Silica / Polyaniline Composite Nanoparticle Produced in an Inverse

Microemulsion Solution for the Electrochromic Applications


# Dissertation

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# Ausführliche Zusammenfassung

Komposite Silica/Polyanilin-Nanopartikel wurden im Rahmen dieser Arbeit synthetisiert und als elektrochrome Filme getestet. Die Kompositstruktur wurde gewählt, um die Haltbarkeit der Filme zu verbessern. Der Durchmesser der Partikel wurde unter 100 nm ausgelegt um diese für optische Anwendungen verwenden zu können. Dazu wurde, zur Kontrolle der Partikelgröße, zur Synthese die Mikroemulsionsmethode verwendet.

Die Mikroemulsionslösung bestand aus Cyclohexan, 1-Hexanol, Triton X-100 und einer wässrigen Phase. Um eine stabile Mikroemulsion des Systems zu erhalten, wurden unterschiedliche Verhältnisse untersucht. Eine stabile Emulsion wurde beim Verhältnis von 65.4 Gew.% Cyclohexan, 30.4 Gew.% Tensid und 4.2 Gew.% wässrige Phase erhalten. Das oberfächenaktive Tensid bestand aus einem 2:1 Gemisch von 1-Hexanol und Triton X-100.

Es konnte gezeigt werden, dass Silica Partikel in den inversen Myzellen dargestellt wurden, wenn zu dem Cyclohexan TEOS, sowie ein saurer Katalysator gegeben wurde. Mehrere male wurde berichtet, dass dichte, sphärische Nanopartikel hergestellt werden aus basischer Mikroemulsionslösung unter Verwendung basischer Katalysatoren. Azide Kataylysatoren konnten in der Arbeit anderer Gruppen nicht so häufig gefunden werden. Daher schien es notwendig zu Untersuchen, ob Nanopartikel auch aus aziden Myzellen dargestellt werden können, da azide Bedingungen zur Synthese des Polyanillins notwendig sind. Die Partikelgröße wurde bestimmt und verglichen mit der von Partikeln, die aus einer basischen Mikroemulsion, durch Zugabe von $NH_3$, dargestellt wurden. Die Partikelgröße der sauer hergestellten Partikel war mit 11.9 nm deutlich kleiner als die der Partikel aus basischem Milieu, die eine Durchmesser von 38.3 nm aufwiesen. Messung der spezifischen Oberfläche der Partikel konnte zeigen, dass die Partikel aus der aziden Mikroemulsion poröser waren. Basierend auf diesen Messungen konnte ein Mikrostrukturmodell vorgeschlagen werden.

Da gezeigt werden konnte, dass poröse Silica Nanopartikel aus azider Mikroemulsionslösung dargestellt werden können, war der nächste Schritt dieser Arbeit die Synthese von Komposit Nanopartikeln. Die Darstellung der Silica/Polyanilin-Komposit-Nanopartikel wurde ebenfalls in einer Mikroemulsion durchgeführt.

Monomeres Anilin, sowie ein polymerisations Agens wurden der wässrigen Phase zugesetzt. Die Partikel wurden mittels Mikrostrukturanalysen, wie TEM und BET (Adsorptions-oberflächenmessungen untersucht. Die TEM Aufnahmen zeigten die Existenz von Partikeln in nano-Grösse, von denen angenommen wurden sie seien Silica/Polyanilin Kompositpartikel. Vergleich der BET Oberfläche vor und nach thermischer Behandlung mit 500 °C zeigten eine deutliche Zunahme. Diese Zunahme der Oberfläche wurde interpretiert als eine Zunahme der Oberfläche durch Thermolyse von Polyanilin aus den Poren des Komposits. Mit diesen Messungen konnte gezeigt werde, dass das Polyanilin in den Silicaporen gebildet wurde. Die Kompositstruktur wurde somit erfolgreich mittels der Mikroemulsions-Synthesemethode erhalten.

Der Hauptgrund für die Synthese der Silica/Polyanilin Kompositnanopartikel war die Erhöhung der thermischen Stabilität. Es konnte bewiesen werden, dass die Kompositstruktur die chemische Stabilität verbessert. So zeigten sich die Partikel resistent gegenüber Ameisensäure, wohingegen sich reines Polyanilin komplett darin gelöst hat. Eine Verbesserung der elektrochromen Eigenschaften konnte ebenfalls für die hergestellten Filme gezeigt werden. Es wird angenommen, dass die Verbesserung der chemischen Stabilität in der Kompositstruktur des Materials begründet liegt. Wenn das Polymer sich in den Poren des Komposits befindet kann es nicht leicht vollständig herausgelöst werden. Der Löslichkeitstest zeigte eine verbesserte chemische Stabilität des Komposit Materials. Die elektrochromen Eigenschaften eines auf FTO beschichteten Glases wurden mit jenen einer reinen Polyanilinschicht verglichen. Der Farbkontrast (bei 600 nm) wurde durch einen Potentialsprung von -0.2 auf +1.0V für beide Filme (Silika/Polyaniline und Polyaniline) herabgesetzt. Der Kompositfilm zeigte jedoch eine langsamere Abnahme als der reine Polyanilinfilm. Diese langsamere Abnahme des Farbkontrasts kann als die Zunahme der elektrochemischen Stabilität gedeutet werden. Das Komposit-Material zeigte größere elektrochemische Stabilität, was durch einen schützenden Effekt der Kompositstruktur verstanden werden kann. Zur Erklärung der Verbesserung der Stabilität wurde ebenfalls ein Mikrostrukturmodell vorgeschlagen.

Im dieser Arbeit konnte gezeigt werden, dass Kompositstrukturen aus Nanopartikeln in einer Mikroemulsionslösung hergestellt werden können. Diese Partikel können womöglich verwendet werden um einen elektrochromen Film mit verbesserten Eigenschaften herzustellen.

## Abstract

Composite nanoparticles of silica/polyaniline were synthesized and tested as an electrochromic material. For the optical application of the particles, the size was designed to be less than 100 nm in diameter, and for the size control of the particles a microemulsion synthesis method was employed. The microemulsion solution was composed of cyclohexane, 1-hexanol, Triton X-100 and aqueous phase. A stable microemulsion composition was selected as 65.4 wt% cyclohexane, 30.4 wt% surfactant and 4.2 wt% aqueous phase, where the surfactant means a mixture of 1-hexanol and Triton X-100. Hexanol-to-Triton X-100 mixing ratio in weight was chosen as 2. It was demonstrated that silica particles could be obtained from the microemulsion solution when TEOS was added to cyclohexane and an acidic catalyst was added to aqueous phase. The preparation of the composite nanoparticles of silica/polyaniline was also performed from the microemulsion solution. Monomer aniline and a polymerization agent were added to the aqueous phase. Microstructure analysis such as TEM and BET surface area measurement showed that polyaniline is incorporated in the pores of silica structure. It was proven that the composite structure enhances the chemical stability of the material, such as resistivity to the dissolution by formic acid, while the pure polyaniline showed complete dissolution. An electrochromic property enhancement was also demonstrated for a film made of the nanoparticles. The electrochromic properties of the electrochromic films deposited on the FTO-coated glass were compared with films prepared by the deposition of pure polyaniline by a chemical polymerization. The composite films showed increased electrochemical durability.

## Kurzzusammenfassung

Komposite Silica/Polyanilin-Nanopartikel wurden im Rahmen dieser Arbeit synthetisiert und als elektrochrome Filme getestet. Der Durchmesser der Partikel wurde unter 100 nm ausgelegt um diese für optische Anwendungen verwenden zu können. Dazu wurde, zur Kontrolle der Partikelgröße, zur Synthese die Mikroemulsionsmethode verwendet. Die Mikroemulsionslösung bestand aus Cyclohexan, 1-Hexanol, Triton X-100 und einer wässrigen Phase. Um eine stabile Mikroemulsion des Systems zu erhalten, wurden unterschiedliche Verhältnisse untersucht. Eine stabile Emulsion wurde beim Verhältnis von 65.4 Gew.% Cyclohexan, 30.4 Gew.% Tensid und

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# Contents

## 1. Introduction

Electrochromism describes a phenomenon of material color change in a persistent but reversible manner produced by electrochemically induced oxidation-reduction reactions. Electrochromic materials can be applied to various kinds of products such as smart windows and display devices. Among those applications, there have been lots of efforts to develop electrochromic display devices (ECDs). Especially flexible display devices are now attracting much attention worldwide since they can facilitate new technological demands such as bending and folding of paper-like displays. High electrochromic efficiency, short response time, long operating life time and reduction of energy consumption are the most important requisites of the materials for the paper-like displays [1-3]. Among those properties, the operation life time is the most important barrier to overcome for a realization of ECDs.

There are two types of electrochromic material: a) inorganic transition metal oxides (TMOs), b) organic polymer materials. The TMOs have been studied longer than the organic materials that they have been studied since 1960s [2-4]. However, organic materials are gaining attentions recently, because of their faster response and longer operating life time compared to the inorganic materials. Among the organic electrochromic materials, conducting polymers are considered as one of the most suitable materials for ECDs since they are easy to process and have high degree of color tailorability, which means one material can exhibit more than one color according to doping percentage, choice of monomer, and applied potential [2]. Among the conducting polymer films, polyaniline- and polypyrrole-films exhibit properties close to practical applications especially in terms of response time [2]

However, there are still problems for conducting polymers. The operating life time of electrochromic conducting polymers is still limited to $10^6$cycles while more than $10^8$ cycles are required for acceptable multimedia display. In general, the electrochemical stability of material is being considered as one of the key factors determining the operating life time of device [5-7]. Therefore it is necessary to improve electrochemical stability of material to achieve prolonged operating life time.

There have been lots of studies to improve electrochemical stability by making inorganic-organic composite structure [8, 9]. Among the composite structure, the inorganic-organic hybrid structure is one of the most frequently tried methods to improve the chemical stability of organic material [10]. In this study, as a feasible way

of achieving enhanced electrochemical stability of electrochromic polymer material, an optical nanocomposite of silica and polyaniline was tried. An inverse microemulsion system was employed to produce nano-sized porous silica particles and silica / polyaniline composite particles. The synthetic method employing inverse microemulsion is frequently used to produce nano-sized particles either inorganic or organic [11]. By using the nano-sized micelles as a reaction reservoir, the size of synthesized particle could be controlled in the range of 30 ~ 100 nm.

A production of porous silica particle was tried and the characterizations on the obtained particle were performed before the production of composite nanoparticle. The composite nanoparticle of silica / polyaniline was then synthesized from an inverse microemulsion solution. The obtained composite nanoparticles were applied on an electrochromic cell in form of electrochromic film for test devices. The electrochromic characterizations on the film made of composite nanoparticle and the test device were also performed. The enhancement of electrochromic durability for the composite material was checked by a comparison with a pure polyaniline film which was prepared by a chemical polymerization method.

## 2. Literature review

### 2.1. Electrochromism

#### 2.1.1. Definition

Electrochromism describes a reversible color change of material produced by electrochemically induced oxidation-reduction reactions. It is one of several types of chromism of materials. As thermochromism and photochromism mean material color changes made by heat and light, respectively, electrochromism refers that the color change is caused by an electric potential. In most cases, the color change in electrochromism can be driven by rather low electrical potential of the order of a fraction of volt or a few volts [1-3]

The color change of material means variation in transmittance and/or reflectance change in visible range, which is originated from different electronic absorption bands according to a switching between oxidation and reduction state of material. When electric potential is applied on electrochromic material, forced oxidation or reduction is derived, and the individual color is originated from the corresponding oxidation or reduction state of the material. For electrochromic materials the characteristic color change is reversible, since the oxidation and reduction state can be converted reversibly by switching potential.

#### 2.1.2. Application fields

The application area for the electrochromism is rather broad, that it covers from smart window glazing and optical modulators to information displays [2, 12-15]. The smart windows are typical examples. The electrochromic property is used to control the amount of light and heat to pass through the windows. Usually the electrochromic material is in form of thin film coated on a window glass. The transmittance modulation has also been applied at the automobiles to automatically tint rear-view mirrors in various lighting conditions. The electrochromic application fields are illustrated in Fig. 1.
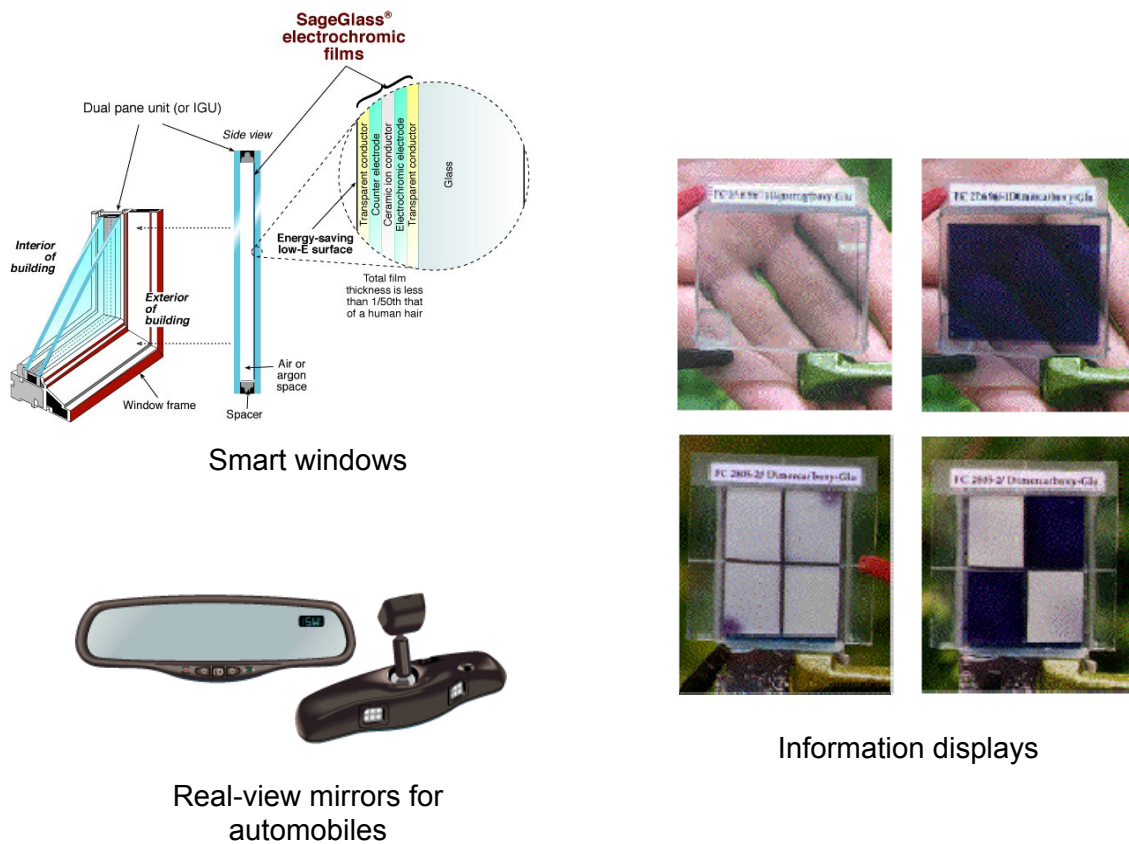
Fig. 1    Application fields of electrochromic devices: Smart windows [16], information displays [17], and real-view mirrors for automobiles

Since the smart windows control the transmittance of heat as well as the transmittance of visible light, the working definition of electrochromism has now been extended to include devices for modulation of radiation in the near infrared, thermal infrared and microwave regions. When color for electrochromic materials is used, this can now mean a response by detectors at these wavelengths, and not just by the human eyes.

Nowadays electrochromic material draws much attention as being used in the display devices. Electrochromic display device (ECD) is being considered as one of the candidates for the conventional liquid crystal display (LCD), since ECD has many advantages over LCDs. Among these advantages the most important are low energy consumption, wider viewing angle, high contrast rate, and possibility to achieve multiple colors with a single material [2, 17]. When a new redox state of electrochromic material

is established by the applied electric pulse, then it is maintained after the potential is switched off. This means the colored or bleached state of the material can be sustained for a considerable time without applying electrical power. This is so-called "color memory effect" of electrochromic material. Because of the color memory effect, energy consumption for the electrochromic display device could be drastically reduced, and this would be a big advantage over other emissive devices. The low power consumption is especially advantageous when it is applied to mobile devices with limited power source.

The possibility for a flexible display is another attraction for electrochromic material. Using polymeric electrochromic material and plastic substrate with a transparent conductive coating, it is possible to build all-plastic flexible display device. There are lots of papers and patents about the flexible display devices [18-22]. In these cases, gel-type electrolyte is also needed. The gel-type electrolyte immobilizes liquid electrolyte in the polymer network [23, 24].

Recently, ITO-coated polymer films are readily available which would provide the plastic substrate for a flexible device. The flexible electrochromic displays are frequently tried with the plastic substrate, flexible electrochromic material, and gel-type electrolyte. The flexible electrochromic displays would facilitate increasing technical demands for foldable display devices. The examples for the flexible electrochromic display devices are given in Fig. 2.
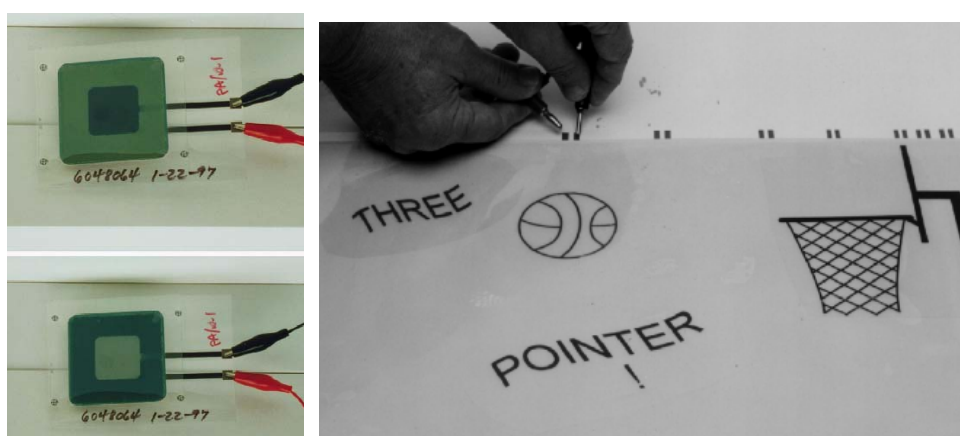


Fig. 2 Flexible electrochromic devices [24].

### 2.1.3. Materials

There are two types of electrochromic material: a) inorganic transition metal oxides (TMOs) such as $WO_3$, $V_2O_5$, $Nb_2O_5$, etc., b) polymers such as polypyrrole, polyaniline, polythiophene, viologens, etc [2, 3, 13]. The electrochromic phenomenon was first discovered from the inorganic material [2, 3]. Ever since the discovery of electrochromism in TMOs, almost all efforts have been devoted to the inorganic materials.

Recently, polymer electrochromic materials are gaining attentions rapidly, because of their faster color change [2, 25]. Polymers are also exhibiting longer operation life time. The comparisons for the two categories of electrochromic materials are given in Table 1 below.

Table 1    Comparisons of inorganic transition metal oxides and polymers as electrochromic materials [2].

| Property | Inorganic Materials | Polymers |
| --- | --- | --- |
| Method of Preparation | Needs sophisticated techniques such as vacuum evaporation, spray pyrolysis, sputtering, etc. | The material can be easily prepared by simple chemical, electrochemical polymerization and the films can be obtained by simple techniques such as dip-coating, spin coating, etc. |
| Processibility of the Material | The materials are poor in processibility. | The materials can be processed very easily. |
| Cost of Making Final Product (Device) | High as compared to the polymer based devices. | Low cost as compared to the inorganic materials. |
| Colors Obtainable | Limited number of colors are available from a given material | Colors depend on the doping percentage, choice of the monomers, operating potential, etc. Hence, large number of colors is available with the polymeric materials. |
| Contrast | Contrast is moderate. | Very high contrast can be obtained. |
| Switching Time (ms) | 10-750 | 10-120 |
| Life Time (cycles) | $10^3$-$10^5$ | $10^4$-$10^6$ |

### 2.1.3.1. Inorganic materials

For inorganic electrochromic material, tungsten oxide ($WO_3$) is most typical. The electrochromism actually was first discovered in $WO_3$ films, it still remains most frequently studied material and as a consequence most feasible candidate among inorganic electrochromic materials for the devices.

The electrochemically induced oxidation and reduction state in $WO_3$ film can be represented by a simple reaction equation as Eq. 1.

$$WO_3 + xM'^+ + xe^- \leftrightarrow M'_x WO_3 \qquad\qquad \text{Eq. 1}$$

$M'^+$ denotes metal ions such as $H^+$, $Li^+$, $Na^+$, and $K^+$. The left side of the equation represents bleached state where the material becomes optically transparent, and the right side is colored state with dark blue color.

Electrochromic color change could also be observed from other transition metal oxides such as $WO_3$, $MoO_3$, $V_2O_5$, $LiO$, $Nb_2O_5$, and etc. Since the color change of material comes from non-stoichiometric redox state, many transition metal oxides which tend to have non-stoichiometric state are electrochromic in nature.

Transition metal oxides films can be made by several processing technique such as vacuum evaporation [26], sputtering [27], spray pyrolysis [28], chemical vapor deposition [29], and sol-gel chemical method [30]. For a low cost production of electrochromic film on the large area substrate for the smart windows of buildings, sol-gel chemical process would be most preferred.

Generally, transition metal oxides are exhibiting slower response to potential switching than organic polymer materials. Operation life time of the inorganic material is also limited to lower range than polymers (Table 1). However, because of the extensive studies on the material, the transition metal oxides are still widely used to smart window system and transmission modulation devices. The electrochromic mechanism and kinetics are relatively well understood for the transition metal oxides.

### 2.1.3.2. Organic materials

It is considered that conducting polymers such as polyaniline, polypyrrole, polythiophene, and etc are suitable material for the ECDs, since they exhibit faster response and longer operating life compared to transition metal oxides as was summarized in Table 1.

From some organic material such as conducting polymers, electrochromic behavior is frequently observed. Usually classical polymers are distinguished from metals with their poor electrical conductivity. Recently, a new class of polymers was developed to provide wide variety of electrical conductivity. The conducting polymers were extensively studied in academic research field and industrial side world-wide [31]. The conducting polymers are also accepted as one of the suitable materials for electrochromic displays. The conducting polymers are easier to be processed than inorganic materials and their color could also be controlled by changing the doping level, changing monomer species, or changing the applied potential. Conducting polymer films are showing properties close to the practical application in terms of response time (Table 1).

Since the transition metal oxides are intrinsically electrochromic because they have different redox states, conducting polymers which have also different redox states are intrinsically electrochromic, too. In Table 2, the observed electrochromism in conducting polymers is given.

Table 2    Polymer electrochromic materials and Electrochromism observed in CPs [2].

| Polymer | Anion |
|---|---|
| Polypyrrole | $ClO_4^-$ |
| Polythiophene | $ClO_4^-$ |
| Polymethylthiophene | $BF_4^-$ |
| Poly-3,4-dimethyhlthiophene | $ClO_4^-$ |
| Poly-2,2'-bithiophene | $CF_3^-$, $SO_3^-$ |
| Octacyanophthalocyanine | $H^+$ |
| Polyaniline | $Cl^-$ |

Among conducing polymers polyaniline attracts many attentions due to its outstanding properties. It is one of the sol-called doped polymers, where the conductivity results from a process of partial oxidation and reduction. The conductivity of polyaniline is easily controllable. One of the most frequently tried applications for polyaniline is as the electrochromic material [32]. Polyaniline also has environmental stability. Unlike the other conducting polymers, polyaniline is also processable by melting or by making solution [33]. It means that polyaniline products can easily be shaped into any required form. Polyaniline films can easily be obtained by polymerization of aniline using some polymerizing agents such as ammonium persulphate [34] or benzoyl peroxide [35]. Also a UV photo processing can be used for the polymerization [36]. Therefore, the polyaniline could be obtained by selecting a proper processing method among those available choices according to the purpose.

For the organic material the oxidation and reduction reaction can be explained differently from inorganic materials. Polyaniline shows typical electrochromic behavior, and it is related with different phases of polyaniline which are formed by oxidation and reduction of the material. The intrinsic oxidation state of polyaniline can be given as in Fig. 3 [37].

As oxidation proceeds, polyaniline changes its phase from completely reduced phase leucoemeraldine to completely oxidized phase pernigraniline. During the oxidation and reduction, polyaniline changes its color. The colors of each oxidation state of polyaniline were summarized in Table 3.

## Leucoemeraldine
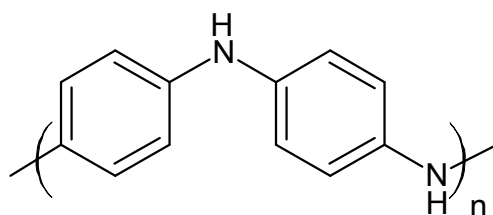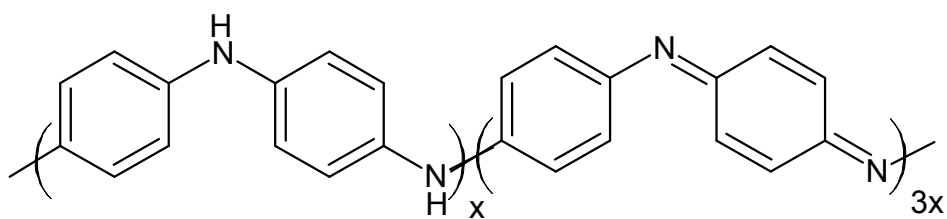


## Photoemeraldine
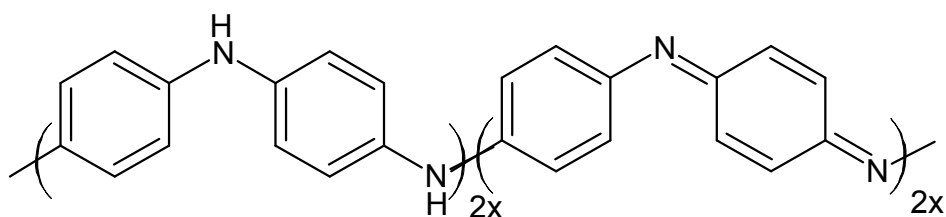


## Emeraldine
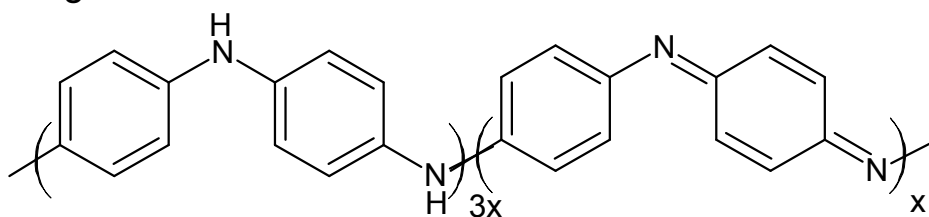


## Nigraniline
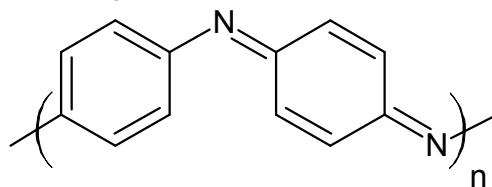


## Pernigraniline



Fig. 3 Intrinsic oxidation states of polyaniline

Table 3    Colors of each four oxidation state of polyaniline [37, 38].

| Oxidation state | leucoemeraldine | photoemeraldine | Emeraldine | nigraniline | pernigraniline |
|---|---|---|---|---|---|
| Color | pale yellow or colorless | light green | green or dark green | blue or dark blue | violet |

### 2.1.4.  Device structure

There are two types for the structure of electrochromic devices. The first type of device is constructed by depositing two electrochromic electrodes either inorganic or organic on the transparent conducting glass substrates. These two electrodes are separated by electrolyte layer which gives electrical contact and pathway for the ions to be injected to or ejected from the electrochromic material [2, 13]. Complementary electrochromism of these two materials produces maximized visible color contrast for the device. It is common structure for smart windows. In this type of device, the color change is persistent, that the colored state or the bleached state will be maintained even in the absence of applied potential. In Fig. 4, the structure of complementary electrodes in electrochromic device is given.
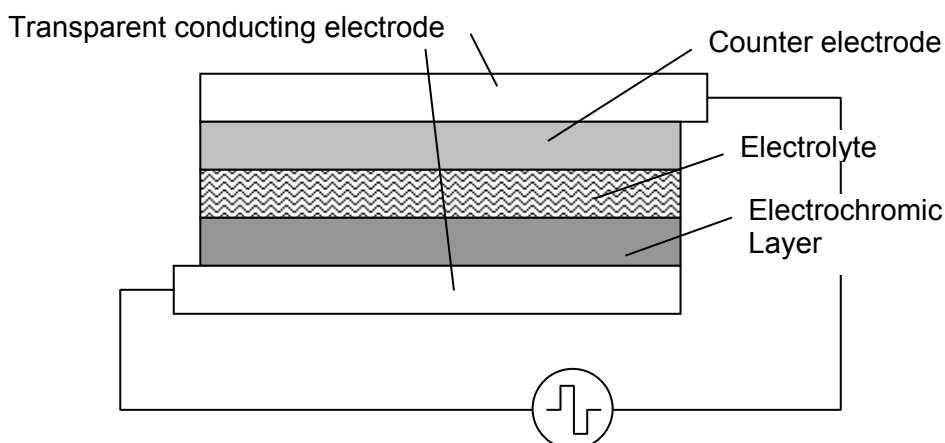


Fig. 4  Schematic diagram of electrochromic cell comprising complementary electrodes.

In the second type of structure, two complementary electrochromic materials are dissolved into a solution, and the solution is kept in between two transparent

conducting glasses [39]. As can be expected from the simple device structure, this type of device is easy to build. The reactions are very fast for this type of device, since the injection or extraction of charges is occurring on every surface of dispersed electrochromic particles. The color contrast is controllable simply by changing the concentration of material dissolved into the solution. The main drawback of this system is that the colored stated is not maintained without potential or current. The two types of colored molecules can freely diffuse through the solution and can react with each other to turn back to bleached state.
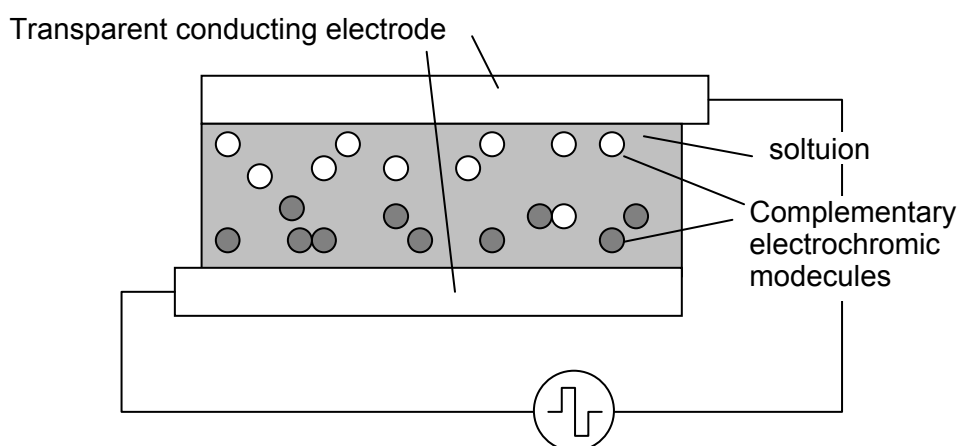


Fig. 5     Schematic  diagram  of  electrochromic  cell  with  two  complementary electrochromic materials dissolved into solution

Basically these two device structure have five layers as transparent conductive electrode / electrochromic layer / electrolyte / counter electrode (ion storage layer) / transparent conductive electrode. However in some cases four-layer structure without counter electrode could be employed for the electrochromic characterization. H. Hu et al [40] demonstrated that four-layer structured electrochromic cells with polyaniline thin film as the electrochromic layer is also working to show color changes. In this case the counter electrode was omitted. The polyaniline film was deposited on the transparent electrode by a simple chemical polymerization of aniline in an acidic aqueous solution. For a quick and simple demonstration of electrochromic working of developed material, this four layer structure could readily be used.

### 2.1.5. Electrochromic characterization

For an extensive study on the electrochromic behavior of material, it is necessary to investigate working electrode separately from the other compartments such as electrolyte and counter electrode. Three-electrode cell configuration[41, 42], facilitates this purpose. Tree-electrode cell is an electrochemical cell containing a working electrode, a counter electrode, and a reference electrode. A current may flow between the working and counter electrodes, while the potential of the working electrode is measured against the reference electrode. This setup can be used in basic research to investigate the kinetics and mechanism of the electrode reaction occurring on the working electrode surface, or in electroanalytical applications. As is shown in Fig. 6, the operation potential for electrochromic working electrode separated from overall cell potential can be checked by measuring potential drop between working electrode and reference electrode.



Fig. 6 Schematic illustration for 3-electrode cell

The electrochromic materials are usually fabricated as thin films on a substrate coated with the conductive transparent electrode such as ITO or FTO. The coatings of the electrochromic material are done either by dry physical coating processes such as
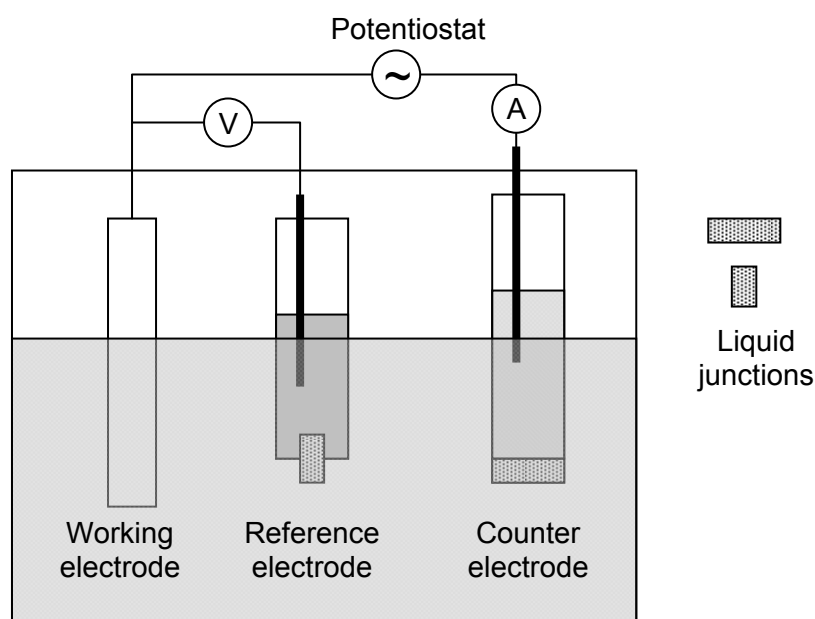
chemical vapor deposition (CVD) and sputtering or by wet chemical coating processes such as dip-coating and spin-coating. Sol-gel derived dip- or spin-coating is frequently used for the simplicity of the process and the possibility to be used in the low-cost film deposition on large scale substrates.

For a characterization of electrochromic material the cyclovoltammogram, the response behavior, and the operation life cycle would be most frequently investigated. For a characterization of polyaniline electrochromic films, the cyclovoltammogram is also frequently used[43]. The cyclovoltammogram is a measure of the currents passes through the electrochromic cell according to applied potentials on the material. The current variation is usually measured while the applied potential is scanning through a certain range, for example from -1 volt to +2 volt with a certain scanning speed. Since redox reactions involve charge insertion or extraction from the electrochromic layer, the absolute value of current is increasing drastically showing a current peak when the applied potential passes a certain level. By examining these current peaks, the identification for each redox reaction could be performed.

The response characteristic of the electrochromic material can be investigated by measuring time for a transmittance of light at a selected wavelength to reach certain level after the potential is switched [44]. The operation life cycle for an electrochromic material is a measure of maximum number of potential switching maintaining certain level of optical transmittance difference between the switching.

### 2.1.6.  Technical requirements according to the application field

With the innovations in electrochromic materials ever since the discovery of phenomena, it is expected that commercial products will soon be realized. The required technical profile for smart window is less hard than that for information display. For the smart windows of buildings a process technology that can enable large area coating with low production cost is to be employed. A list of typical requirements for the smart windows can be given as bellows [45];

- Continuous range in solar and optical transmittance, reflectance, and absorptions between bleached and colored states,

- Contrast ratio of at least 5:1,

- Coloring and bleaching times (response time) of a few minutes,

- Operating glass surface temperatures of -20 °C ~ 80 °C,

- Switching with applied voltages of 1 ~ 5 V

- Open circuit memory of a few hours (maintains a fixed state of transmission without corrective voltage pulses),

- Acceptable neutral color,

- Large area with excellent optical clarity,

- Sustained performance over 20 ~ 30 years,

- Acceptable cost ($100/m$^2$).

When electrochromic materials are used in the smart windows, response speed of the material doesn't have to be very fast so that over 30 seconds or even several minutes of response time is no problem. However, when information display is concerned, response time and operation life cycle number are very important properties for material. When electrochromic device is compared with the other non-emissive display devices such as field effect liquid crystal displays, the most noticeable drawbacks for the material are write/erase time and operation life. The comparison for the devices is given in Table 4.

Table 4    A properties comparison for ECDs and other non-emissive devices [2].

| Properties | Electrochromic Displays (ECDs) | Field Effect Liquid Crystal (FELC) Displays | Dynamic Scattering Liquid Crystal(DSLC) Displays |
|---|---|---|---|
| Viewing angle | wide | narrow | narrow |
| Optical mode | Transition, Reflection, Projection | Transition, Reflection, Projection | Transition, Reflection, Projection |
| Color | Two or more | B/W or dye | B/W |
| Voltage (V) | 0.25 - 20 | 2 - 10 | 10 - 30 |
| Power (µW/cm$^2$) | 1 - 10 | < 0.1 | 1 - 10 |
| Energy (mJ/cm$^2$) | 10 - 100 | | |
| Color memory | Yes | No/Yes | No/Yes |

| Write time (ms) | 100 -1000 | 20 | 20 |
|---|---|---|---|
| Erase time (ms) | 100 - 500 | 1 - 500 | 100 |
| Operation life | $10^5$ - $10^6$ cycles | > 2 × $10^5$ hr | > 1 × $10^4$ hr |

With wide viewing angle, color memory, and color tailorability, electrochromic display device provides advantages over the conventional display systems, but the slow response to potential switching and limited operation life are major blockage for display application.

### 2.1.7. Problems

Electrochromic device has working electrode and counter electrode (or ion storage layer), which are separated by suitable electrolyte either liquid or solid. This structure is quite analogous to rechargeable electrochemical battery. Not only the structure, but the whole phenomena occurring in the device are basically same. Therefore, the technical limitations of batteries are persisting also in the electrochromic devices. Usually, rechargeable batteries are suffering limited number of charging/discharging cycles, and this is also the main problem of electrochromic devices.

Therefore it could be said that the most urgent problem to be solved for electrochromic display device is the limited operation life cycle. As was mentioned in the previous sections, even though the inorganic materials have been studied longer, the organic electrochromic materials such as conducting polymers are being considered as feasible candidate for display devices, because of their faster response and longer operating life. The conducting polymers are even easier to process than inorganic electrochromic materials and they have high degree of color tailorability.

The response times of polymer materials reach down to 10 ms which is quite close for the display device application. On the other hand, even the maximum operation life time of polymers films is only $10^6$ cycles as was summarized in Table 1 and Table 4.

The limited operating life of the polymers is closely related with electrochemical stability of the materials. There have been reports discussing the limited stability of conducting polymers [5-7]. For some conducting polymers such as polypyrrole and

polyaniline, electrochemical degradations of the materials are observed when sufficiently high anodic potentials are applied [46].

It has been also demonstrated that the electrochemical stability of polymer materials could be improved by forming composites with chemically stable inorganic (i.e. $SiO_2$, $Al_2O_3$) particles or matrixes [47-50]. Those composites are made by dispersing inorganic nanoparticles into the polymer matrix or by incorporating polymers into a host inorganic matrix. Fu et al. pointed out, that the strong interaction between the surface group of silica particle and polymer reduces the direct interfacial reaction between polymer and attacking electrolytes.

Frailty of mechanical stability is another problem for conducting polymer films. They will rapidly become brittle with mechanical degradation after being polymerized [51, 52]. Therefore, the monolithic films of conducting polymers are not the favorable forms to be applied to the flexible displays because of the brittleness of the films. There have been several researches about improving mechanical flexibility of conducting polymer films by making composites with more flexible polymers such as polyethylene [53] or polyimide [54].

Thus the main objective of this study may be providing a new feasible or effective way to ensure higher chemical stability of the material and as a result to enhance the operation life time of the whole electrochromic device.

## 2.2. Inorganic-organic hybrid composites

As was described in the previous sections, the problem for the electrochromic material is the limited operation life. With the limited operation life cycle, electrochromic display device cannot be materialized. From the previous studies of Mažeikienè et al [5, 6], it was known that the operation life is mainly governed by the electrochemical stability of electrochromic material. The electrochromic material would be applied either to working electrode or to ion storage electrode. For both of the electrodes the electrochemical stability is an important parameter to determine the operation life time. There have been efforts to improve electrochemical stability of polymer. Ak et al [55] demonstrated that by a copolymerization a reasonable switching stability of electrochromic device. B. Ballarin et al [56] showed that a novel sonogel-carbon-polythiophene microstructured material could increase the stability of redox-active phase. This would be an example of increasing stability by employing a nanocomposite

structure. It could also be said that the chemical and/or mechanical stability of polymer can be improved effectively by making composites with inorganic material such as silica.

One of the most frequently used and at the same time one of the most effective ways to improve chemical stability of organic material is a hybrid composite structure with inorganic components [57]. H. Schmidt showed that the organically modified glasses exhibit properties so close to those of inorganic component that they could be considered as glasses. The introduction of organic components into glass structures by a sol-gel techniques leads to hybrid materials. Utilizing the sol-gel wet chemical process, it was possible to prepare the organically modified glasses in a low temperature. The low temperature condition would be quite essential to make organic-inorganic hybrid material to keep the organic part alive during the preparation process. The materials prepared through this method behave more like inorganic glasses, even with high contents of organic groupings. It was also shown that the surface hardness of the hybrid material is close to that of inorganic glasses. The thermoplastic behavior also showed that the material is quite similar with the inorganic glasses rather than polymers. It was also shown that by a chemically controlled condensation the phase separation could be avoided, and the highly homogeneous and transparent composite structure can be obtained. With this previous work of H. Schmidt, it could also be possible to conceive that in this work the mechanical and chemical properties enhancement of organic electrochromic material would be achieved by using the hybridization.

Generally it can be said that organic polymers have mechanical flexibility, toughness, and formability, while inorganic ceramics have excellent durability to chemical attacks, high thermal stability, and surface hardness. By the favorable combination of these properties, superior properties of inorganic-organic hybrid material could possibly be achieved.

For the last decades, inorganic-organic nanocomposite materials have gained much attention since they shows interesting and still unexplored properties [10]. There are several ways to produce polymer / inorganic nanocomposites [58-60]. For example, sol-gel fabricated silica nanoparticles can be dispersed into a polymer matrix to form composites. A particle size controlling and a surface modification of the obtained nanoparticles should also be employed for those attempts.

Inorganic-organic hybrid composites can be classified into one of three types; 1) dispersion of inorganic particles into organic bulk medium [61], 2) hybrid material in form of film [62], 3) core-shell particles with inorganic core and organic shell, or vice versa [63, 64]. The purpose of the hybrid is rather diverse that it covers from improving chemical and/or mechanical stability of organic material [65, 66]. For the case of electrochromic composite material, electro-activity of hybrid composite material will mainly come from organic part while inorganic part is improving chemical, mechanical, and thermal stability of the system.

Silica is one of the most frequently used inorganic materials for the hybrid [67], since various kinds of organosilanes were available as the precursors for synthetic reactions. Sol-gel method provides preferable reaction condition with superior properties of material such as complete mixing down to molecular level.

Silica/polyaniline composites are frequently tried. Jang et al [68] prepared silica/polyaniline composite film using sol-gel process. They prepared uniform crack-free film by mixing preformed polyaniline powder into silica precursor solution and by casting the solution onto a substrate.

Azevedo et al [69] demonstrated that formic acid can be used as an effective solvent for polyaniline. The polyaniline solution was also mixed with TEOS to produce silica/polyaniline composite glass. The sol-gel reaction, i.e. hydrolysis and polycondensation of TEOS to form silica was catalyzed by formic acid. Thus formic acid acts as solvent and catalyst at a same time.

For a hybrid structure of silica and polyaniline, the synthesis of both materials would necessarily be performed in a same temperature range. For this purpose a sol-gel synthetic method for silica at room temperature would be employed. If silica has to be prepared by melting, polyaniline could not stand that high temperature. Generally, polyaniline could be obtained either by chemical polymerization or electrochemical polymerization. For a hybrid with silica polyaniline would rather be produced by the chemical polymerization process where an electrical potential load is not necessary.
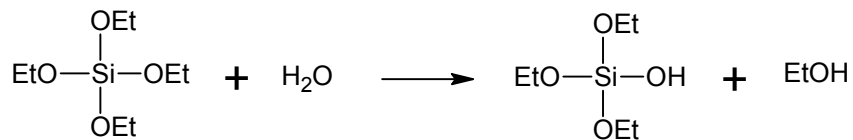
### 2.2.1. Sol-gel chemistry of silica

For the inorganic-organic hybrid, sol-gel synthetic reaction is most frequently employed [67, 70, 71]. Sol-gel method provides much simple way to produce the

composite material at low temperatures like ambient temperatures. Through the sol-gel reaction method, inorganic parts of the composite can easily be made using metal alkoxides. The metal alkoxides can simply be converted to oxides without further heat treatment at high temperatures.

For example silica can be obtained by a series of hydrolysis and polycondensation of silica precursors. Most frequently used silica precursor is tetraethoxysilane (TEOS). The hydrolysis and polycondensation of TEOS into silica can be represented as in Fig. 7.

Hydrolysis

OEt                                     OEt
|                                       |
EtO—Si—OEt  +  H₂O  ⟶  EtO—Si—OH  +  EtOH
|                                       |
OEt                                     OEt

Water condensation

OEt            OEt                  OEt    OEt
|              |                    |      |
EtO—Si—OH  +  HO—Si—OEt  ⟶  EtO—Si—O—Si—OEt  +  H₂O
|              |                    |      |
OEt            OEt                  OEt    OEt

Alcohol condensation

OEt            OEt                  OEt    OEt
|              |                    |      |
EtO—Si—OH  +  EtO—Si—OEt  ⟶  EtO—Si—O—Si—OEt  +  EtOH
|              |                    |      |
OEt            OEt                  OEt    OEt
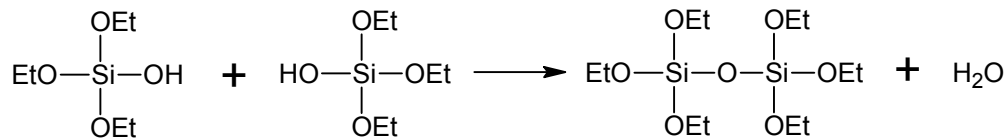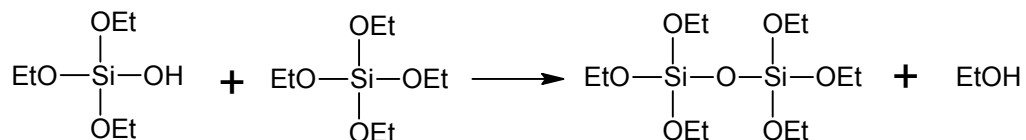
Fig. 7 Hydrolysis and polycondensation of TEOS

Sol-gel reaction which produces inorganic material at low temperatures is much useful especially when a simultaneous synthesis of inorganic and organic components is necessary. This is the usual case for inorganic-organic composite fabrications.

When both inorganic and organic components are synthesized in one liquid solution, it happens that the synthetic reactions of both components would necessarily be done under the same catalytic condition. Usually polymers require acidic condition of polymerization, which means silica also have be synthesized in an acidic condition.

As was well understood, in an acidic solution, silica tends to form 3-dimensional network rather than to grow into spherical dense particles [72]. By the hydrolysis and condensation primary silica particles are produced. At low pH, the dissolution rate of primary particle is low (Fig. 8) that the growth of primary silica particles is limited and instead they aggregate with each other to form 3-dimentional framework. On the other hand at high pH, the dissolution rate of primary particle is high enough for larger particles to grow by absorbing the dissolved silica, which is usually referred as Ostwald ripening. With this process dense spherical silica particles with wide variety of sizes as 10 nm to several μm could be obtained from basic solutions [73].
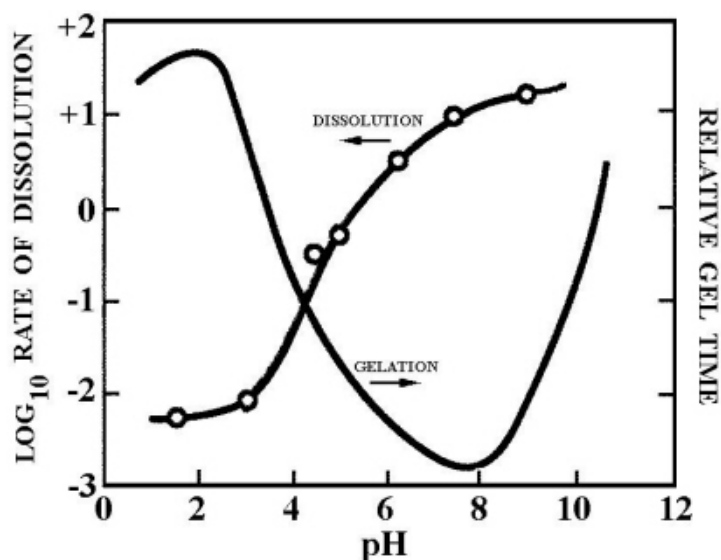


Fig. 8 Dissolution rate and relative gel time as a function of pH [72].

When a silica / polyaniline hybrid material is concerned especially in a form of composite nanoparticles rather than a core-shell particle, porous silica structure would be advantageous since polyaniline could be incorporated into the pore space

### 2.2.2. Chemical polymerization of polyaniline

Polyaniline is easily processable among the conducting polymers. The conductivity of polyaniline can be varied in a wide variety according to its redox state and/or to its doping state [74, 75]. It also has environmental stability that it could also be used for protecting metal surface from corrosion [76].

Polyaniline can be fabricated either by chemical or electrochemical polymerization from the monomer anilines. The electrochemical polymerization is more common to obtain polyaniline [77, 78]. For the last several decades, numerous studies were done on the electrochemical polymerization. However, the chemical polymerization is also an attractive method, since it is more simple and adjustable to a mass production of polyaniline.

For the chemical polymerization of polyaniline, so-called polymerization agent is needed. Ammonium peroxodisulfate (APS) is most frequently used polymerization agent [79, 80]. Normally, polyaniline salts are prepared from an acidic solution containing HCl by adding monomer aniline and APS. The efficient polymerization of aniline is achieved in an acidic medium.

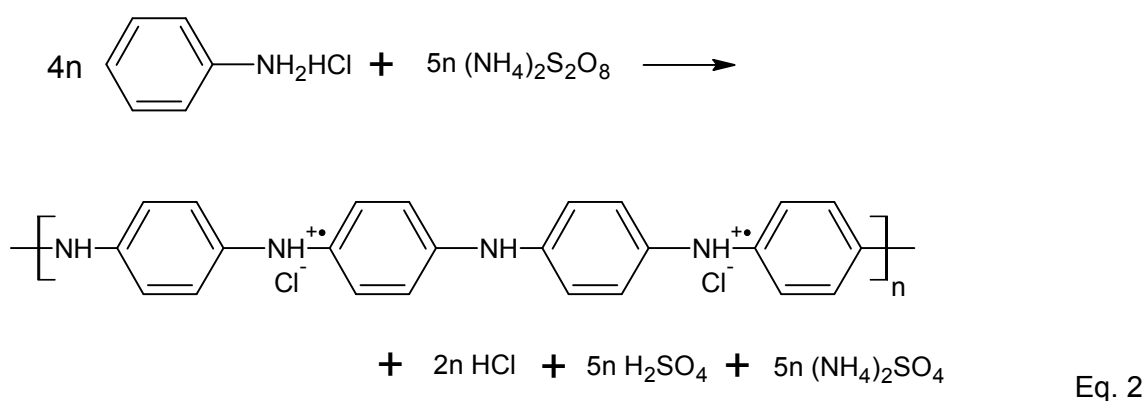When aniline is dissolved into aqueous solution containing HCl, aniline will exist as an anilinium cation. In the acidic solution, aniline hydrochloride is a starting monomer for the polymerization reaction. When APS is added to the solution, the oxidative polymerization starts soon. The overall reaction where polyaniline hydrochloride, i.e. emeraldine salt is produced can be given as Eq. 2.

$$4n \quad \text{C}_6\text{H}_4-\text{NH}_2\text{HCl} \; + \; 5n \; (\text{NH}_4)_2\text{S}_2\text{O}_8 \longrightarrow$$

$$\left[ \text{NH}-\text{C}_6\text{H}_4-\overset{+\bullet}{\underset{\text{Cl}^-}{\text{NH}}}-\text{C}_6\text{H}_4-\text{NH}-\text{C}_6\text{H}_4-\overset{+\bullet}{\underset{\text{Cl}^-}{\text{NH}}}-\text{C}_6\text{H}_4 \right]_n$$

$$+ \; 2n \; \text{HCl} \; + \; 5n \; \text{H}_2\text{SO}_4 \; + \; 5n \; (\text{NH}_4)_2\text{SO}_4 \qquad \text{Eq. 2}$$

The pure, i.e. unsubstituted, form of polyaniline which could easily synthesized by an oxidative chemical polymerization are usually insoluble in common organic solvents [81]. Since polyaniline is hardly soluble to organic solvents or infusible, for a better processibility production of polyaniline particles especially in the form of colloidal dispersion are frequently tried [82, 83]. The colloidal dispersion of polyaniline can be applied on the surface of other material in a form of film, or can be mixed with other matrix to form bulks.

As an electroactive material, polyaniline would rather be prepared in a form of thin film. For polyaniline film preparation, in situ chemical polymerization coating methods could also be used [84, 85]. Wan et al demonstrated that composite polyaniline film can be produced by an in situ chemical polymerization coating onto a transparent conducing substrate.

## 2.3. Microemulsions

When a new electrochromic material is developed, it would be deposited onto a transparent conducting substrate. For the film deposition, it would be more desirable for the electrochromic material to be dispersed into liquid solution in a form of particle for further processing. In this case, the size of the dispersed particle is a critical parameter for the transparency of the deposited film.

Since the electrochromic devices utilize optical transmittance change of material, the electrochromic coating should be optically transparent. For the optically transparent coating, the size of dispersed particle should be kept under 100 nm. When the particles with sizes larger than 100 nm are dispersed, the film usually shows haze because of optical scattering. Thus a special technique to control particle size is needed.

To control the size of nanoparticles, a special synthetic environment is needed. Among the synthetic methods the microemulsion solution method is frequently tried to produce nanoparticles. The microemulsion solution could provide micelles in a well controlled nano-size range. When the particle is synthesized from the individual micelles of microemulsion, the size of produced particles is controlled within the size of micelles. In the past several decades, microemulsions have been studied worldwide because of their big application possibilities to the field of chemical nanoparticle synthesis, cosmetics, pharmaceuticals, agriculture, and bio-organic reactions [86-88].

There are two types of microemulsions which are oil-in-water (O/W) microemulsion and water-in-oil (W/O) microemulsion. Both microemulsions are transparent and optically isotropic liquid media. The water-in-oil microemulsion is composed of continuous oil phase and discrete nanometer-sized aqueous droplets.  And the aqueous droplets are dispersed in the media and stabilized by ionic and non-ionic surfactants or surfactant mixtures. In the W/O microemulsions, nano-meter sized aqueous droplets will act as a nano-sized reactor where the nanoparticle is synthesized.

In case of silica particle formation, the hydrolysis and polycondensation of the silica precursor (in general tetraethoxysilane, TEOS) occur in the aqueous droplets [87, 88].

### 2.3.1. Hydrophilic-lipophilic balance of surfactant

When a W/O microemulsion solution is used as a reaction medium for the nanoparticle production, the aqueous micelles of the solution must be maintained during the reaction period. For a stability of microemulsion solution, the surfactant is an important component. For an effective dispersion of aqueous phase into oil phase, a cosurfactant system, the mixture of two different surfactants, could necessarily be used [89, 90]. When a cosurfactant system is employed, the amount of aqueous dispersed phase could be controlled in a wider range then single surfactant system, and the stability of the aqueous micelles could also be enhanced.

The mixing ratio of surfactant and cosurfactant would rather be decided by taking a hydrophilic lipophilic balance (HLB) of surfactants into account. The type of microemulsion (i.e. O/W or W/O) can be predicted on the basis of the relative hydrophilic-lipophilic properties of surfactant. According to the HLB concept, a specific numerical value could be assigned to each of the surface-active agents, and the numerical value represents hydrophilic-lipophilic balance of the surfactant system. HLB number of surfactants is defined as a numerical scale from 0 to 20. HLB = 0 implies 100% hydrophobic and 20 implies 100% hydrophilic. For an inverse microemulsion where aqueous phase is dispersed into oil phase, surfactants with lower HLB number (< 10) are required [91]. Most nonionic surfactants fall in between the two extremes. Most surfactant manufacturers provide HLB values of their reagents. The HLB number of 1-hexanol is known to be 6.05 [89] and that of Triton X-100 is 13.50 which is given by the chemical company (see appendix).

The overall HLB value of the mixture is calculated as the sum of the fraction $\times$ individual HLB number. When two different surfactants such as Triton X-100 and 1-hexanol are mixed with weight ratios $x_{\text{Triton X-100}}$ and $x_{\text{1-hexanol}}$, the HLB number of the mixed surfactant $\text{HLB}_{\text{mixed}}$ is given as Eq. 3.

$$\text{HLB}_{\text{mixed}} = \text{HLB}_{\text{Triton X-100}} \cdot x_{\text{Triton X-100}} + \text{HLB}_{\text{1-hexanol}} \cdot x_{\text{1-hexanol}}$$

Eq. 3

Given that the hexanol-to-Triton X-100 weight ratio is 2, the HLB can be calculated as 8.53.

### 2.3.2. Composition of microemulsion

In addition to the HLB number, relative composition of each components of microemulsion, i.e. the amount of oil phase, surfactant, and aqueous phase, must be controlled to obtain a stable microemulsion solution.

From the literatures, several types of the microemulsion systems for making inorganic nanoparticles were surveyed and summarized as in Table 5. For the comparison of those systems, water-to-surfactant molar ratios were calculated. With larger value of water-to-surfactant ratio, more amount of water phase can be mixed into the microemulsions system with a given amount of surfactant. Since the particles are formed in the water droplets, more particles can be produced with more water phase.

Table 5    Some microemulsion systems in the literatures.

| System | Product | Water-to-surfactant molar ratio | Ref. |
|---|---|---|---|
| Triton X-45 / cyclohexane / water | Silica seed particles for titania coated silica | 2.33 | [92] |
| (Triton X-100:hexanol)[1] / cyclohexane / Water | Titania | 18.1 | [93] |
| NP-5 / cyclohexane / $NH_4OH$ | Silica | 0.7-5.4 | [94] |
| (NP-5:NP-9)[2] / cyclohexane / $NH_4OH$ | Silica | 4.2 | [95] |
| Hypermer B246 / $C_{12}(OE)_5$ / HCl / isooctanol / isooctane | Silica | 4.0 | [96] |

Among the microemulsion systems in Table 5, (Triton X-100:hexanol) cosurfactant system shows highest water-to-surfactant molar ratio, which means this system is advantageous over other systems if the water phase has to be dispersed more with the same amount of surfactant.

---

[1] Surfactatn mixture of Triton X-100 and hexanol
[2] Mixture of NP-5 and NP-9

### 2.3.3. Production of nanoparticles from microemulsions

The use of W/O inverse microemulsion as a reaction media, to obtain silica particles for chromatographic applications is a common practice in industry[86]. In the W/O microemulsions, nano-meter sized aqueous droplets will act as the nano reactors where the formation of nanoparticles takes place through the sol-gel processes. In case of silica particle formation, the hydrolysis and polycondensation of the silica precursor (in general tetraethoxysilane, TEOS) occur in the aqueous droplets [87, 88].

As catalysts for those reactions, ammonia or hydrochloric acid can be used. It is reported that relatively small dense silica particles could be obtained using ammonia as a catalyst, while large mesoporous particles with hydrochloric acid [96, 97]. Esquena et al. claimed that they've got the mesoporous silica particles from a W/O microemulsion system using HCl as catalyst.

Microemulsion technique also can produce organic-inorganic nanocomposites when organic and inorganic precursors were mixed in a dispersed droplet [88]. There are several examples for organic-inorganic composites produced by microemulsions [98-101]. V. Uricanu et al prepared an organic-inorganic hybrid films using organoalkoxysilane to create inorganic network combined with polymer network. The composite film showed high resistance against solvent attack. Y. Deng et al produced magnetic polymeric composite nanoparticles using inverse microemulsion process. Y. Lu et al claimed that they could produce nonporous discontinuous structure using microemulsion technique, one being hydrophilic polymer and the other being hydrophobic polymer. Even though there are lots of examples for composite nanostructures, but there is no noticeable report about making nanocomposite between silica and electrochromic conducting polymers with microemulsion processes.

### 2.4. Summary of the state-of-the-art

Electrochromism refers a reversible and persistent color change of material during the electrochemically induced oxidation and reduction. Electrochromic films have been applied to the devices such as an efficient smart windows and a high contrast non-emissive information displays. As a feasible candidate for the conventional emissive displays, electrochromic displays are attracting much attention recently. Electrochromic

displays have many advantages over conventional LCDs such as wider viewing angle, high contrast rate, and possibility of achieving multiple colors with a single material.

From the literature survey [2, 3, 13], it was found that there are two types of electrochromic material: a) inorganic transition metal oxides, b) polymers such as polyaniline. Ever since the discovery of electrochromism in transition metal oxides, almost all efforts have been devoted to the inorganic materials. In recent years, however, polymer materials are gaining attentions because of the possibility of being applied to the flexible display devices. By a summary of the results of other researchers' previous works [2, 25], It could be said that conducting polymers such as polyaniline and polypyrrole are more suitable material for the electrochromic displays since they exhibit faster response and longer operating life than the inorganic material. However, it still has problems for the display applications.

The response times of polymeric materials could reach down to 10 ms, which is short enough for a display device application. On the other hand, the operation life time runs far behind compared to liquid crystal. Even though the operation life cycle of conducting polymers is larger than inorganic material, but the maximum operating life cycle of polymer films is only $10^6$ cycles while the average operating life cycle of conventional LCDs is more than $10^8$ cycles. Therefore, it could be said that an enhancement of operation life time is necessary for the electrochromic displays to be realized.

From the literature survey [5-7], it could be found that the limited operating life time of the polymers might be closely related to the electrochemical stability of the materials. For some conducting polymers such as polypyrrole and polyaniline, electrochemical degradations occur when sufficiently high anodic potentials are applied [46]. This means the electrochemical stability must be increased for an enhancement in operation life time of the electrochromic material. The next question would be how we could increase the electrochemical stability of polymer electrochromic material.

It has been demonstrated that the electrochemical stability of polymer materials could be improved by forming composites with chemically stable inorganic (i.e. $SiO_2$, $Al_2O_3$) particles or matrixes [47-50]. Actually the inorganic-organic nanocomposite materials have gained much attention since they shows interesting and still unexpected properties [10]. Those composites are made by dispersing inorganic nanoparticles into the polymer matrix or by incorporating polymers into a host silica matrix. With many

efforts of former research works, we could find several different ways to produce polymer nanocomposites [58-60]. As example, sol-gel fabricated silica nanoparticles can be dispersed by compounding in a polymer matrix to form composites. The strong interaction between the surface group of silica particle and polymer seems to reduce the direct interfacial reaction between polymer and attacking electrolytes [49].

With the literature survey, it could be simply concluded that for the enhancement of operation life time of polymer electrochromic material the increase in electrochemical stability is necessary, and for the increase of electrochemical stability of the material the inorganic-organic composite structure could be used. Then the next step is to select materials for this study to show an example of increase in stability by using the composite method.

As an electrochromic polymer, polyaniline was selected. Polyaniline is the well-known and frequently studied conducting polymer which could easily polymerized in an aqueous condition only by using appropriate oxidation agent. A synthetic method of polyaniline is rather well established by former research works. The conductive polyaniline films can be easily obtained by a polymerization of corresponding monomer aniline either by using oxidation agents such as ammonium peroxodisulfate [34] and benzoyl peroxide [35] or by an electrochemical polymerization. A UV photo processing can also be used for polymerization [36].

As an inorganic part of the composite, silica was selected. Silica is a frequently used material for the inorganic-organic composite structures [67]. Using a well-established sol-gel chemical process, silica-organic composite material could be easily made while keeping temperature within a range where the organic part could survive without losing its structural integrity. Thus in this study, the silica/polyaniline composite structure was explored for the enhancement of chemical stability of polyaniline as an electrochromic material.

To obtain enhanced electrochemical stability without losing the response speed of material, the structure of the composite was designed as nanoparticle. Since the material would be applied to an optical electrochromic device, to avoid Rayleigh scattering, the size of the particle would rather be suppressed under 50 nm. The increased surface area of nanoparticle could maintain the response speed.

For this purpose, a particle size controlling method which will guarantee the composite particle size to be under 100 nm is necessary. To control the size of

nanoparticles, microemulsions have been studied worldwide. Microemulsion has big application possibilities such as chemical nanoparticle synthesis, cosmetics, pharmaceuticals, agriculture, and bio-organic reactions [86-88]. There are two types of microemulsions which are oil-in-water (O/W) microemulsion and water-in-oil (W/O) microemulsion.

The use of W/O inverse microemulsion as a reaction media, to obtain silica particles for chromatographic applications is a common practice in industry [86]. In these cases, W/O microemulsions are transparent and isotropic liquid media. They are composed of continuous oil and discrete nanometer-sized aqueous droplets which are dispersed in the media and stabilized by ionic and non-ionic surfactants or surfactant mixtures. In the W/O microemulsions, nano-meter sized aqueous droplets will act as a nano-sized reactor. In case of silica particle synthesis, the hydrolysis and polycondensation of the silica precursor occur in the aqueous droplets [87, 88].

From the literature survey it was also found that using the microemulsion technique organic-inorganic nanocomposites can be produced when organic and inorganic precursors were mixed in an emulsion droplet [88]. There are several other examples for organic-inorganic composites produced by microemulsions [99-101].

With these findings from the literature survey, it could be once more summarized as in Fig. 9 that the slow response and limited operation life time of the electrochromic material must be overcome for the further application to the display devices. Until now the electrochromic films were prepared by depositing either inorganic transition metal oxides or organic polymers showing the limited operation life time. However, no noticeable work has been done with the inorganic-organic composite material in form of nanoparticle to overcome the limited operation life time. The limited operation life time could be ascribed to the limited electrochemical stability of the material, and the stability of the organic material was found to be increased with the hybridization with the inorganic components. Therefore, in this study, the necessary enhancement of electrochemical stability of polyaniline for the enhanced operation life time could be tried by making silica/polyaniline composite nanoparticle. For that purpose of preparing composite material in form of nanoparticle, a microemulsion synthesis method would be employed, since it could provide the stable nano-sized reaction reservoir. The electrochemical stability would be expected to be enhanced by the composite structure of organic electrochromic material with inorganic support, and at the same time the fast

switching could also be expected when the composite material is prepared in form of nanoparticle with extended specific surface area.
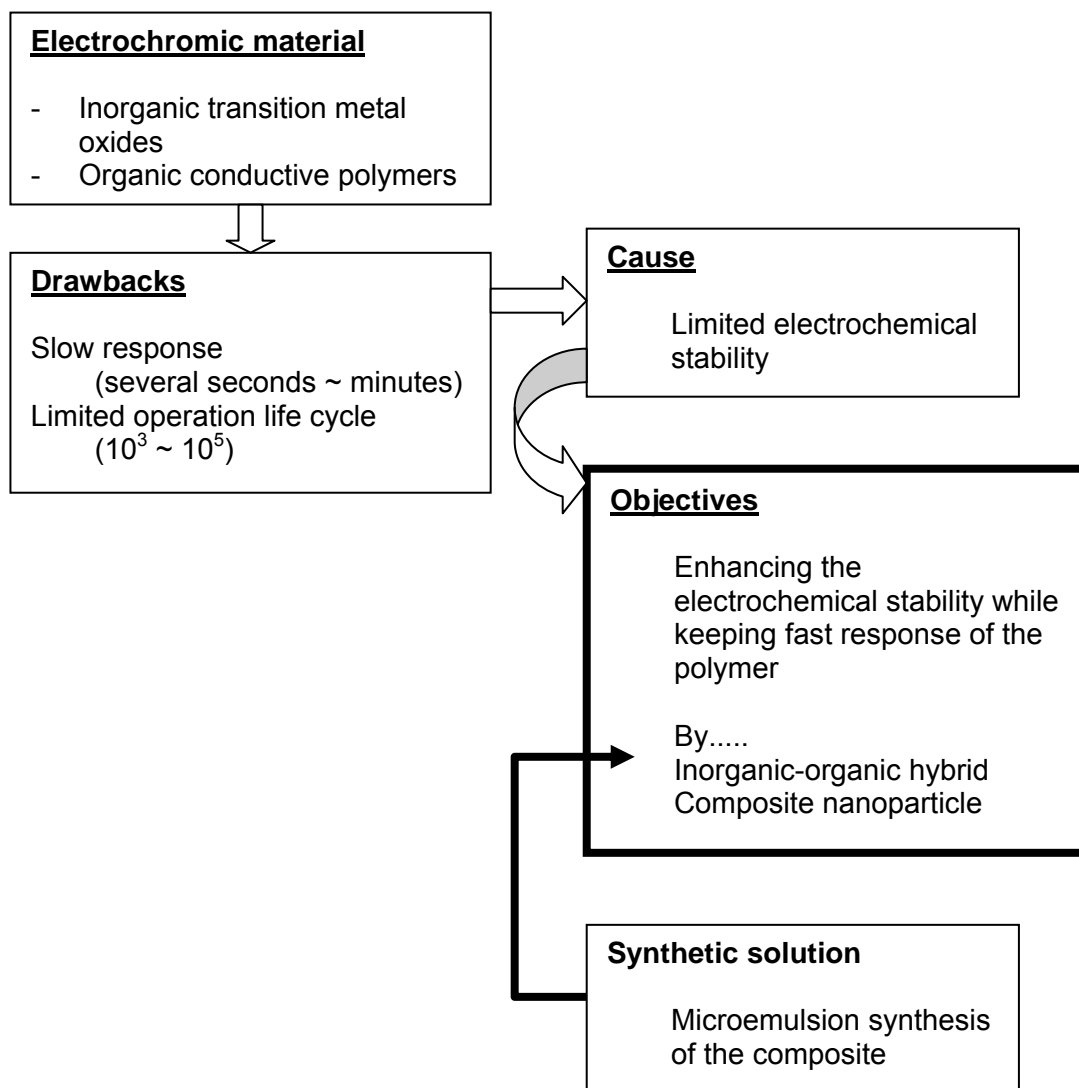


Fig. 9    The summary of the state-of-the art, and derived objective and corresponding solution.

For this trial, there is one more thing which should be considered for selecting a synthetic condition. It's the catalyst for the synthetic reaction of silica and polyaniline. The catalyst for producing silica nanoparticle from microemulsion is mostly ammonia. It is reported that relatively dense silica particles could be obtained using ammonia [87, 94], i.e. in basic condition. However, the polymerization of polyaniline will mostly occur

in acidic solution. Therefore, the synthetic reaction of silica nanoparticle would necessarily be done in an acidic condition, since both the synthetic reaction of silica and polyaniline should occur in a same reaction media.

From the literatures, it could be found that relatively large mesoporous particles could be obtained from microemulsion solution with hydrochloric acid [96, 97]. J. Esquena et al. claimed that they got the mesoporous silica particles from a W/O microemulsion system using HCl as catalyst. Even though there are a few examples, the making porous silica nanoparticle from an acidic microemulsion seems to be an uncommon practice.

Regarding the inorganic-organic composite nanoparticle production, there is no noticeable report about making nanocomposite between silica and electrochromic conducting polymers with microemulsion processes. Therefore, it could be a rather new challenge for producing silica / polyaniline composite nanoparticle as the electrochromic material.

Thus in this study, a new method for the enhancement of electrochromic properties of polymer material would be proposed and the corresponding scientific significance can be stated as follows;

1) Inorganic-organic composite structure of material is used for the electrochemical stability enhancement of the electrochromic polymer.

2) A production of porous silica nanoparticle and composite nanoparticle of silica/polyaniline is tried using an acidic catalyst rather than basic catalyst which is not so commonly tried.

3) For the preparation of composite nanoparticle of electrochromic material, a microemulsion synthetic process is used.

## 3. Objective

As a result of the literature survey, it can be stated that a considerable improvement in chemical stability of electrochromic material is necessary for an enhancement of operation life time of electrochromic polymers. It could also be understood from the results of many research works that the chemical stability of polymer material should be able to be improved by making composites with inorganic component [57]. Therefore the objective of this study can be condensed as improving electrochemical stability of polymer electrochromic material by forming a composite with inorganic component. Through the investigation on the feasibility of making electrochromic nanocomposite particles with microemulsion a new way to produce inorganic-organic composite nanoparticle would be proposed. This nanostructure material is also suitable for the flexible electrochromic film with improved operating life time.

Polyaniline is a typical conducting polymer, showing electrochromic behavior, and with lot of studies [32-36] on polyaniline, the electrochromic phenomena is well understood. For an inorganic-organic composite nanoparticle, polyaniline was selected as the polymer electrochromic material because it has been studied many times as an electrochromic material that the electrochromic behavior is well understood. With the understanding, the improvement effect on the electrochromic properties of composite structure could also be well explored. In terms of composite structure, polyaniline has another advantage. Since the composite structure between polyaniline and inorganic material has been the object of extensive studies, the synthetic method and properties of material is relatively well understood. The well established processing method of polyaniline is easy to comply with. Polyaniline can simply be prepared by a chemical and/or electrochemical polymerization from aqueous solutions.

As the inorganic component of composite, silica was selected. Silica is one of the most frequently studied inorganic materials for inorganic-organic hybrid. It is quite resistant to a wide variety of chemical attacks. In addition to this, silica is normally an electrical insulator, which means it will not interfere with the electrical properties of the polymer. Silica nanoparticles are easily obtainable through several well established low temperature sol-gel production methods. This is quite essential part for the choice of silica. Since both the polyaniline and silica would necessarily be synthesized in a same

temperature condition. The sol-gel synthetic method could facilitate the room temperature synthesis of silica rather than high temperature melting.

Normally the electrochromic material should maintain optical transparency. Therefore, it is also necessary to make the composite material in a form of nanoparticle and to keep the size of the particle under a certain level to avoid haze when applied to the coating. The size of composite particle should be suppressed under 100 nm. In this study, the composite was designed in a form of nanoparticle. The particle size was targeted under 50 nm.

To control the size of the composite particle, microemulsion synthesis method was employed. Microemulsion is composed of continuous oil phase and discrete nanometer-sized aqueous droplets which are dispersed in the oily media and stabilized by ionic and/or non-ionic surfactants. As can be seen from the previous works, microemulsion is regarded as an efficient way to make monodispersed nano-sized particles. Especially for silica nanoparticle production, microemulsion method is frequently employed. In some cases, composite nanoparticles were also obtained from the inverse microemulsions.

The silica precursor TEOS will be mixed into the continuous oil phase, and be made to diffuse into the aqueous phase by a hydrolysis at the interface. The hydrolyzed TEOS will form mesoporous silica network after the further polycondensation in the aqueous phase [72]. During the reaction, monomers will also be polymerized by the polymerizing agent in the pores of the silica.

If the sol-gel reaction to form silica and the chemical polymerization of polyaniline are occurring simultaneously in the aqueous phase, composite particles in the size range of around 50 nm might be produced. This is possible, because silica could be synthesized in aqueous solution through sol-gel reaction, and polyaniline could also be polymerized in aqueous solution through chemical polymerization process. As the precursors for the silica and the polyaniline, TEOS and aniline were respectively selected.

Since polyaniline can be synthesized effectively in an acidic aqueous solution where HCl is contained as an acidic catalyst, it is designated that silica is also synthesized under an acidic condition. As the polymerization agent for polyaniline, ammonium peroxodisulfate (APS) was selected. APS is most frequently used polymerization agent [79, 80].

Sol-gel synthesized silica tends to form 3-dimentional network of primary particle aggregation, i.e. gel. In the gel network, solutions are trapped in the void spaces which are formed in between the silica network backbone. In the solution the aniline and APS are contained. Therefore, the polymerization of aniline might proceed in the voids of silica gel network. With these reactions, the composite nanoparticle might be produced from the aqueous micelles of microemulsion

If polyaniline is trapped inside the open pores of inert silica particles both chemically and physically as is illustrated in Fig. 10, the electrochemical stability of the polymer will be improved while an electrical contact is maintained through the particles.

A schematic illustration for the composite nanoparticle and its electrical signal flow through the particle could be given as in Fig. 10.
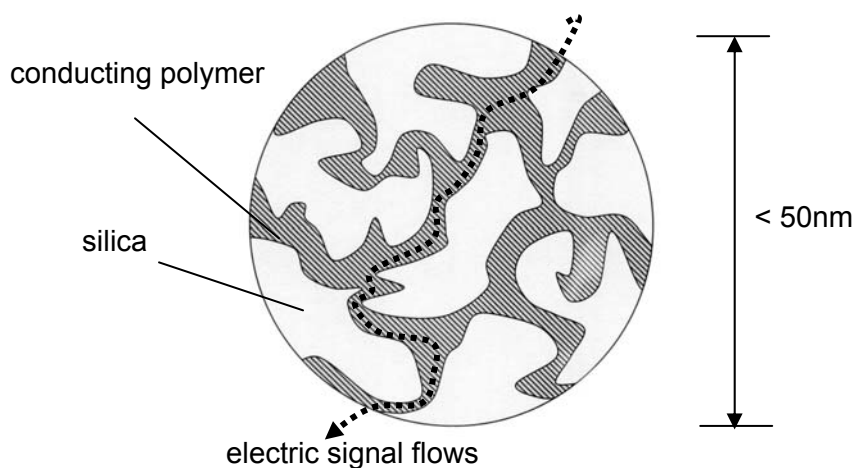


Fig. 10 A schematic drawing of the composite nanoparticle

At first, the production of silica particle will be checked from an acidic microemulsion of which micelles are containing HCl as an acidic catalyst. There are many reports regarding the productions of silica particle from microemulsions using $NH_3$ as a basic catalyst, but very few reports are found using acidic catalyst.

For the particle characterization, transmission electron microscopy (TEM) and BET surface area measurement technique will be used. BET surface area measurement technique is particularly for porosity of particles produced from acidic microemulsion.

If the porous silica particles are successfully obtained, silica/polyaniline composite particle will be tried in the microemulsion. As the analytical tools TEM, Fourier Transform Infrared (FTIR) spectroscopy and BET surface area measurement will be used. The BET surface area measurement technique combined with heat treatment for the composite particle would give the information about the structure.

The obtained composite particle will be deposited onto a transparent conducting glass substrate. With the coated sample, electrochromic properties of the composite material will be checked and compared with those of pure polyaniline film. With the comparison of durability against cyclic switching potential, the enhanced operation life of composite material would be verified.

## 4. Experimental part

Experimental works in this study can be divided into four parts; 1) finding microemulsion composition which will be used for the synthesis of particles, 2) checking the possibility of the synthesis of silica nanoparticle, 3) trying silica/polyaniline composite nanoparticle in microemulsion solution, and 4) checking the electrochromic properties of the composite material.

Before the start of particle production, as a reservoir for the synthetic reaction stable microemulsion condition must be checked. With the checked conditions for the stable microemulsions, a production of pure silica particle was tried. The production of pure silica particle from the microemulsion solution was followed by a synthesis of silica / polyaniline composite nanoparticle. And finally the obtained composite material was then deposited on an ITO-coated glass substrate for a further electrochromic characterization.

## 4.1. Preparation of microemulsion

### 4.1.1. Microemulsions composition selection

The objective of this study is to obtain composite nanoparticle comprising silica as a chemically stable inorganic part and polyaniline as a functional electrochromic polymer part. The composite nanoparticle was synthesized in the microemulsion solution, which controls the shape and the size of the produced particles. In the W/O microemulsions, nano-meter sized aqueous droplets will be formed and they are acting like nano-sized reactors where the formation of nanoparticles takes place through the sol-gel processes.

For a selection of microemulsion composition, it was first be considered that as much water as possible is desirably dispersed into oil medium with a fixed amount of surfactant added. Since the surfactant must be washed away after the particle formation is ended, less amount of surfactant would be desirable. As was discussed at Table 5 in the literature review, a cyclohexane / (Triton X-100 : hexanol) / aqueous phase system has larger water-to-surfactant molar ratio as 18.1 compared to other known microemulsion systems with the ratio from 0.7 to 5.4. Thus in this study, an

inverse (W/O) microemulsion system of cyclohexane / (Triton X-100 : hexanol) / aqueous phase was selected. Triton X-100 is a non-ionic surfactant. The chemicals used are cyclohexane, hexanol, surfactant, precursor of silica, aniline, oxidative polymerization agent, HCl. They were used as received.

Hexanol was used as cosurfactant [102], and cyclohexane is an oily medium. For a microemulsion system which uses Triton X-100 as a surfactant, it is advantageous to disperse more water phase into oil phase when a cosurfactant is mixed with the surfactant. This gives higher water-to-surfactant molar ratio of the system (see Table 5) [102]. This high water-to-surfactant molar ratio ensures that more aqueous phase can be dispersed in the oily medium and as a result more particles could be produced from a microemulsion solution. Using the co-surfactants is also helpful to obtain stable microemulsion while changing the portion of dispersed water phase in a relatively wide range. This could give more freedom to select a better composition for the composite particle production.

At first, a stable microemulsion composition was investigated by changing concentration of Triton X-100 and by changing water-to-surfactant ratio. The composition of microemulsion could be given as the mixing weight ratio for cyclohexane / surfactant / aqueous phase, where surfactant represents mixture of Trion X-100 and 1-hexanol. In this study, this weight ratio of mixing was used to represent the composition of the prepared microemulsion solutions.

The compositional range investigated was cyclohexane 50.0 ~ 80.0wt%, surfactant 12.5 ~ 45.0wt% and water phase 0.0 ~ 12.5wt%. The mixing ratio of Triton X-100 and hexanol was changed according to the HLB of the mixed surfactant. The HLB of the mixed surfactant was changed in a range of 8 ~ 11.

A composition limit of the stable microemulsion could be defined as the point where the micelle concentration exceeds the critical micelle concentration (CMC) for a given mixture of surfactant and continuous medium (in this case cyclohexane) [102]. When the micelle concentration exceeds the CMC by drop-wise addition of the water phase, the solution will become translucent from being transparent. This is because of the phase separation from the microemulsion solution. Therefore, the point of the water phase dispersion limit could be checked as the point where first haze of the solution is appearing. The experimental procedure for the microemulsion composition study is given in Fig. 11.
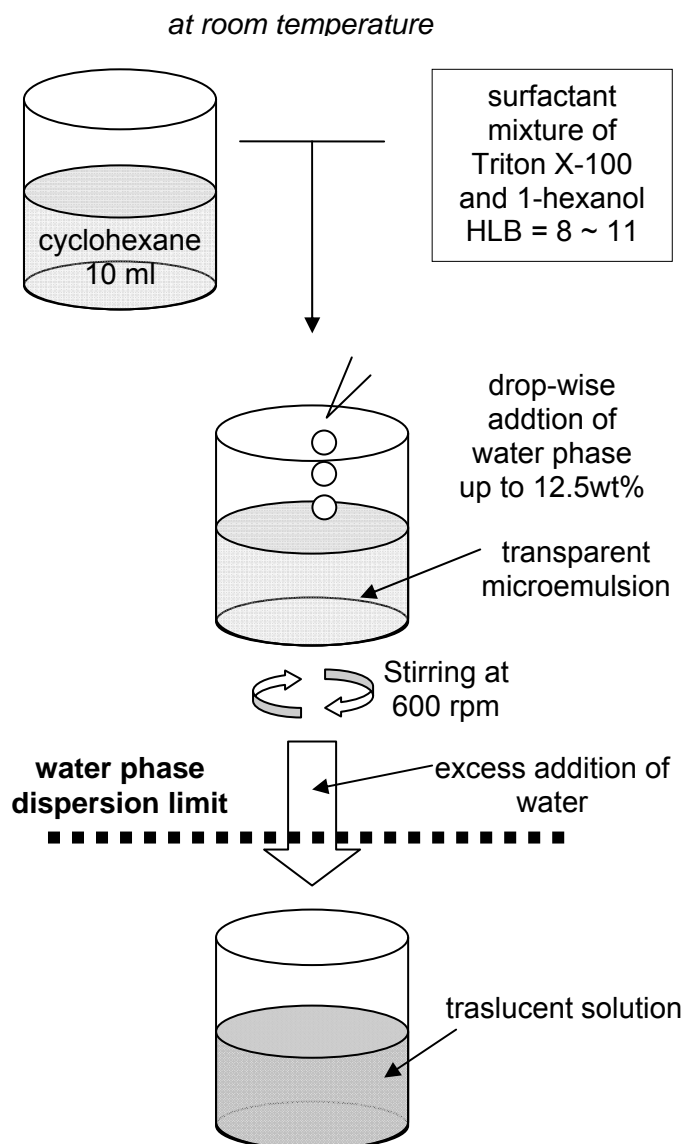
*at room temperature*



Fig. 11 Experimental procedure for checking the composition limit of stable microemulsion (The composition of the solution is given in Table 6 in "Results and Discussions" Part.)

10 ml of cyclohexane was first poured into a glass ware and the mixture of surfactant (Triont X-100 : hexanol) was added. The amount of surfactant mixture was from 1.0 to 6.4 grams according to the designated composition of the microemulsion solution. With the solutions having different mixing ratios of cyclohexane and surfactant, the water phase dispersion limit was checked by checking he haze point while adding

water phase drop-wise. The investigated composition range and its results are given in Table 6 in the "Results and Discussions" part.

The whole experiments were done at room temperature. The mixture of cyclohexane and surfactant was transparent before the addition of water phase, and before reaching the water phase dispersion limit the solution was remained transparent. With these processes the composition limit for stable dispersions of aqueous phase into cyclohexane was obtained.

### 4.1.2. Micelle size characterization

Since the synthesis of composite particle is occurring in the aqueous micelles of microemulsion solution, the size of micelle is an important condition for particle production. The size of particle is confined within the size of micelles. In this study, a production of particle with size less than 50 nm was pursued. Therefore micelle with the size in a similar range would be preferred. To investigate the effects of pH of aqueous phase and mixing ratio of 1-hexanol and Triton X-100 on the size of micelle, the micelle sizes were characterized while the pH and the surfactant mixing ratio were changed.

With the microemulsion composition selected from composition determination experiment, effects of pH of aqueous solution and mixing ratio of 1-hexanol / Triton X-100 on the size of micelles were investigated. The selected composition is given in "5. Results and Discussions" part. The micelle sizes were measured by dynamic light scattering method using photon correlation spectrometer (PCS). For the micelle size measurement by PCS, the microemulsion solution samples were used as received without dilutions. About 2 ml of solution was taken from the prepared microemulsion solutions and injected into one-end closed borosilicate glass tube. Each of the prepared samples was then placed into a toluene reservoir for the measurement.

To see the effect of pH micelles sizes were checked when aqueous phases with different pH values were dispersed into the microemulsion solution. The pH of aqueous solutions was selected as 2, 7, and 12. The effect of mixing ration of hexanol-to-Triton X-100 on the size of micelles was also checked. All the measurements were done in an ambient atmosphere.

## 4.2. Synthesis of porous silica particles

Before the synthesis of composite nanoparticle, a synthesis for pure silica nanoparticles from microemulsion was tried. Polyaniline is produced usually from acidic solutions. For composite particle production, silica and polyaniline are synthesized simultaneously from the same reactor, i.e. micelle. Therefore silica also has to be obtained from the acidic micelles. In this experiment, the production of silica nanoparticle from acidic micelles was demonstrated.

### 4.2.1. Silica synthesis

At first the silica formation in the microemulsion with an acidic catalyst was tried demonstrating that the silica particles could be obtained from an acidic microemulsion solution. For silica particle synthesis TEOS was used as a precursor. The silica precursors were dissolved into the cyclohexane, and the concentration of the precursor was determined by water-to-TEOS molar ratio which was selected as 20 for the whole experiments in this study.

The acidic catalyst of silica sol-gel synthesis was HCl. It was dissolved into aqueous phase before it was dispersed in the microemulsion solution. For a comparison, silica particle was also prepared by using basic catalyst. For a basic catalyst, $NH_3$ was used. The concentrations of HCl and $NH_3$ were adjusted by checking the pH of solution. For an acidic aqueous solution, the pH was 2 and for a basic solution, the pH was 12.

Triton X-100, 1-hexanol and TEOS were first mixed into cyclohexane, and then the prepared aqueous phases were added drop-wise into the mixed solvent, respectively. After the addition of aqueous phase, the microemulsion solution was kept under mild stirring for 24 hrs at room temperature. The whole experimental procedure is given in Fig. 12.
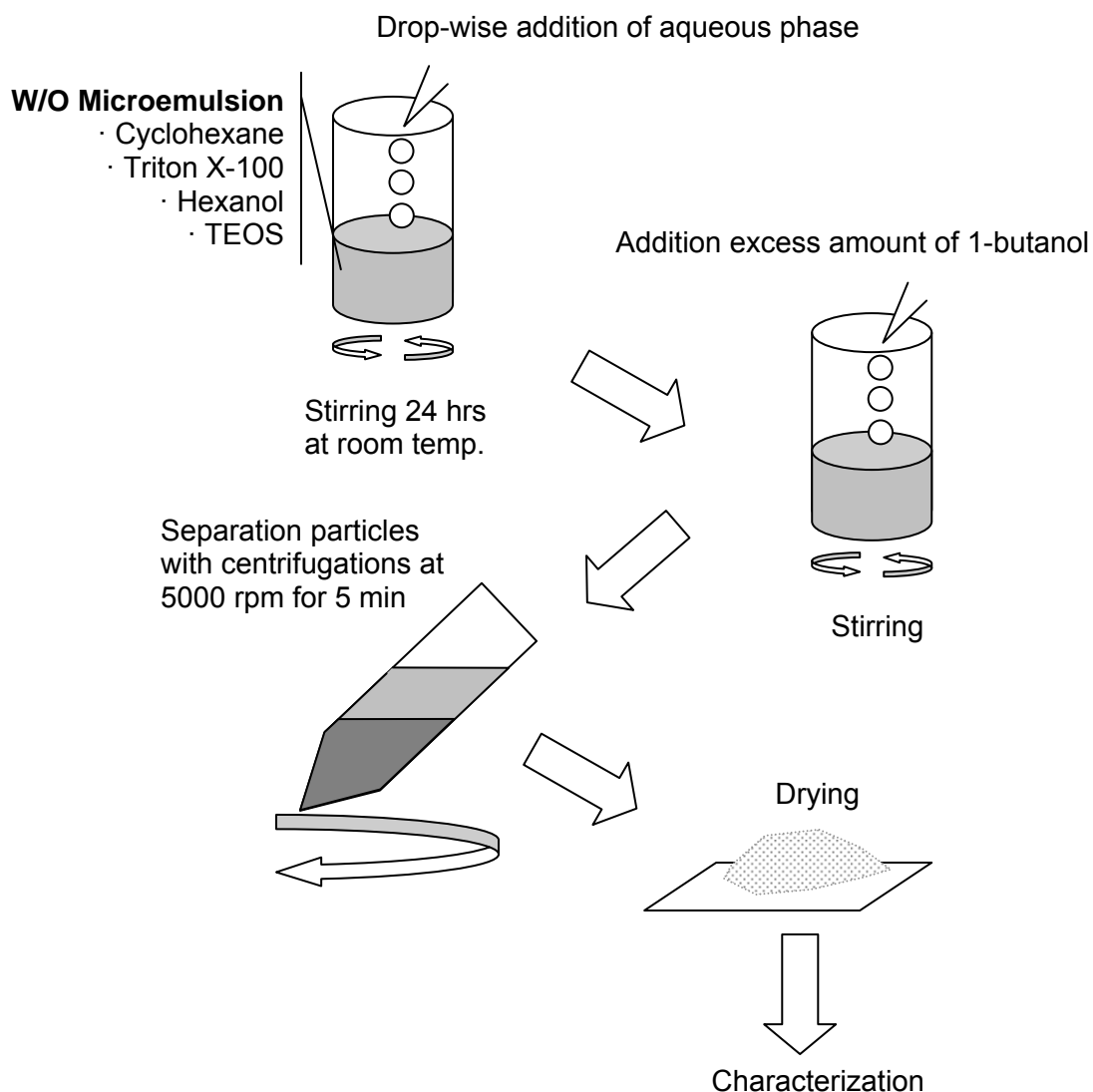
Fig. 12 A schematic illustration for the process of silica particle synthesis.

### 4.2.2. Characterization

For the characterization of particle size and structure, transmission electron microscopy (TEM, see appendix) and BET surface area measurement were performed. For TEM, the microemulsion solution containing silica particle was used. After 24 hrs of stirring, one drop of acidic and basic microemulsion solution was placed on a carbon coated Cu-grid and dried. The dried sample was placed under the microscopy and investigated.

For the further investigations on the structure, particles were extracted from microemulsions. For the extraction of particle from the solution, excess amount of 1-butanol was added to the microemulsions. The addition of 1-butanol leads to the drastic decrease of the critical micelle concentration (CMC) of the microemulsion system [102]. By decreasing the CMC, phase separation will happen, and the particles in the micelles are flocculated. When 1-butanol was added to microemulsions, solutions rapidly became translucent which is the sign of flocculation of particles. This flocculation phenomenon will be discussed in "5. Results and Discussions". Then the solutions were centrifuged at 5,000 rpm for accelerating sedimentation of the flocculated particles. The extracted particles were washed with ethanol to remove the surfactant and the other solvents which probably remains at the surface of the particles. The washing was repeated five times, followed by a drying in a vacuum oven at 120 °C for 12 hrs.

To identify the obtained particle, Fourier transform infrared (FTIR) spectroscopy (see appendix) was performed with the extracted samples in the wave number range from 600 to 2000 cm$^{-1}$. Pellet type samples were prepared by mixing with KBr and pressing.

To investigate the structure of particle, porosity was also checked by a BET surface area measurement technique.

### 4.3. Synthesis of composite particles

With the synthesis composition where porous silica particles were successfully obtained, a production of silica/polyaniline composite particles were tried.

#### 4.3.1. Composite particle synthesis

The microemulsion composition was the same as was used for pure silica particle production. As a precursor for silica TEOS was also used. TEOS was dissolved into cyclohexane. Aniline was used as a precursor of polyaniline. To ensure the synthesis of polyaniline in aqueous micelle, aniline was dissolved into the aqueous solution before dispersion.

Mixed solutions of cyclohexane, hexanol, Triton X-100, and TEOS were first prepared. Two kinds of aqueous solutions were prepared: one with HCl and aniline and

the other with HCl and APS. These two solutions were dispersed to form two microemulsion solutions. Later on, these two microemulsion solutions were mixed. When the aqueous phases were completely dispersed, transparent microemulsion solution was obtained. The mixed solution was kept stirring at room temperature for 24 hrs. The whole experimental procedure to produce silica and silica/PANI composite particles from microemulsion is described in Fig. 13.
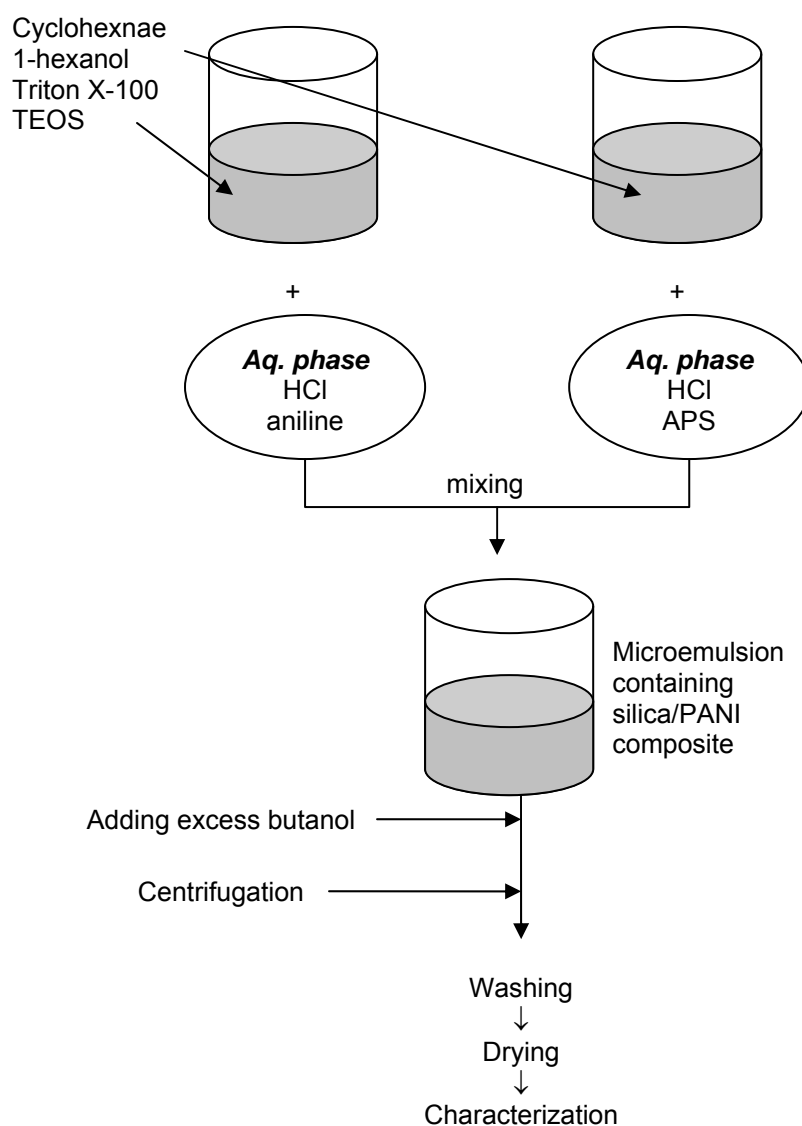


Fig. 13.  The schematic representation of the experimental procedure to produce the silica and silica/PANI composite particles from the microemulsion solutions

### 4.3.2. Characterization

The characterizations of the prepared particle were performed while comparing the pure silica particle obtained from acidic microemulsion.

To determine the size and the shape of composite particle TEM photos were taken. TEM sample was prepared by placing one drop of microemulsion solution containing composite particle on a carbon coated Cu-grid. It was dried and investigated under the microscope.

After 24 hrs of reaction, particles were extracted from the microemulsion solutions. Micelles were broken by adding excess amount of 1-butanol. From the translucent solution, the particles could be separated with the centrifugation. In this study, the solution was centrifuged at 5,000 rpm for 5 minutes. The extracted particles were washed with ethanol to remove the surfactant and the other solvents which probably remains at the surface of the particles. The washing was repeated five times, followed by a drying in a vacuum oven at 120 °C for 12 hrs.

To identify the obtained particle, Fourier transform infrared (FTIR) spectroscopy (see appendix) was performed with the extracted samples in the wave number range from 600 to 2000 cm$^{-1}$. Pellet type samples were prepared by mixing with KBr and pressing.

To understand a physical structure of silica / polymer composite particle, BET surface area measurement technique was used. For the BET surface area measurement, particle sample was dried at 150 °C in vacuum for 2 hrs. The change of the surface area during a heat treatment up to 500 °C in air was investigated. By comparing the surface areas before and after heat treatment, the microstructure of particles was discussed.

To check the enhancement of chemical stability of the composite material, dissolution characteristic of the sample into a formic acid solution was checked. Formic acid is known as an effective solvent to dissolve polyaniline [69]. 10 mg of composite particles were added to the 50 ml of formic acid. The solution was kept under stirring with magnetic bar at room temperature for 24 hrs. The extent of dissolution for the composite sample was compared with pure polyaniline. After the dissolution, remaining particles were separated from the solution by a centrifuge and subsequently were

washed with ethanol and dried at 120 °C in vacuum. FTIR analysis results were compared for the samples before and after the dissolution.

Thermal analysis up to 500 °C in air was also done to measure the weight loss from the composite particle. Before the thermal analysis, the composite particle sample was dried at 150 °C in a vacuum oven to eliminate the effect of the water or solvent evaporation from the weight loss.

## 4.4. Electrochromic cells

The objective of this study is to demonstrate that silica/polyaniline composite structure is serving the enhancement of durability of the material. To check the enhancement in electrochromic properties, the obtained composite particles were deposited on a transparent conducting glass in a form of film. It was assembled into a 3-electrode cell and a 3-layered parallel device. For a comparison, a pure polyaniline film was also prepared by a conventional chemical polymerization coating process.

### 4.4.1. Cell preparation

The synthesized particles were extracted from the microemulsion solution and washed with ethanol 5 times to remove remaining solvents. The washed particles were then dispersed into ethanol again. The dispersion of particle in ethanol was used as the coating solution for spin-coating.

A spin-coating was performed with the prepared solution by injecting 0.25 ml on the rotating substrate which is 5 cm × 5 cm glass coated with fluorine-doped tin oxide (FTO). The substrate was kept rotating at 2000 rpm for 30 minutes after the injection for further drying. The injection and drying were repeated to adjust the thickness of coating. The prepared coating was then heat treated at 150 °C for 2 hrs. The overall process for preparing coating sample was illustrated in Fig. 14.

Aqueous sol.
HCl + aniline

Aqueous sol.
HCl + APS

Keep stirring
for 24 hrs.

Cyclohexane
1-hexanol
Triton X-100
TEOS

Separating
particles with
centrifugations

1-butanol

Particle
characterization

Drying

Dispersion in
ethanol
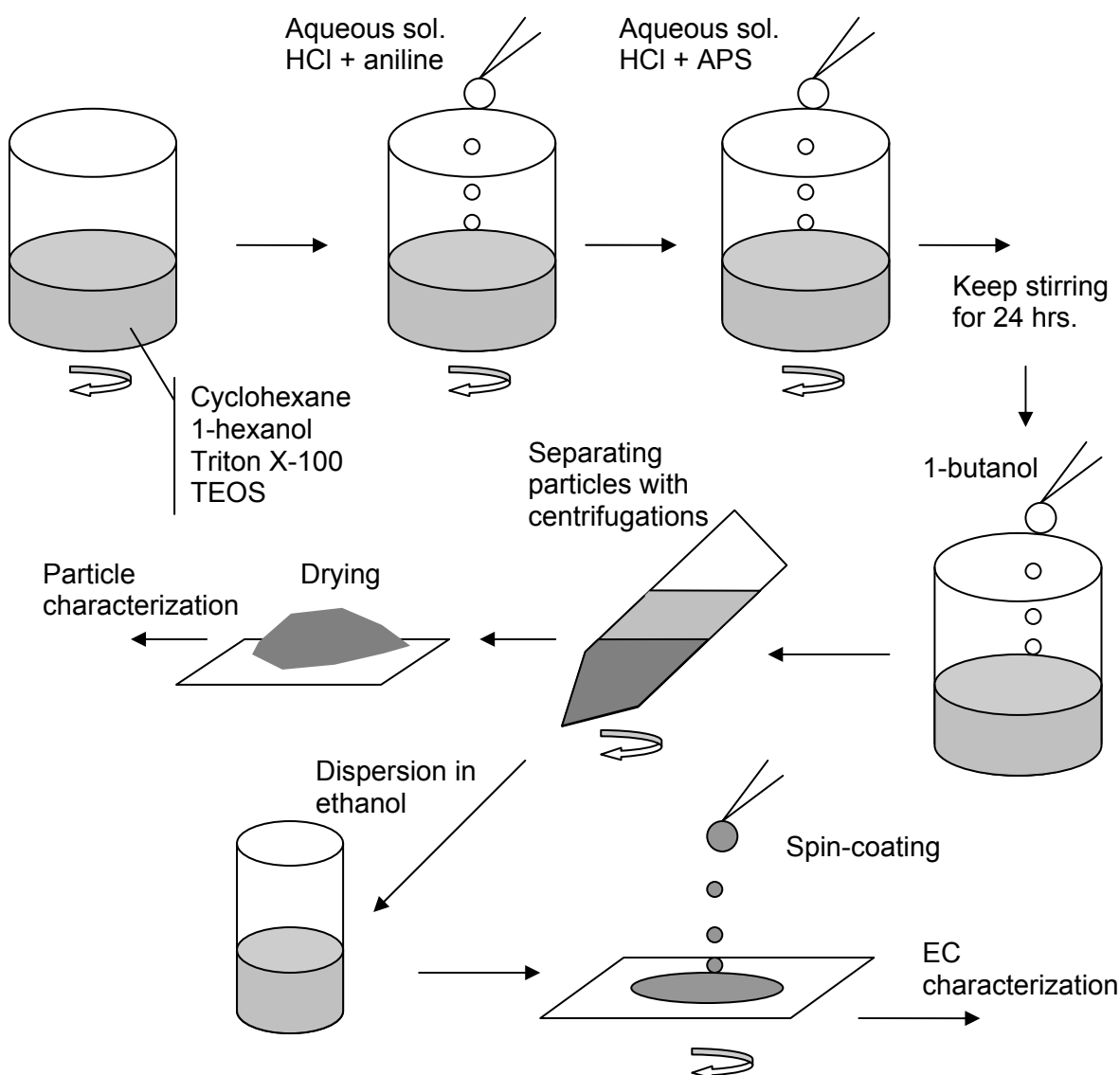
Spin-coating

EC
characterization

Fig. 14   The schematic representation of the experimental procedure to produce the silica and silica/PANI composite particles from the microemulsion solutions.

For a comparison of electrochromic properties, pure polyaniline film was also prepared on FTO-coated glass. The polyaniline film was prepared by a conventional chemical polymerization coating which was carried out in the aqueous solution containing HCl, aniline and APS.

The coating solution for polyaniline was prepared by mixing two solutions which contain HCl + aniline and HCl + APS, respectively. FTO-coated glass with dimension 5 cm × 5 cm was put into the mixed solution and kept for 24 hrs at room temperature.

The coated sample was then thoroughly washed with distilled water. The washed sample was dried at 150 °C for 2 hrs.

For the electrochromic properties measurement, 3-electrode cells (see Fig. 6) were prepared with the prepared composite and polyaniline films. For the electrolyte of the cell, aqueous solution of 1 M $H_3ClO_4$ was prepared. A saturated calomel electrode was employed as the reference electrode and Pt-plate was used as the counter electrode.

With the prepared 3-electrode cell, cyclovoltammogram, transmittance in the visible region and durability test were performed.

With the prepared films of composite and pure polyaniline, a 4-layer electrochromic cell was prepared as illustrated in Fig. 15. The cell comprises aqueous electrolyte, sealing and two FTO-coated glasses on one of which the electrochromic layer was deposited. The electrolyte which is aqueous solution of 1 M $H_3ClO_4$ was filled in the cell. No counter electrode was employed. Two cells were prepared with composite and pure polyaniline film, respectively.
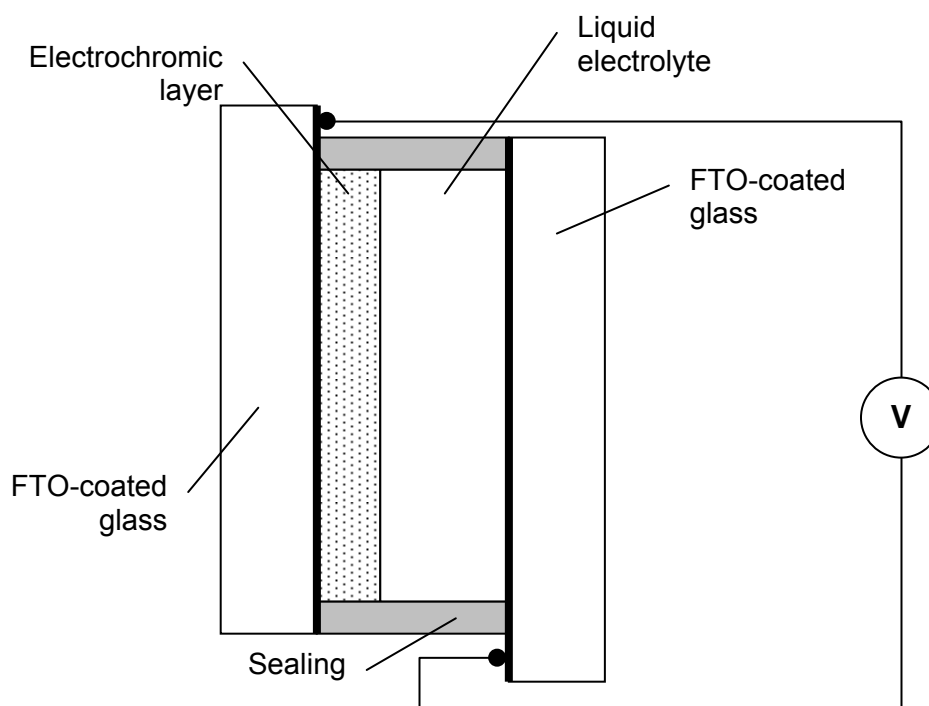


Fig. 15 Schematic diagram of 4-layer electrochromic cell

### 4.4.2. Electrochromic properties characterization

Electrochromic properties characterization was done for the prepared 3-electrode cells.

Using a potentiostat (see appendix) cyclovoltammetry was performed on both the composite and pure polyaniline films. The potential was scanned from -0.2 to 1.0 Volt with the scanning speed of 50 mV/sec.

Transmittance spectra in the visible range from 400 to 800 nm were obtained using UV/VIS spectrometer (see appendix) and potentiostat. For a bleached state, a cathodic potential of -0.2 Volt against reference electrode was applied on the electrochromic layer. For a colored state, an anodic potential of +1.0 Volt was applied.

To check response, coloration contrast and durability of electrochromic layer, transmittance at a fixed wavelength of 600 nm was monitored while potential was switching between -0.2 and +1.0 Volts. Duration of each step was 30 sec.

## 5.  Results and Discussions

As pointed out in the chapter 3, the main objective of this study is to obtain an electrochromic property enhancement effect by the composite material. Thus the objective of the synthesis part is to prepare a silica/polyaniline composite material with suitable properties. For an optical application the composite should be synthesized in a form of nanoparticle in order to avoid light scattering. The production of nanoparticle needs a special technique to ensure a size control in nanometer range. Since the microemulsion synthesis method was employed for the preparation and the size control for the nanoparticles, the first step of experimental work was about establishing the stable microemulsion solution conditions. Then the influences of the micelle size on the silica particle synthesis in the microemulsion solution were investigated. Then it was demonstrated that both silica and polyaniline could be synthesized from the microemulsion solution.

It could be found from literatures that silica and polyaniline are produced usually from different pH conditions of micelles. In most cases, nano-sized silica particles were produced from basic micelles as was demonstrated by Arriagada et al [87]. On the other hand, polyaniline was usually synthesized in an acidic condition [79, 80]. However, in this study, silica and polyaniline had to be synthesized simultaneously in the same micelles. Therefore, a new synthetic condition has to be found either for producing silica particle in an acidic micelle or for producing polyaniline in a basic micelle. However, the oxidative chemical polymerization of aniline in basic solutions is not common. Then it would be easier to find a processing condition to produce silica nanoparticle from an acidic solution.

In sol-gel chemistry, silica bulk could usually be obtained from an acidic solution [72]. For the particle production, the basic condition usually employed for the solution. That's why we could find many tries of silica nanoparticle production from microemulsion solutions containing basic micelles rather than acidic micelles. However, a few examples about using acidic micelles could also be found. Esquena et al [96] demonstrated the production of silica from a microemulsion solution containing acidic micelles. If the silica particle could also be obtained from the acidic condition, then a simultaneous synthesis of silica and polyaniline in an acidic micelle could be also be possible, and, in this study, this was tried.

Then the electrochromic properties for the produced composite particles had to be characterized and compared with pure polyaniline to see the properties enhancement for the composite. The electrochromic properties characterization was done following the general method such as cyclovoltammogram, visible light transmittance change, response time, and operation life cycle.

The whole experimental works in this study were performed following the steps:

1) Finding out stable microemulsion solution conditions with water phase at pH 7 before the addition of TEOS,

2) Producing porous silica particle from the microemulsion solution by adding TEOS to the stable microemulsion solution found from step 1),

3) Producing silica/polyaniline composite particle from microemulsion solution by adding TEOS to the microemulsion solution and by dissolving aniline and ammonium peroxodisulfate (APS) to the water phase,

4) Subsequent preparation and characterization of electrochromic cell using the obtained composite particle,

and hence the results of the experiments were also organized following these steps. A schematic diagram of experimental procedure could be given as in Fig. 16.
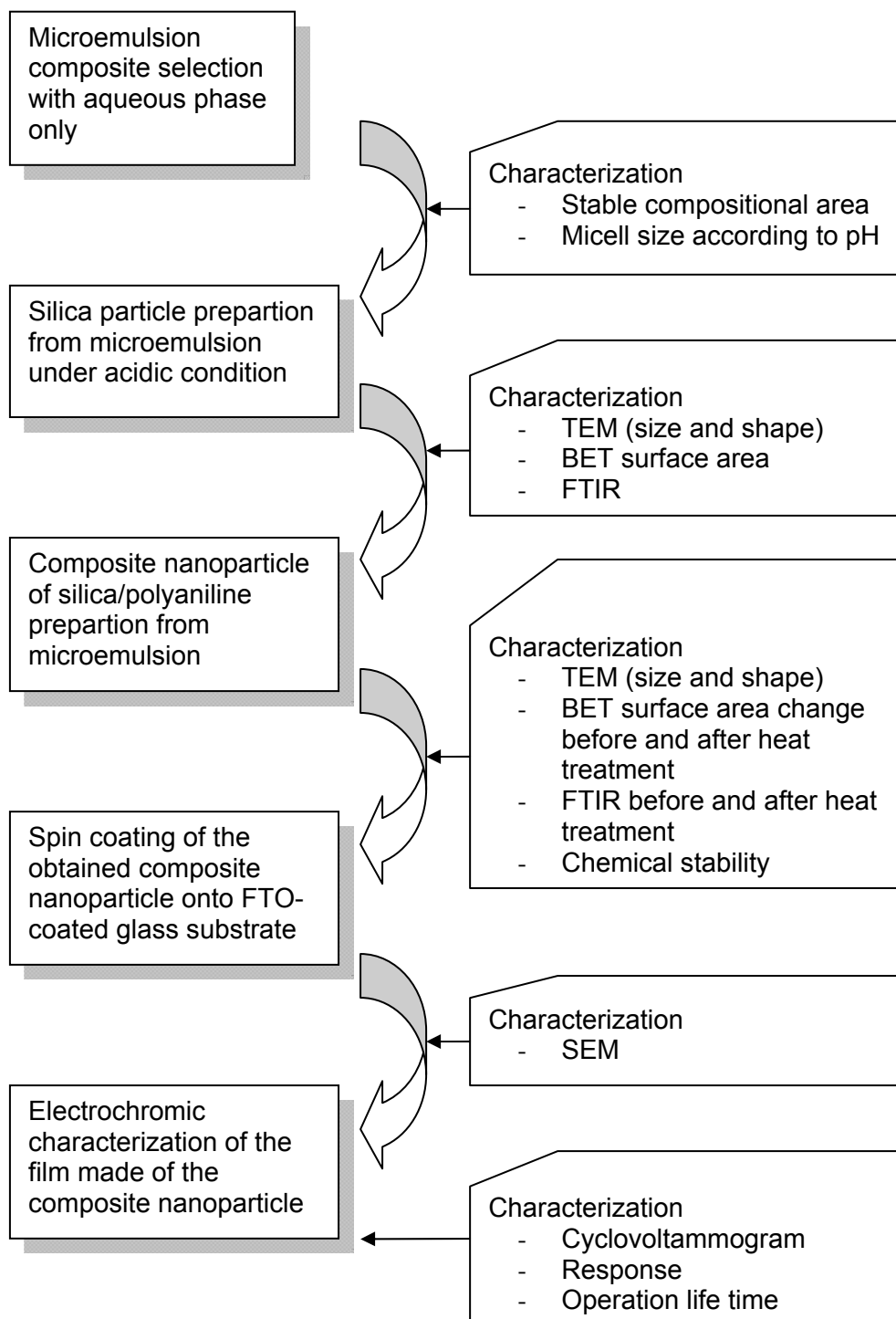
Microemulsion composite selection with aqueous phase only

Characterization
- Stable compositional area
- Micell size according to pH

Silica particle prepartion from microemulsion under acidic condition

Characterization
- TEM (size and shape)
- BET surface area
- FTIR

Composite nanoparticle of silica/polyaniline prepartion from microemulsion

Characterization
- TEM (size and shape)
- BET surface area change before and after heat treatment
- FTIR before and after heat treatment
- Chemical stability

Spin coating of the obtained composite nanoparticle onto FTO-coated glass substrate

Characterization
- SEM

Electrochromic characterization of the film made of the composite nanoparticle

Characterization
- Cyclovoltammogram
- Response
- Operation life time

Fig. 16 A schematic presentation of the whole experimental works

## 5.1. Stable microemulsion solution

In this section, the selection for a composition of stable microemulsion without TEOS and polyaniline was carried out. Cyclohexane, Triton X-100, 1-hexanol, and aqueous phase were mixed and checked whether the stable microemulsion conditions were formed. The aqueous phase in this case is just water at pH 7 without anything else.

Subsequent investigation on the micelle sizes were also done for different compositions and pH values of aqueous phase.

The stability of microemulsion solution and the size of micelles are the important parameters for a production of composite nanoparticle. In the first stage of experimental works, it was intended to get the composition for stable microemulsion solution and the corresponding size of micelle. The relative composition of cyclohexane, 1-hexanol, Triton X -100, and aqueous phase were investigated for different hydrophilic lipophilic balance (HLB) values of surfactant and pH values of aqueous phase.

As a microemulsion solution is a thermodynamically stable dispersion of aqueous droplets into an oily medium, the stable microemulsion solution is generally a transparent solution with no phase separation. The stable state of microemulsion must be sustained for several hours up to several days, since the sol-gel reaction or the chemical polymerization of polyaniline could last for as much as several hours up to one or two days. A HLB is one of the most important parameters to determine the state of microemulsion solution. At different HLB conditions, cyclohexane, 1-hexanol : Triton X-100 cosurfactant system and aqueous phase were mixed to get transparent microemulsion solutions.

The pH of aqueous phase is also an important parameter since the synthetic reaction is undergone at different pHs. The synthesis of silica and polyaniline is performed in a same micelle at a lower pH. The production of silica nanoparticle from an acidic solution is not so common, where as the particle production from a basic solution is frequently tried. Therefore the production of silica in acidic and basic micelles was checked and compared. For that comparison, it is also necessary to check the composition range for stable microemulsion solutions at different pHs.

As was described the experimental part, at room temperature the aqueous phase was dispersed into the mixed solution of cyclohexane, Triton X-100, and 1-hexanol by a stirring at around 600 rpm.

While varying relative amount of each component as cyclohexane, Triton X-100, 1-hexanol, and aqueous phase, solutions were mixed and its transparency was checked by bare eyes. The complete dispersion could be verified by the transparency of the solutions, since thermodynamically stable microemulsion solution doesn't have any phase separation after a dispersion of aqueous phase.

When the aqueous phase is dispersed into an oil phase and acts as the nano-sized reactors for the nanoparticle productions, the size of produced silica nanoparticle will be confined within the size of micelle. Therefore, the size of micelle is another important parameter for nanoparticle production. As was demonstrated by other microemulsion studies, the size of micelles in microemulsion can be changed by varying the composition of microemulsion [103, 104] or by varying the pH of the dispersed aqueous micelle [105]. The sizes of micelles of the stable microemulsion solutions were checked by a dynamic light scattering method as was described in the experimental section.

The results of these investigations were used to keep the microemulsion stable and to control the size of the micelles for further synthesis of the nanoparticle.

### 5.1.1.  Composition range for the stable microemulsion

As a first step, composition change of the solution was performed to obtain a composition range for the stable microemulsion. The composition range for stable microemulsion could be characterized by the amount of water phase dispersed into the solution at a given concentration of surfactant.

The selected microemulsion system in this study is cyclohexane / Triton X-100 : 1-hexanol / aqueous phase, where cyclohexane is the oil phase and Triton X-100 : 1-hexanol is a cosurfactant system. Therefore the compositional change was done by varying those main components of microemulsion; cyclohexane, surfactant mixture, and water phase.

As was described in the experimental part, investigation for stable microemulsion composition was done by dispersing water with pH = 7 without TEOS and polyaniline.

The stable microemulsion composition could generally mean the dispersion limit of water phase into the oily medium cyclohexane in presence of the surfactant. The dispersability of water phase into cyclohexane, i.e. water-in-oil (W/O) microemulsion, can be controlled by changing the HLB of the surfactant system. As was generally explained in the literature [91], the HLB values lower than 10 would be preferable for the better dispersion of the water into the oil. Therefore, in this study, the HLB value of the surfactant system was changed around the point HLB = 10.

The surfactant mixture was prepared by mixing Triton X-100 and 1-hexanol. By changing the mixing weight ratio of these two components, the HLB value of the surfactant mixture was modified. In this experiment, three different mixing weight ratios (Triton X-100 to 1-hexanol) were tried as 1:2, 1:1, 2:1 to change the HLB values around 10, and the resultant HLBs of the surfactant mixture were given as 8.53, 9.78, and 11.02, respectively. The HLB of the surfactant mixture can be given by the HLBs for the components (Triton X-100 and 1-hexanol) and the relative mixing weight ratio as described in Eq. 3. Different amounts of the surfactant mixtures were dissolved into 10 ml of cyclohexane. The detailed experimental condition is given in Table 6.

Table 6    The investigated composition range for stable microemulsion compositions. The water phase used in this system was just distilled water. The pH of water phase was checked as 7.

| # | cyclohexane (g) | Surfactant mixture | | | | | water phase maximum (g) | total weight (g) |
|---|---|---|---|---|---|---|---|---|
| | | Triton X-100 (g) | 1-hexanol (g) | T/H | sub sum (g) | HLB | | |
| H1-1 | 10.00 | 1.36 | 0.68 | 2.00 | 2.03 | 11.02 | 0.41 | 12.44 |
| H1-2 | 10.00 | 1.79 | 0.90 | 2.00 | 2.69 | 11.02 | 0.55 | 13.24 |
| H1-3 | 10.00 | 2.24 | 1.12 | 2.00 | 3.36 | 11.02 | 0.81 | 14.17 |
| H1-4 | 10.00 | 2.65 | 1.33 | 2.00 | 3.98 | 11.02 | 1.08 | 15.05 |
| H1-5 | 10.00 | 3.30 | 1.65 | 2.00 | 4.95 | 11.02 | 1.30 | 16.25 |
| H2-1 | 10.00 | 0.95 | 0.95 | 1.00 | 1.90 | 9.78 | 0.70 | 12.60 |
| H2-2 | 10.00 | 1.28 | 1.28 | 1.00 | 2.57 | 9.78 | 0.89 | 13.46 |

| | | | | | | | |
|------|-------|------|------|------|------|------|------|-------|
| H2-3 | 10.00 | 1.59 | 1.59 | 1.00 | 3.17 | 9.78 | 1.24 | 14.41 |
| H2-4 | 10.00 | 2.10 | 2.10 | 1.00 | 4.20 | 9.78 | 1.56 | 15.76 |
| H2-5 | 10.00 | 3.05 | 3.05 | 1.00 | 6.10 | 9.78 | 1.62 | 17.72 |
| H2-6 | 10.00 | 3.86 | 3.86 | 1.00 | 7.73 | 9.78 | 1.67 | 19.39 |
| H3-1 | 10.00 | 0.52 | 1.04 | 0.50 | 1.56 | 8.53 | 0.84 | 12.40 |
| H3-2 | 10.00 | 0.88 | 1.76 | 0.50 | 2.64 | 8.53 | 1.22 | 13.87 |
| H3-3 | 10.00 | 1.23 | 2.47 | 0.50 | 3.70 | 8.53 | 1.66 | 15.37 |
| H3-4 | 10.00 | 1.82 | 3.65 | 0.50 | 5.47 | 8.53 | 2.03 | 17.50 |
| H3-5 | 10.00 | 2.49 | 4.97 | 0.50 | 7.46 | 8.53 | 2.20 | 19.66 |

After the surfactant mixture was dissolved into 10 ml of cyclohexane, water was added to the solution up to its dispersion limit. The dispersion limit of aqueous phase was measured by the transition point of the solutions from transparent to translucent. When the aqueous phase is dispersed in cyclohexane where the cosurfactant system was dissolved before the dispersion, no phase separation is observed for a stable microemulsion. With no phase separation, the solution is transparent. Therefore, a stable microemulsion can be confirmed simply by checking the transparency of the solution with bare eyes.

The photos for the transparent solutions within the composition range for stable microemulsion and for the unstable solutions beyond the dispersion limit of aqueous phase are given in Fig. 17.a and b, respectively.

The HLB of the surfactant is a determining parameter for the type of microemulsion either W/O or O/W. The lower HLB number favors W/O microemulsion. Therefore, it is expected that more aqueous phase could be dispersed for the microemulsion with lower HLB number. By checking the dispersion limit of the aqueous phase (Fig. 17) at the given concentration of cosurfactant, a ternary phase diagram was obtained as is given in Fig. 18.
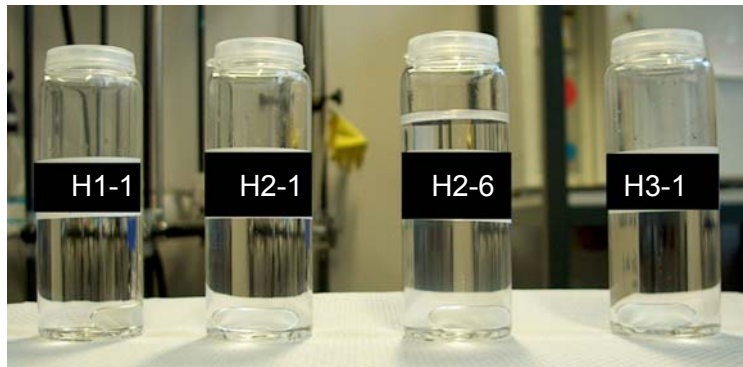
(a)



(b)

Fig. 17 Microemulsion solutions: (a) transparent solutions within the stable microemulsion composition range and (b) translucent solutions beyond the dispersion limit of aqueous phase.
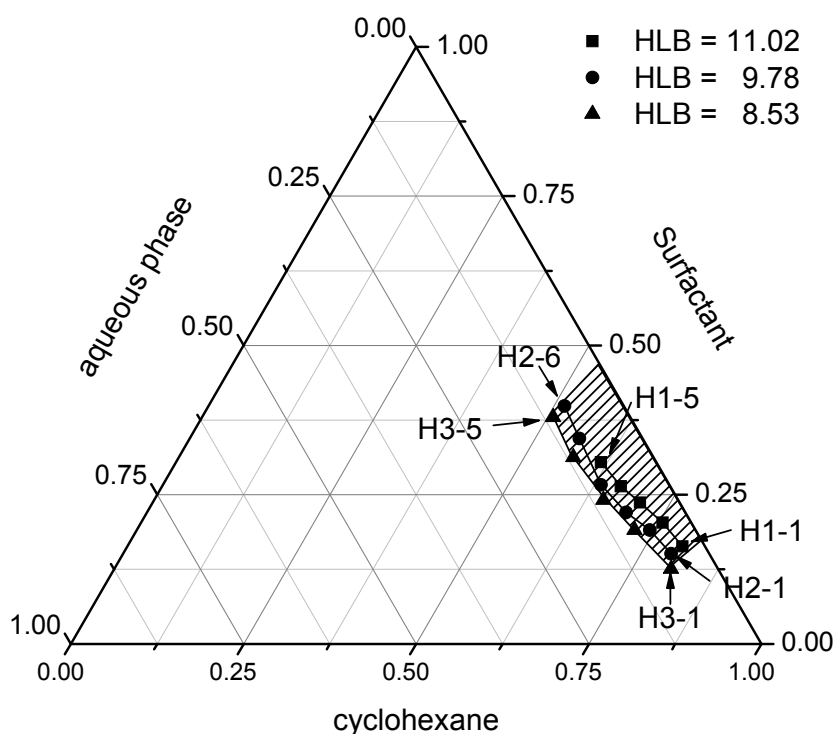
Fig. 18  A ternary phase diagram of cyclohexane / surfactant (Triton X-100 : 1-hexanol) / water phase system at room temperature for different HLBs indicated above (The pH of water phase was 7. The scale of each axis is in weight ratio.)

The shaded area on the graph is represents stable microemulsion composition range. As was expected, the results showed that more aqueous phase could be dispersed into solutions at a given amount of surfactant with a surfactant mixture having lower HLB number.

This result also corresponds to the purpose of cosurfactant system. The mixture of Triton X-100 and 1-hexanol is a frequently used cosurfactant system. The cosurfactant system is to enhance the degree of aqueous phase dispersion [89, 90]. Lower HLB number for the cosurfactant system means larger amount of 1-hexanol in the mixture. When the 1-hexanol – to – Triton X-100 mixing ratio was increased, the HLB number is decreases.

It would also be desirable to use as small amount of Triton X-100 as possible, since Triton X-100 must be washed away from the synthesized particle. For smaller amount of Triton X-100 addition, more 1-hexanol is needed. However, when 1-hexanol is dissolved into solution, it could act as a cosolvent for the aqueous phase [93]. In this case, the aqueous phase is dissolved into cosolvent rather than be dispersed in form of the nano-sized aqueous droplets.

Whether the added 1-hexanol is acting as a cosolvent or not could be checked by a laser light scattering. Generally, the colloidal dispersion of aqueous phase in cyclohexane cannot be seen by bare eyes, since the solution is completely transparent. The alternative way to check the dispersion is to use scattering of visible laser light. The laser light is scattered when it passes through the solution containing aqueous droplets. The scattering was shown as the blurring of light line. When 1-hexanol – to – Triton X-100 weight ratio is larger than 2.5, i.e. the HLB number of mixed cosurfactant system is smaller than 8.17, the scattering was not observed, which means the aqueous phase was dissolved into the cosolvent. Therefore the HLB of cosurfactant system was kept higher than 8.53.

In addition to the HLB effect to the dispersion limit, pH of the aqueous phase could also affect the degree of dispersion in microemulsions. To get the stable microemulsion composition range, one more ternary phase diagram was drawn while the aqueous phases with different pH values were dispersed. For this investigation the HLB of surfactant mixture was set to 9.78, which corresponds to 1-hexanol-to-Triton X-100 = 1. The pHs of the water phase were selected as 2, 7 and 12, and the pH values were controlled by adding aqueous HCl solution for acidic case and $NH_3$ solution for basic case. The dispersion limit was checked with the same method as described above at page 54. The detailed experimental condition is given in Table 7.

The result for the investigation for the effect of pH on water phase dispersion limit is given in Fig. 19. As can be seen from the ternary phase diagram, the aqueous phases with lower pH values could be dispersed slightly more than those with higher pH.

Table 7 The investigated composition range for stable microemulsion compositions. The water phase pH in this system was changed as 2, 7 and 12. The HLB of the surfactant mixture was set to 9.78.

| # | cyclohexane (g) | surfactant mixture | | | water phase maximum | | total amount (g) |
|---|---|---|---|---|---|---|---|
| | | Triton X-100 (g) | 1-hexanol (g) | sub sum (g) | pH | amount (g) | |
| P1-1 | 10.00 | 0.93 | 0.93 | 1.85 | 2.00 | 0.96 | 12.81 |
| P1-2 | 10.00 | 1.22 | 1.22 | 2.44 | 2.00 | 1.27 | 13.72 |
| P1-3 | 10.00 | 1.53 | 1.53 | 3.06 | 2.00 | 1.38 | 14.44 |
| P1-4 | 10.00 | 2.04 | 2.04 | 4.08 | 2.00 | 1.64 | 15.73 |
| P1-5 | 10.00 | 3.13 | 3.13 | 6.26 | 2.00 | 1.96 | 18.22 |
| P1-6 | 10.00 | 4.07 | 4.07 | 8.14 | 2.00 | 2.21 | 20.35 |
| P2-1 | 10.00 | 0.95 | 0.95 | 1.90 | 7.00 | 0.70 | 12.60 |
| P2-2 | 10.00 | 1.28 | 1.28 | 2.57 | 7.00 | 0.89 | 13.46 |
| P2-3 | 10.00 | 1.59 | 1.59 | 3.17 | 7.00 | 1.24 | 14.41 |
| P2-4 | 10.00 | 2.10 | 2.10 | 4.20 | 7.00 | 1.56 | 15.76 |
| P2-5 | 10.00 | 3.05 | 3.05 | 6.10 | 7.00 | 1.62 | 17.72 |
| P2-6 | 10.00 | 3.86 | 3.86 | 7.73 | 7.00 | 1.67 | 19.39 |
| P3-1 | 10.00 | 1.06 | 1.06 | 2.11 | 12.00 | 0.35 | 12.46 |
| P3-2 | 10.00 | 1.32 | 1.32 | 2.64 | 12.00 | 0.78 | 13.42 |
| P3-3 | 10.00 | 1.64 | 1.64 | 3.28 | 12.00 | 1.10 | 14.39 |
| P3-4 | 10.00 | 2.13 | 2.13 | 4.26 | 12.00 | 1.39 | 15.66 |
| P3-5 | 10.00 | 3.11 | 3.11 | 6.21 | 12.00 | 1.45 | 17.66 |
| P3-6 | 10.00 | 3.91 | 3.91 | 7.82 | 12.00 | 1.44 | 19.26 |
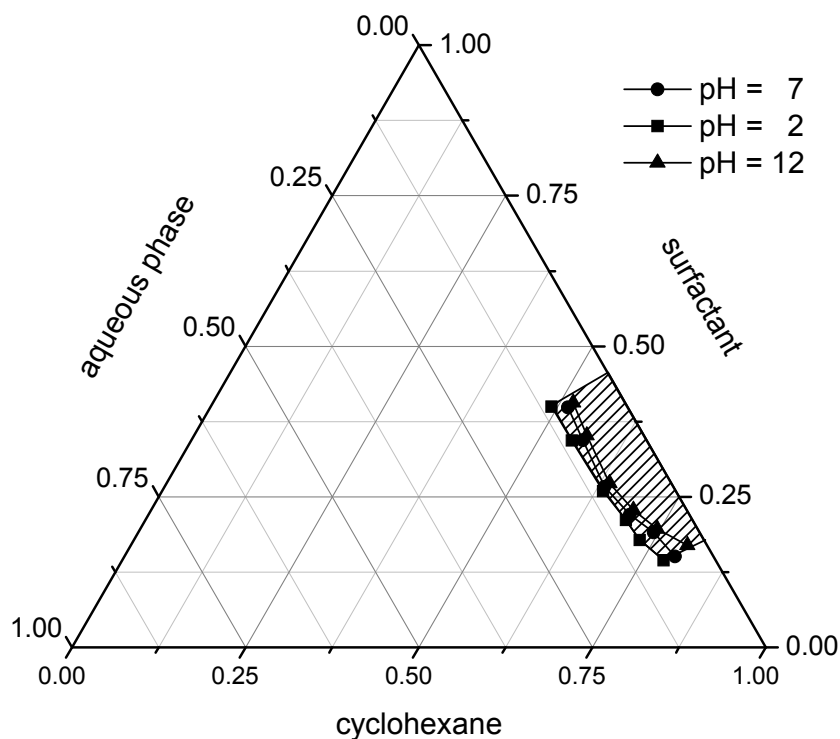
Fig. 19  A ternary phase diagram of cyclohexane / surfactant (Triton X-100 : 1-hexanol) / aqueous phase system for different pHs of the aqueous phase as indicated above; the HLB number of cosurfactant system was 9.78.

From the results of stable microemulsion composition range, one composition point was selected for further investigation and particle synthesis. The composition was selected from the shaded area from Fig. 18 and Fig. 19. The selected composition would necessarily ensure a stable microemulsion solution for the tested HLB conditions of surfactant mixture and for all pH ranges of the water phase. It should be pointed away from the water phase dispersion limit lines. With these considerations, the selected composition could be given as;

65.4 wt% cyclohexane

30.4 wt% surfactant

4.2 wt% aqueous phase.

### 5.1.2. Size of the micelles

Before the synthesis of particles from the microemulsion solutions, the size of micelle was checked to confirm whether it is suitable for the nanoparticle synthesis. The micelles in microemulsion solution were used as reactors for particle synthesis. The size of produced particle would be confined within the size of micelle. Therefore the size of the micelle is an important parameter, which has to be checked before the particle synthesis is tried.

The size of micelle was measured using a proton correlation spectrometer (PCS). As was described in the Experimental part at page 39, small amount of microemulsion sample was put into a borosilicate tube and the tube was placed into toluene reservoir. The microemulsion samples were prepared with a selected composition above (65.4 wt% cyclohexane, 30.4 wt% surfactant and 4.2 wt% aqueous phase) for different HLB numbers of surfactant mixture at a fixed pH 7 of dispersed water phase.

At first, time needed for microemulsion dispersion to reach equilibrium micelle size was checked. For the measurement the microemulsion solution samples were prepared by dissolving a cosurfactant system having HLB number as 8.53 into cyclohexane. An aqueous phase with pH = 7 was subsequently dispersed in the cyclohexane solution. All the process was done at room temperature. After mixing the aqueous phase, samples were picked up at 10, 75, 315, and 1100 minutes of stirring, and the micelle size measurements were done using PCS. The results are given in Fig. 20.

The measured size of micelle remained almost same regardless of the stirring time. This means that the dispersion of aqueous phase reaches equilibrium within 10 min after mixing. When the water was first added to the solution, the stirring is necessary to make the solution homogeneous faster. However, once the solution become transparent with water droplet dispersion, the stirring seems to do no affecting role for the transparent state of the microemulsion solution. The transparent state was maintained when the stirring was stopped. No haze or no phase separation was observed from the microemulsion solutions stored in the shelf for several days or for months. Therefore, it could said that the microemulsion solution is stable within the time span for the synthetic reaction
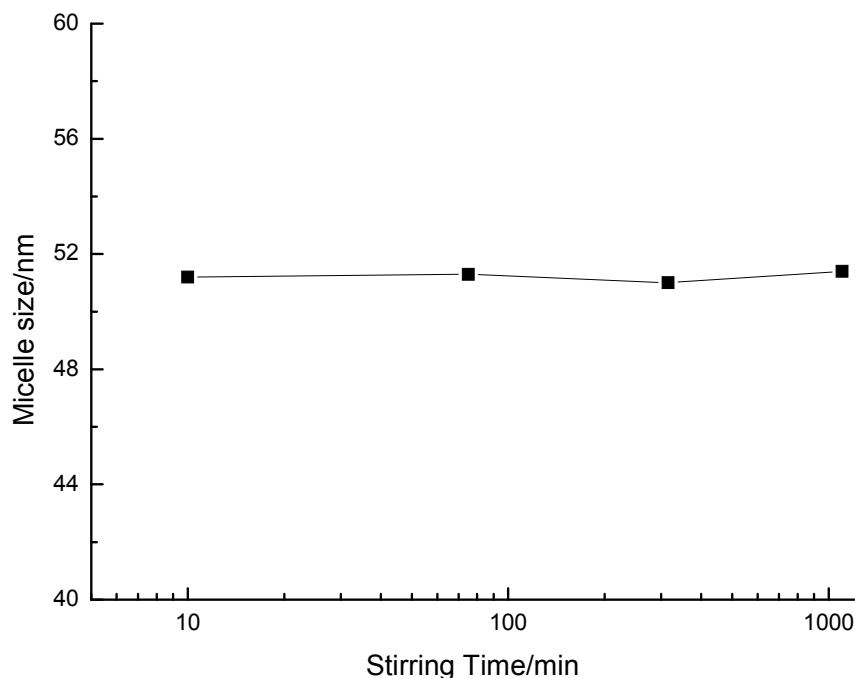
Fig. 20  Micelle size obtained by PCS (see the "Experimental part" at page 39) vs. the stirring time, with a composition 65.4 wt% cyclohexane, 30.4 wt% surfactant and 4.2 wt% aqueous phase, and the pH of aqueous phase = 7

The aqueous phase in this study will have different pH values since the particle synthesis is to be tried in acidic and in basic conditions for a comparison of particle synthesis according to the pH values of aqueous phases. Therefore, it is also necessary to see the pH effect on the size of aqueous micelle, before the start of silica particle synthesis. For this investigation, three different microemulsion samples were prepared by dispersing aqueous phases with pH = 2, 7, and 12. The pHs of the water phases were set by either HCl or $NH_3$ right before the dispersion into the microemulsion solution. The composition of the resultant microemulsion solutions were also set to the composition selected from the phase diagrams (Fig. 18 and Fig. 19) as 65.4 wt% cyclohexane, 30.4 wt% surfactant and 4.2 wt% aqueous phase. The HLB number of mixed surfactant system was 8.53. Micelle sizes were measured also by PCS for those three samples and the measurement results are given in Fig. 21.
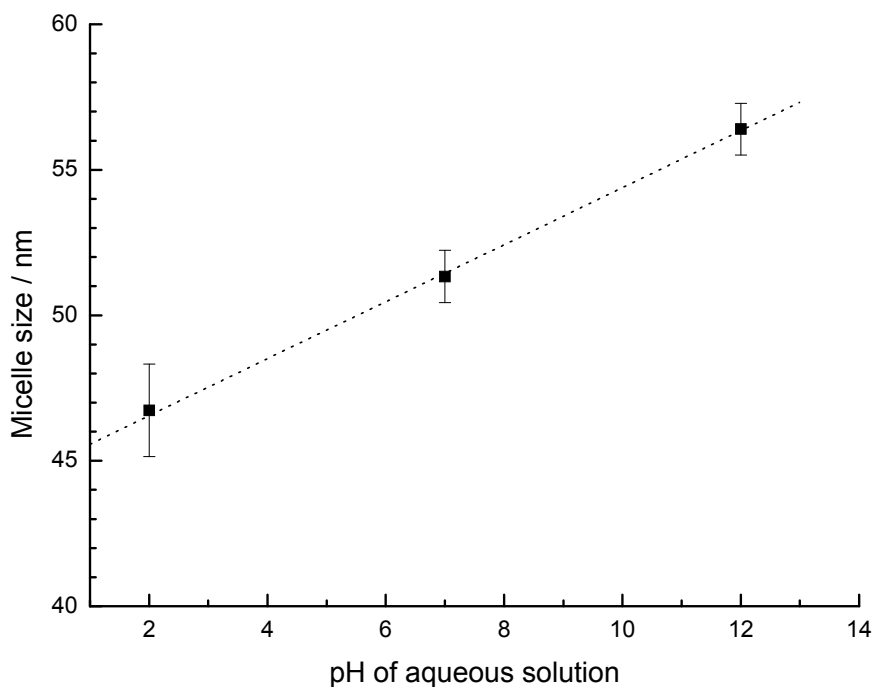
Fig. 21   Micelle size according to the pH of the aqueous phase under the condition of
HLB number of the surfactant mixture as 8.53, with a microemulsion
composition 65.4 wt% cyclohexane, 30.4 wt% surfactant and 4.2 wt%
aqueous phase

For pH values 2, 7 and 12, micelles were obtained in the size range of 45 to 55 nm.
The size of micelles increased with increasing pH. The effect of pH on the size of
micelles in the microemulsion solutions was frequently observed. Rahman et al [106]
pointed out that at a higher pH the dispersed aqueous phase could have increased size
of micelles.

However, the size of micelles still stays below 60 nm in all pH range of the aqueous
solution in this study. With the size range of micelles, the production of nanoparticle
within ~50 nm in size would be possible.

As was observed from the micelle size to time experiment (Fig. 20), the
microemulsion solution also showed the stability once the water phase was dispersed.
No haze or no phase separation was observed after the transparency of the solution
obtained. With the given microemulsion composition as 65.4 wt% cyclohexane, 30.4

wt% surfactant and 4.2 wt% aqueous phase, it could be said that the water droplets were stably dispersed throughout the pH range of 2 to 12.

As was explained above by the microemulsion composition experimental data in Fig. 18, the mixing weight ratio of Triton X-100 and 1-hexanol influences the degree of water phase dispersion. The smaller HLB number of mixed surfactant system increases the degree of dispersion of aqueous phase into microemulsion solutions. The change of degree of dispersion could also affect the size of micelles. Therefore, in this study, the effect of HLB number of surfactant mixture on the micelle size was investigated.

To investigate the effect of HLB of surfactant mixture on the size of micelle, micelle sizes were measured while the mixing ratio of 1-hexanol – to – Triton X-100 was changed that the resulting HLB number of the surfactant mixture was changed from 8 to 11. The microemulsion composition was also the selected one as 65.4 wt% cyclohexane, 30.4 wt% surfactant and 4.2 wt% aqueous phase. The results are given in Fig. 22. Micelle size was decreased as the HLB number of mixed surfactant system was increased. The more 1-hexanol was added, the smaller was the size of micelles.

Usually short chain alcohols such as hexanol are frequently used as the cosurfactant in the microemulsion system. However, as in the study of Yamaguchi [107], the added alcohol could be acting as water-soluble cosolvent as well. In this study, the lipophilic cosurfactant 1-hexanol was added to the microemulsion solution. The added 1-hexanol could also act as a water-soluble cosurfactant. In this case the water could be dissolved into the cosolvent. Then less amount of water would participate in forming aqueous micelle dispersion. Therefore, the observation of micelle size decrease could be ascribed to the cosolvent effect of 1-hexanol.

From the phase diagrams in Fig. 18 and in Fig. 19, a composition of microemulsion was selected as 65.4 wt% cyclohexane, 30.4 wt% surfactant and 4.2 wt% aqueous phase. The HLB number was selected as 8.53 which corresponds to 1-hexanol – to – Triton X-100 mixing ratio in weight as 2. This composition gives stable microemulsion at aqueous phase pH of 2, 7, and 12. The sizes of micelles prepared with the given composition were within range of 45 to 55 nm.
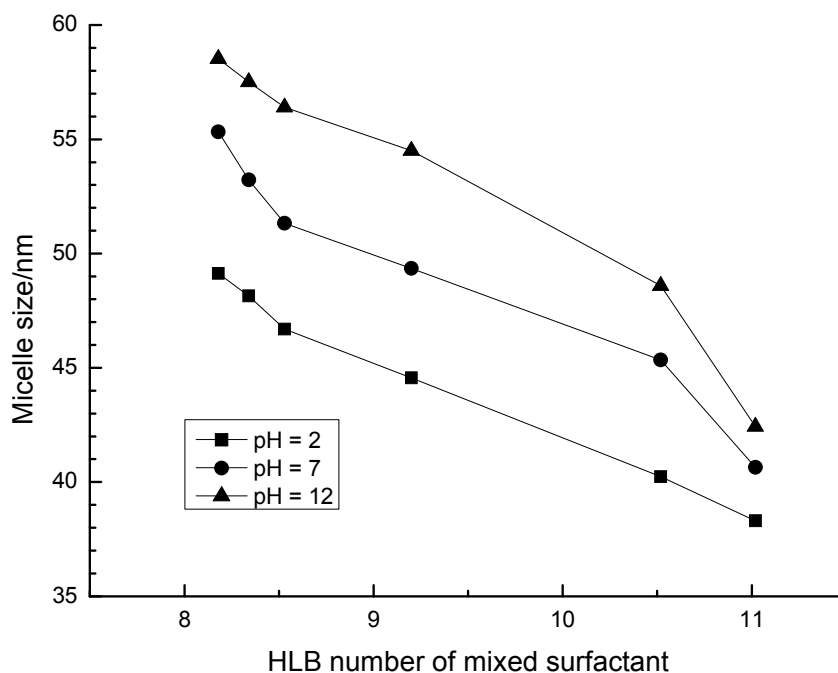
Fig. 22   Micelle size change according to the HLB number of surfactant mixture (Triton X-100 : 1-hexanol) for different pHs of aqueous phase as indicated in the inset of the graph (The composition of microemulsion was selected as 65.4 wt% cyclohexane, 30.4 wt% surfactant and 4.2 wt% aqueous phase.)

## 5.2.  Synthesis of porous silica particle from microemulsion

The composition for the stable microemulsion solution was selected from the studies on the composition range. The size of micelle in the microemulsion for the given composition was characterized. The next step is to verify that silica nanoparticles could be synthesized from the selected microemulsion solution containing acidic aqueous micelles. Then the synthesis of silica / polyaniline composite nanoparticle would follow.

Since the synthetic reaction for aniline into polyaniline usually requires acidic conditions [79, 80], silica must be synthesized in the acidic micelles for the production of composite particle. In this section, the synthesis of silica nanoparticle from microemulsion solution was examined.

Sol-gel synthesized silica in form of nanoparticle is one of the most frequently studied materials for various kinds of applications such as e.g. high performance liquid chromatography [108], drug delivery [109], inorganic-organic hybrid nano composites [71], optical coatings [66] and more. When the nano-sized silica particle is applied in functional coatings, it exhibits advanced properties such as high scratch resistance, chemical stability and optical transparency [58]. Recently many attentions are drawn to silica-organic hybrid nano-composites, since they are expected to have superior physicochemical properties [59, 60].

Several methods have been reported regarding the production of porous silica particles. One of them is utilizing an inverse microemulsion to control the size of the silica particles. The aqueous micelles which are about 50 nm in diameter act as the reaction vessels. Since the sol-gel reaction is confined in the nano-sized reaction vessels, the size of the silica particle and its distribution can be controlled by controlling the size of the micelles. Arriagada et al. [94] have produced monodispersed silica nano particles with diameters of around 50 nm using the inverse microemulsion. They used TEOS as the silica source and ammonia as the catalyst for the hydrolysis and the polycondensation. In almost all the other microemulsion synthesis, a basic catalyst is used [92, 94]. When the particle growth is taking place under basic conditions, the resulting particles would be dense and spherical, following the Ostwald ripening model [72]. Silica particles obtained from the basic micelles in the microemulsion are therefore also dense and spherical.

However, the synthetic reaction of polyaniline will usually occur in the presence of acidic catalyst. In this study, polyaniline will be synthesized by chemical polymerization process. For the chemical polymerization of aniline, ammonium peroxodisulfate is used as an oxidative polymerization agent. Because of the APS, the aqueous would solution become acidic. Therefore, when the silica/polyaniline composite structure is concerned, acidic catalyst would rather be used for the synthesis of silica.

To produce the composite nanoparticle from the microemulsion solution the silica particle would necessarily be synthesized from the micelles under the acidic condition. However, not many examples for the utilization of an acidic catalyst in the synthesis of silica nanoparticle from microemulsions are found in the literatures. There have been attempts to use emulsions which provide much larger micelles than the microemulsion. Esquena et al [96] demonstrated that porous silica particles could be obtained from an emulsion system, but the size of the particles were over 1 $\mu$m. Few examples could

also be found about using acidic micelles in a microemulsion for producing porous silica particles. Wang et al [110] made nano sized (~30 nm) porous silica particles from a microemulsion solution using sodium silicate as the silica source. However, the obtained silica particles were inevitably containing the sodium as an unwanted impurity. Therefore, a more refined precursor must be used for particle production to avoid the impurities.

In this section the possibility of producing silica nanoparticles from an inverse microemulsion was demonstrated using TEOS and HCl as an acidic catalyst. The size, the shape, and the surface area of obtained particle were compared with that obtained using basic catalysts. The synthesis method which uses the acidic micelles could be applied later on to produce silica/polyaniline composite nanoparticles.

### 5.2.1.  Particle synthesis from the microemulsion

A synthesis of silica particles were tried in the microemulsion solutions with the composition 65.4 wt% cyclohexane, 30.4 wt% surfactant and 4.2 wt% aqueous phase, which was selected by the stable microemulsion composition experiment results (see Fig. 18 and Fig. 19). As a precursor of silica TEOS was added into the solution as was illustrated in Fig. 12.

The water-to-TEOS molar ratio is an important parameter for silica sol-gel reaction, since water is a key component for the hydrolysis reaction of TEOS for a given microemulsion solution composition, the amount of dispersed aqueous phase was fixed. Then the water-to-TEOS molar ratio is to be controlled by changing the concentration of TEOS which is dissolved into cyclohexane.

To select the water-to-TEOS ratio, the literatures were referred, which were dealing with silica synthesis from microemulsions. Esquena et al [96] selected water-to-TEOS molar ratio as 6, Osseo-Asare et al. [94] 7.8, and Fu et al. [92] larger than 7.5. These cases were using surfactants other than Triton X-100. When Triton X-100 and acidic aqueous phase were employed, the water-to-TEOS molar ratio could reach up to 63 [111].

In this section, production of silica from the microemulsion solution was observed at various water-to-TEOS molar ratios. At first the calculated amount of TEOS was dissolved into cyclohexane. Then the surfactant system was dissolved into the solution.

The aqueous phase was then dispersed into the cyclohexane solution containing the TEOS and the surfactant. Solutions with different amount of TEOS were prepared and the mixed solutions were kept under mild stirring (600 rpm) at room temperature for 24 hr. The mixed solutions were all transparent all through the reaction time. After 24 hr of stirring, the access amount of 1-butanol were added into the solutions, and then it was checked whether precipitation was occurring. To compare silica production according to the pH of the aqueous phase, two sets of samples were prepared using acidic (pH = 2) and basic (pH = 12) aqueous phase, respectively. The results were given in Table 8.

Table 8    Production of silica from the microemulsion solution with various water-to-TEOS molar ratios

| Water-to-TEOS molar ratio | pH of aqueous solution | |
|---|---|---|
| | 2 | 12 |
| 10 | Gel like precipitation [1] | Gel like precipitation [1] |
| 15 | Gel like precipitation [1] | Precipitation |
| 18 | Precipitation | Precipitation |
| 20 | Precipitation | Precipitation |
| 22 | Precipitation | Precipitation |
| 24 | Precipitation | No precipitation |
| 30 | No precipitation | No precipitation |
| 40 | No precipitation | No precipitation |

[1] The precipitation was observed during the stirring of solution.

The precipitations observed in this experiment are considered as silica. When the precipitations were heat treated up to 500 °C, white powder could be obtained. The following characterizations are to verify that the precipitations are agglomerated silica particles synthesized from the micelles.

At high water-to-TEOS molar ratios, i.e. when small amount of TEOS was added, no noticeable precipitation was observed. It could be said that the water-to-TEOS

molar ration must be kept under 24 for the production of silica from the given microemulsion condition.

However, at low water-to-TEOS molar ratios, the gel-like precipitates were observed during the stirring. It seems that the sol-gel reaction of TEOS into silica is occurring outside of micelles with large amount of TEOS in the cyclohexane. It is not a favorable situation for the controlled synthesis of silica and polyaniline in the microemulsion solution.

From the observations summarized in Table 8, it could be said that for the stable production of silica the water-to-TEOS molar ratio would rather be controlled in the range of 18 to 22 for both of microemulsions using acidic and basic aqueous phases.

### 5.2.2. Characterization of particles

To see the shape and size of the particles TEM investigations were performed. The silica particle was prepared from the microemulsion solutions with the given composition (65.4 wt% cyclohexane, 30.4 wt% surfactant and 4.2 wt% aqueous phase). TEOS was dissolved into cyclohexane, and the water-to-TEOS molar ratio was 20. After stirring at room temperature for 24 hr, one drop of microemulsion solution was placed on the carbon coated Cu grid and was dried to remove solvents. The prepared specimen was then put under TEM.

Fig. 23 shows the TEM micrographs of the silica particles synthesized from the microemulsions containing acidic (Fig. 23.a) and basic (Fig. 23.b) aqueous dispersions, respectively. The particles from the acidic micelles were smaller in size than the particles from the basic micelles. The shapes of the particles are quite different. Particles from acidic micelles showed ellipsoidal shape while particles from basic micelles showed spherical shape.

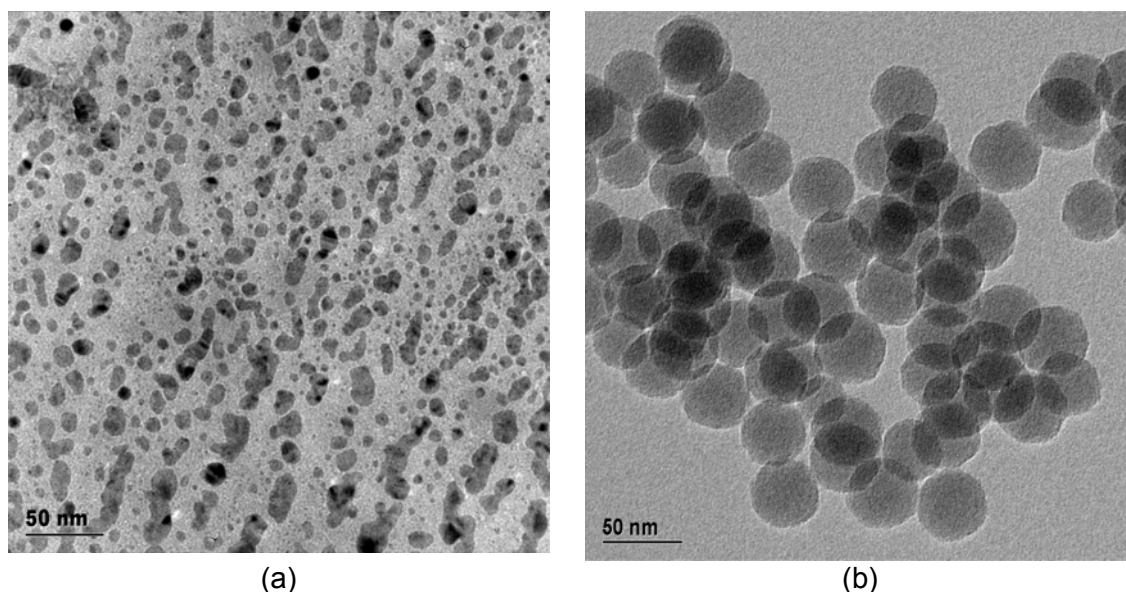(a)                                    (b)

Fig. 23   TEM photo of silica nanoparticles produced from the microemulsions
containing (a) acidic (pH = 2, micelle size ~ 47 nm) and (b) basic aqueous (pH
= 12, micelle size ~ 56 nm) dispersions (The specimens were prepared by
placing one drop of each microemulsion solution on carbon coated Cu-grids.)

The catalyst for producing silica nanoparticle from microemulsion is mostly
ammonia [87, 94]. The production of silica nanoparticle in an acidic condition should be
possible, since the composite particle has to be prepared in a micelle by a
simultaneous synthesis of silica and polyaniline, and the polyaniline usually have to be
prepared in an acidic condition. From the literature survey, it was found that most of the
nanoparticle syntheses from the microemulsion were done under basic conditions
where $NH_3$ was used for catalyst. Even though some cases [97] were reported that the
mesoporous particles could be prepared from the microemulsion, but these still are not
common practice to prepare silica nanoparticle from the microemulsion. In other cases,
they [96] reported the micron-sized silica particles could be obtained from the emulsion
media using acidic catalyst HCl.

In this study, it was demonstrated that the nanoparticle of silica could be obtained
from the microemulsion solution on both of the cases using acidic and basic catalysts.
The microemulsion solution with Triton X-100 : 1-hexanol mixture as the surfactant was

proved to act as a synthesis media for the silica nanoparticle for both the cases using basic and acidic catalyst. When the basic catalyst $NH_3$ was used, the obtained silica particle is spherical and looks quite similar with the particles prepared from other works [87, 94]. The particles from acidic condition showed rather irregular shape and are smaller than the particles from the acidic condition. For more clear understanding, the further characterization was necessary.

For the further investigations such as FTIR and BET surface area measurement, it is necessary to separate the synthesized particles. The microemulsion solution containing silica particles in the micelles are still transparent showing no precipitations even after 24 hrs of reaction time. When the solution was centrifuged with the particles in the micelles, only part of the particle could be separated. Thus an additional treatment like breaking the micelles would be needed for an effective separation of particle.

If the critical micelle concentration (CMC) is reduced by changing composition of microemulsion [102] or by changing temperature [112, 113], then the micelles will be broken and a phase separation will occur. With the phase separation of aqueous phase the synthesized particles will get closer and be flocculated by weak interactions like Van der Waals interaction among the particles [102]. Then the synthesized particles could be separated easily from the microemulsion solution with a simple centrifugation. Usually, the flocculation or the breaking micelles from the microemulsion solutions could be done by adding short chain alcohols such as methanol, ethanol or butanol to the solution [102]. In this study, 1-butanol was used as the short chain alcohol. Ethanol was also tried, but when 1-butanol is used larger amount of sedimentation was obtained from the microemulsion. The addition of excess amount of 1-butanol could reduce the critical micelle concentration of microemulsion and hence aqueous phase separation, and the particles which had been trapped in the aqueous micelles could be flocculated. Then the flocculated particles were separated from the solutions simply by a centrifuge at 5000 rpm.

For the extraction of particle from the microemulsion solution, 1-butanol was added up to the extent where the microemulsion solutions lost transparency and became translucent. The translucent solutions were then centrifuged at 5000 rpm for 5 min to separate particles. The separated particles were washed 5 times with ethanol. The washed particles were then dispersed again into ethanol solution and the TEM

specimens were prepared by placing one drop of each solution on the carbon coated Cu grid. The TEM photographs for the extracted particles are given in Fig. 24.
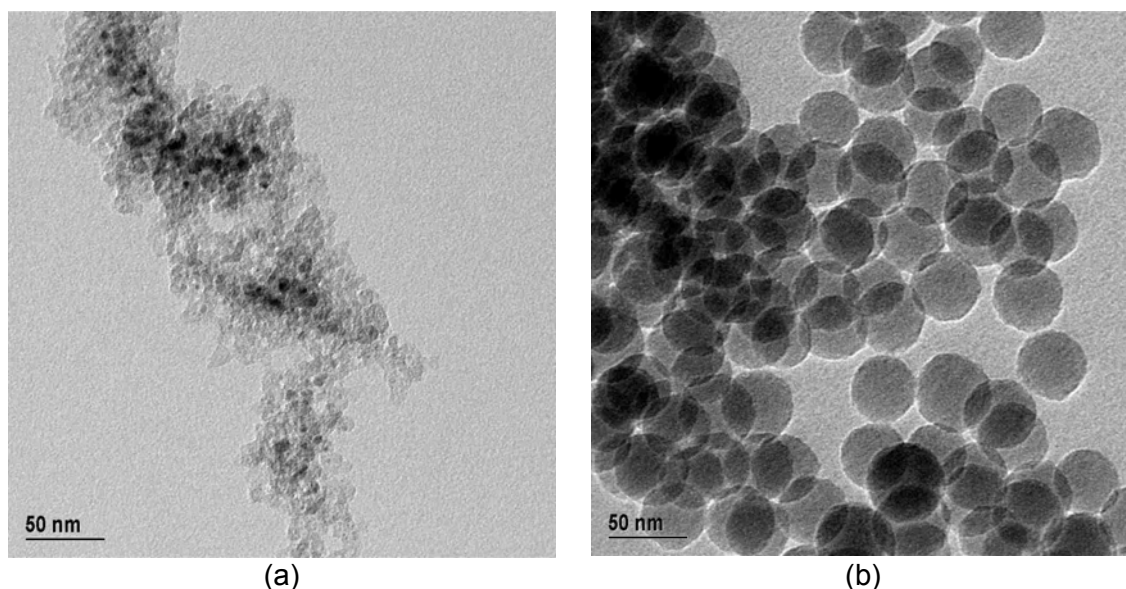


|         (a)          |         (b)          |

Fig. 24   TEM photo of silica nanoparticles produced from (a) acidic (pH = 2, micelle size ~ 47 nm) and (b) basic micelles (pH = 12, micelle size ~ 56 nm) after extracting from the microemulsions and subsequent washing

By comparing TEM photos before (Fig. 24) and after (Fig. 23) the extraction of particles, the extracted particles showed agglomerations. Especially the agglomeration as in Fig. 24.a for particles from the acidic microemulsion is a noticeable difference from the observation in Fig. 23.a. This observation could mean that the synthesis of silica particle is done in the aqueous micelles of microemulsion solution. This is a main purpose to use the microemulsion solution employing the micelles as nano-sized reactors for a production of nano-sized particles. As was discussed in the literature review, various other research works were done to produce nanoparticles either inorganic or organic using the nano-sized reactors in microemulsions [86-88]. In this study, the micelle is also working as the nano-reactors for the production of silica nanoparticle. The well dispersed particles before the extraction (Fig. 23.a) represents that as long as the particles are remaining in microemulsion solution the dispersion maintains. However, when the micelles were broken for the extraction of the particles, the flocculation inevitably produces agglomerations as in the TEM photo (Fig. 24.a).

Apart from the agglomerations after the extraction of particles, it could also be noticed that the particles obtained from each aqueous micelles with different pH values showed big difference in size. For a quantitative view, the particle size distributions were checked with TEM photos as in Fig. 23, and were plotted as in Fig. 25.

The average sizes of the particles synthesized from acidic micelles and basic micelles were 11.9 nm and 38.3 nm, respectively. In addition to the size difference, the particles from the acidic micelles showed wider size distribution compared with the particles from the basic micelles. It was observed from the micelle size investigation as in Fig. 21 that the acidic aqueous micelles are smaller than the basic micelles. The average sizes of obtained particles are following the micelle size trends.
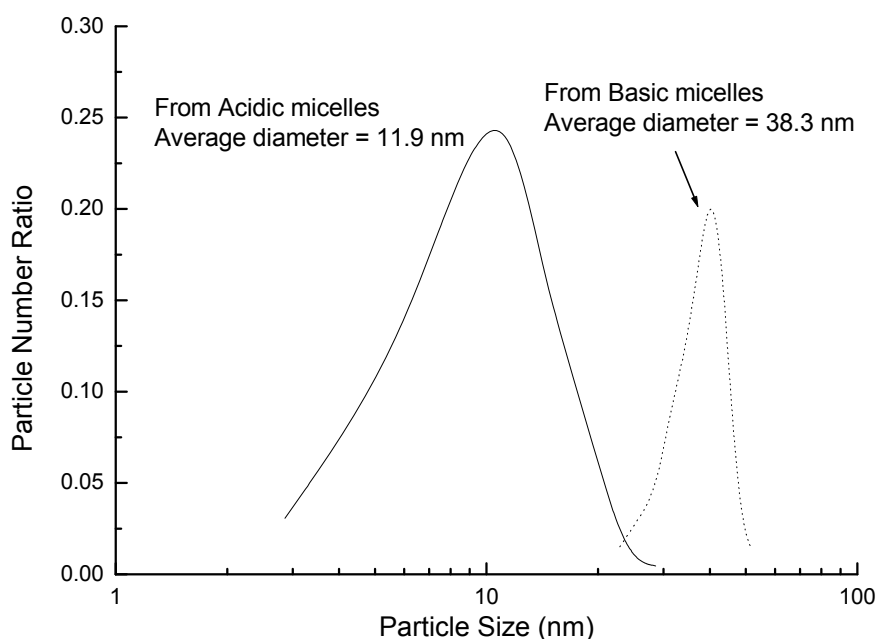


Fig. 25   Particle size distribution obtained from the TEM pictures in Fig. 23(a) (pH = 2, micelle size ~ 47 nm) and (b) (pH = 12, micelle size ~ 56 nm)

It is clear that the obtained particle from the acidic microemulsion solution is silica, since the extracted white powder survived heat treatment up to 500 °C. However, for a more quantitative characterization the composition and chemical structure of the particle were investigated.

To check composition and chemical structure of the silica particle FTIR spectroscopy was done on the particle obtained from the acidic micelles. The FTIR specimens were prepared as follows. The synthesized particles were extracted from the microemulsion and washed with ethanol five times. And the washed particles were dried at 120 °C for 2 hrs. The dried powder was then mixed with KBr, and compacted into a pellet shape. In Fig. 26, a FTIR spectrum for the silica particles from acidic microemulsion is shown.
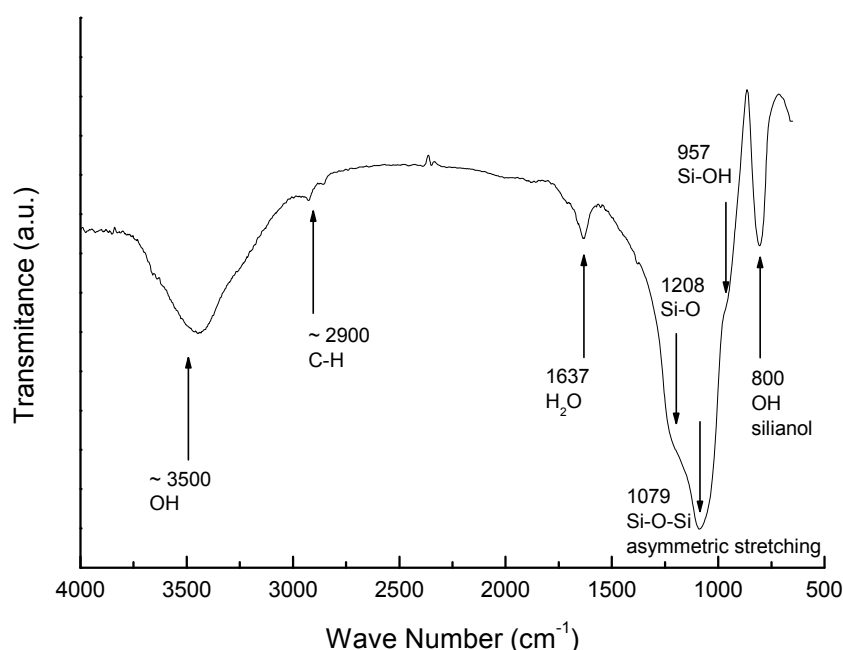


Fig. 26   FTIR spectrum of particles obtained from acidic microemulsion solution with the composition of microemulsion as 65.4 wt% cyclohexane, 30.4 wt% surfactant and 4.2 wt% aqueous phase, and pH of aqueous solution as 2 (The unit of Y-axis is arbitrary unit of transmittance.)

It is a rather typical spectrum for silica material prepared from sol-gel reaction, showing characteristic absorption bands at 1208 and 1079 $cm^{-1}$ for Si-O-Si asymmetric stretching, at 950 $cm^{-1}$ for Si-OH bonding, and at 800 $cm^{-1}$ for OH bending of silanol [114]. From the FTIR spectrum it is once again verified that the obtained particles are silica.

A broad absorption band around 3500 cm$^{-1}$was observed, and it could be assigned as OH bonding in the silica particle or water molecules absorbed. Since the silica was synthesized by a sol-gel process in the microemulsion solution at room temperature and was washed and dried 120 °C for 2 hrs, the water and OH groups bonding could still be seen from the FTIR spectrum. Around 2900 cm$^{-1}$ small absorption bands were also observed and could be assigned as C-H stretching vibration. These could be attributed to the remaining of ethanol from the solvent.

For an investigation on the microstructure of the obtained particle, the surface areas for both the particles from acidic and basic micelles were measured and compared. The particles extracted from the above prepared acidic and basic microemulsion solutions were washed with ethanol 5 times and dried in a vacuum oven at 150 °C to remove the solvent from the particle. Then the two sets (acidic and basic) of powders were put to measure BET specific surface area. In Fig. 27, the nitrogen adsorption and desorption isotherm curves are given.
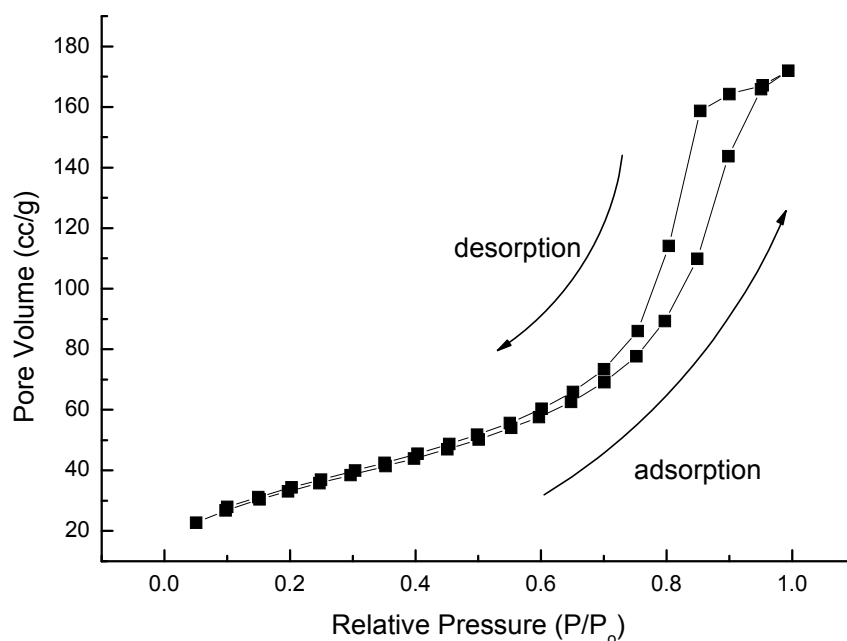


(a)

Fig. 27   Nitrogen adsorption and desorption isotherm of the silica particles obtained from the (a) acidic and (b) basic microemulsion solutions (see Fig. 24).
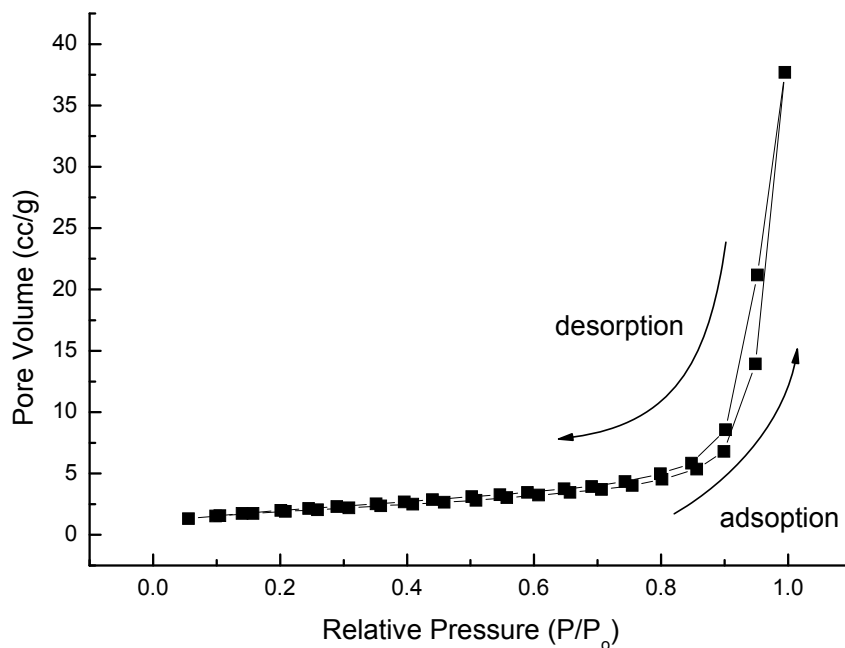
(b)

Fig. 27 continued.

From the isotherm data, the pore size distribution were obtained by using the built-in Barrett, Joyner and Halenda (BJH) algorithm of the BET surface area measurement instrument, and is plotted in Fig. 28. From the pore size distribution curve, it could be seen that the pore volume of the particle prepared from the acidic microemulsion is much larger than that of the particles from the basic microemulsion. The volume of the pores larger than 4 nm showed big differences between the two samples. The peak at around 100 Å (= 10 nm) for the particles from the acidic microemulsion can be considered to represent pores formed by the particles. This showed that the particles must be loosely packed than the particles from the basic microemulsion. The difference in that range of pore size only tells us the degree of particle packing rather than the pore size distribution inside of the particle itself. From the pore size distribution itself it was not easy to see the pores inside the particles.
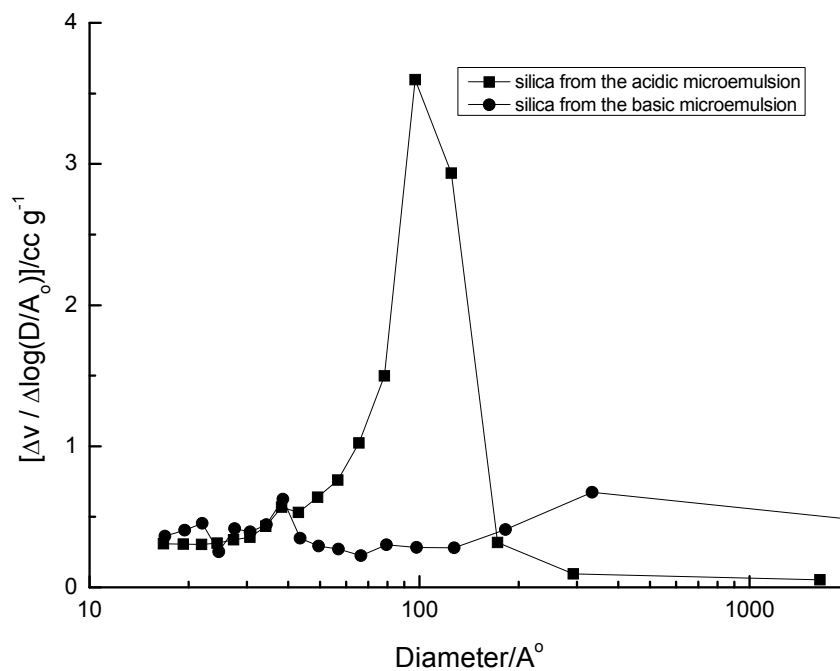
Fig. 28   Pore size distribution comparison between the silica particles prepared from the acidic and the basic microemulsion solutions (see Fig. 24).

The surface areas for the silica particles obtained from the acidic and the basic microemulsion were given in Table 9. The particles from the acidic solution have larger surface areas than the particles from the basic one. Calculated surface areas for those two particles are also denoted in the table. The surface area calculations for the particles were done with the assumption that the particle is a dense sphere with the observed average diameters ($\varphi_{ave}$).

Table 9    Comparison between the calculated surface area, the BET surface area, and the total pore volume for the silica particles obtained from acidic and basic microemulsions

|  | Particles from the acidic microemulsion ($\varphi_{ave}$ = 11.9 nm) | Particles from the basic microemulsion ($\varphi_{ave}$ = 38 nm) |
| --- | --- | --- |
| Measured surface area (total pore volume) | 623 m$^2$/g (1.35 cc/g) | 89 m$^2$/g (0.75 cc/g) |
| Calculated surface area | 210 m$^2$/g | 65 m$^2$/g |

The particle from acidic micelles exhibits larger surface area than that from basic micelle, which was expected from the smaller size of the acidic particles than basic particles. The measured surface area of the particles showed larger value than the calculated one for both of the particle samples. The surface area difference between measured and calculated is pretty much larger for the particles from acidic micelle than from basic micelle. For an interpretation of the observations a microstructure model for the particles were proposed in the next section.

### 5.2.3. Microstructure model for obtained silica particles

In this study, two sets of silica particle samples from acidic and basic micelles were prepared and compared. Those two samples showed different shapes, sizes, and microstructures. To explain the differences, we proposed model for the particle formation as in the schematic illustration of Fig. 29.

The size and shape of the produced particles are governed by the size of the micelle and the different particle formation processes at different pH conditions. When the acidic aqueous solution was dispersed, the size of the micelle is smaller than the basic solutions as was the result of the micelle size measurement shown in Fig. 21. Since the particle growth would be confined to the size of the micelles, the particles resulting from the acidic micelles would be smaller than those from the basic micelles.

The particle growth is also strongly dependant on the pH of the solution where the growth occurs [72]. Brinker et al explained that at higher pH values, the solubility of primary silica particles is high enough to provide monomers to the ripened particles to grow larger, which usually referred to as Ostwald ripening. In this case, dense and spherical particles as in Fig. 23.b respective Fig. 24.b are achieved by a process comprising Ostwald ripening. On the other hand, in the aqueous solutions with lower pH values, primary particle wills remain under 2 nm in size, since the solubility of silica is rather low. In this situation primary particles tend to form a 3-dimentional network in the solution, and thus to gelate. For the case of the microemulsion containing acidic aqueous micelles in this study, the gel would be confined to the size of micelles and the individual gel in each micelle would become an individual particle as is shown in Fig. 23.a.

This difference on silica synthesis is very frequently observed for the sol-gel reactions [72]. Acidic catalyst is used for porous bulk silica, whereas basic catalyst for dense and spherical particles. This common behavior of silica sol-gel reaction was preserved inside the aqueous micelles in this study.

If the gel turns into a particle by the extraction of solvents, it would remain porous even after a shrinking which is expected during the drying. As can be seen from the BET surface area data in Table 9, the experimentally determined surface area of the particle from the acidic solution was 623 $m^2/g$, which is almost three times larger than the calculated surface area. This large surface area indicates that the particles from acidic solutions are porous. On the contrary the particles from basic solutions showed no big difference between the measured and calculated surface areas, indicating a low porosity of these particles.
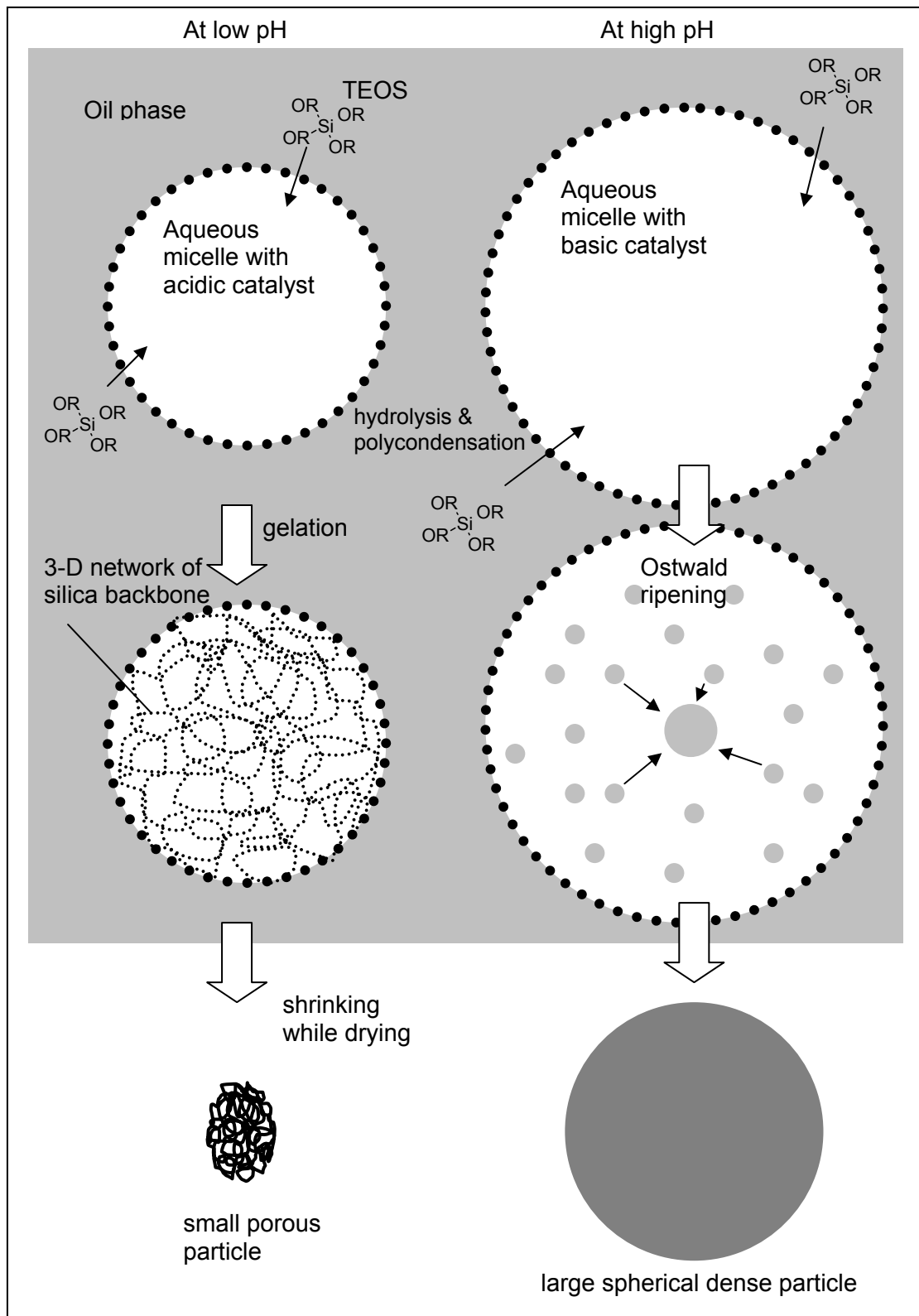
Fig. 29  A schematic description for the different reaction processes in the acidic and basic micelles

It was demonstrated that silica particles with very different microstructures could be obtained from an inverse microemulsion solution using TEOS and various catalysts. The size of the particle obtained from the acidic microemulsion where HCl was used as the catalyst is much smaller as around 11.9 nm than that from the basic microemulsion where $NH_3$ was used as around 38.3 nm. The particle from the micelles containing HCl has larger surface area around 623 $cm^2$/g than the particles from the micelles containing $NH_3$ around 89 $m^2$/g. By comparing these experimental results with the calculated surface areas, it could be said that porous silica particles were obtained from the acidic microemulsion solution. The process demonstrated in this study, could be extended to the preparation of silica/organic hybrid material where the acidic condition would necessarily be involved.

### 5.3. Synthesis of silica/polyaniline composite particle from microemulsion

Since the porous silica nanoparticles were obtained from the acidic microemulsion solution, synthesis of silica/polyaniline composite particle was tried also from the acidic microemulsion solution. The main purpose of inorganic-organic hybrid is to achieve the enhanced electrochemical stability of material. Generally, inorganic-organic hybrid nanocomposites are attracting much attention for their chemical, physical, optical, and electrical properties which is not obtainable with a single component. Silica is the most frequently studied inorganic material for the composites [10]. If the composites are to be used as an optical coating material, then the size must be controlled under 100 nm where the scattering of visible light could be avoided.

There are several well-established methods for producing the composite nanoparticles. Microemulsion method [115, 116] is one of the useful methods to produce monodispersed nanoparticles. When the micelles were used as the nano-reactors, it could suppress the particle growth within the range of 50 nm.

Since 1990, there have been many tries to make the composite nanoparticle using silica from the microemulsion solution. Those tries are about making the composite in one of the three types; a) silica-inorganic core-shell [115, 117], b) silica-organic core-shell [71], and c) silica-metal core-shell [118].

One of the main reasons for those composite structures is the protection from the chemical degradation of functional component. With the help of chemically stable silica, the durability of the organic component is enhanced to a certain extent when the nanoparticle is applied in bulk or film [47, 49]. However, when the silica core and organic shell is concerned, which is the case where the contact with outside should be maintained, the core-shell structure would not be enough for the protection. For this case, a more secured structure is needed to protect the organic component while maintaining the contact with the surrounding substances. A composite structure could be figured where the silica forms a network to hold the polymers mechanically and/or chemically in its network and the contact of the polymer to the outside of the structure is maintained. And this structure has to be reduced to nanoparticles for the utilization of the material to the optical coatings.

In this study we tried a composite nanoparticle where silica forms the skeleton of particle and the organic component is dispersed and interconnected through the voids formed by the skeleton. In a previous chapter [see 5.2 Synthesis of porous silica particle from microemulsion], it was demonstrated that the porous silica nanoparticle could be obtained from the microemulsion solution using the acidic catalyst. By using this reaction method, a polyaniline was incorporated into the pores of the silica particle. Polyaniline is considered relatively well compatible with silica to form hybrid [119], and it also has much interesting electrical properties such as semi-conductivity and electrochromic behavior [37].

### 5.3.1. Particle synthesis from microemulsion

The chemicals for composite particle synthesis are TEOS, aniline, ammonium peroxodisulfate (APS), and HCl. The microemulsion solution with the composition as 65.4 wt% cyclohexane, 30.4 wt% surfactant (Triton X-100 : 1-hexanol), 4.2 wt% aqueous phase was used. TEOS was dissolved into cyclohexane and the amount of TEOS was set according to the water-to-TEOS molar ratio = 20 which was selected by the silica particle preparation experiment above (see Table 8 and page 69).

It was intended that the composite particles were produced by a simultaneous synthesis of silica and polymer in a same micelle. The polymerization of the organic part, aniline in this study, will usually occur in an acidic condition. Therefore, silica also had to be synthesized with an acidic catalyst which was already demonstrated in the

previous sections. Producing silica particles and silica / polymer composites was done following the process which is illustrated in Fig. 13.

Two sets of microemulsion solutions were prepared: (a) with an aqueous phase containing HCl and aniline, (b) with an aqueous phase containing HCl and APS. The concentration data of each component for the two solutions was given in Table 10.

Table 10  The composition for the microemulsion solutions prepared before the mixing.

|  | Solution "(a)" | | Solution "(b)" | |
|---|---|---|---|---|
| Cyclohexane | 65.4 wt% | | 65.4 wt% | |
| Surfactant mixture | 30.4 wt% | 1-hexanol to Triton X-100 weight ratio = 2 | 30.4 wt% | 1-hexanol to Triton X-100 weight ratio = 2 |
| Aqueous phase | 4.2 wt% | HCl to make pH=2 | 4.2 wt% | HCl to make pH=2 |
|  | | 0.225 M aniline | | 0.2 M APS |
| TEOS | Added to make water to TEOS molar ratio = 20. | | Added to make water to TEOS molar ratio = 20. | |

The concentrations of aniline, APS in the aqueous phase were 0.225 M and 0.2 M, respectively. The pH of the aqueous phase was set to 2 using HCl. Before the dispersion of each aqueous phase into the microemulsion solution, the aniline and APS were dissolved into the aqueous phase. Then the aqueous phases were dispersed. Those two microemulsion solutions had same relative composition of cyclohexane, surfactant and aqueous phase. The prepared two microemulsion solutions were then mixed together without delay. The composition of the mixed microemulsion was 65.4 wt% cyclohexane, 30.4 wt% surfactant (Triton X-100 : 1-hexanol), 4.2 wt% aqueous phase. The mixed solution was kept at room temperature for 24 hrs under a mild magnetic stirring at 600 rpm. The color change is presented in Fig. 30.

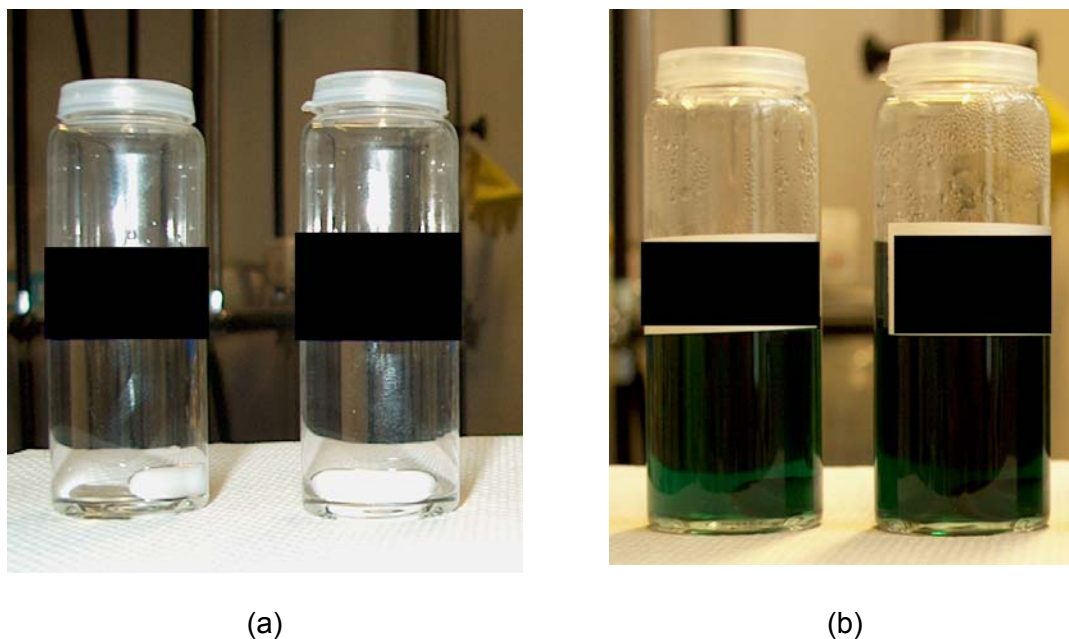(a)                                              (b)

Fig. 30   Color change of the solution during the synthesis of silica/polyaniline
composite particles; (a) just after mixing, (b) 24 hrs after mixing.


Unlike the solution for silica production in the previous sections, the solution containing TEOS and aniline for producing composite particle showed color change from colorless to dark green at about an hour after the mixing. Dark green is the typical color for polyaniline in form of emeraldine salt. This color change is an evidence that polyaniline was synthesized in the solution.

For the characterization of particle, the size and shape of the particle obtained from the microemulsion were checked by the TEM as given in Fig. 31. The size of the particle was found to be around 10 nm. The TEM specimen was prepared by placing a drop of microemulsion solution (Fig. 30.b) with the synthesized particle on a carbon coated Cu grid.
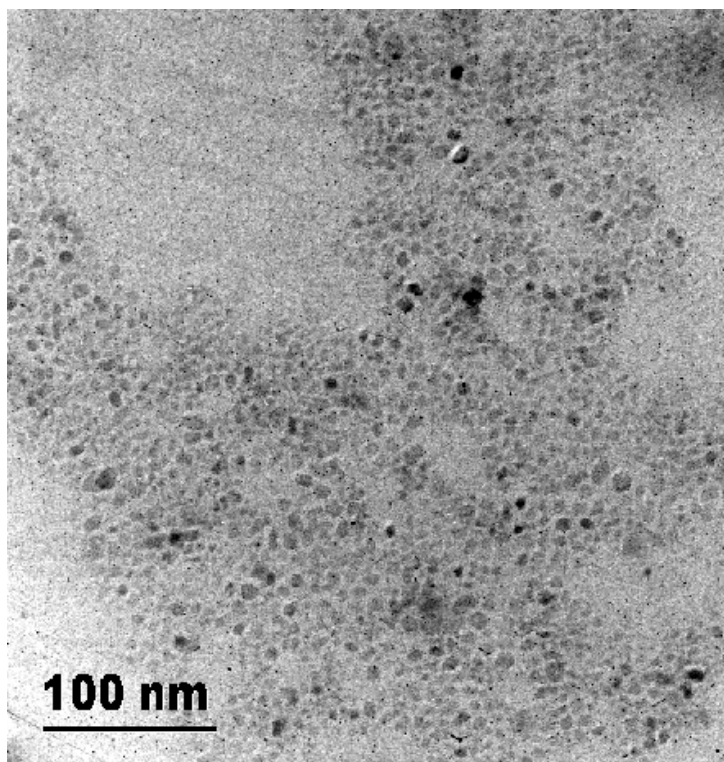
Fig. 31   TEM photo of the composite particle obtained from the microemulsion using TEOS and aniline

The TEM photo shows that particles were obtained from the microemulsion solution using TEOS and aniline, and the obtained particle is rather uniform in size around 10 nm.

To check the components of the obtained particle the FTIR spectroscopes were done on the composite particles and compared with the FTIR spectrum of pure silica particle, which was checked in the previous section. The composite particles were first extracted from microemulsion solution. This was done by adding excess amount of 1-butanol to the microemulsion solution, as was done on the pure silica microemulsion solution to separate particles. When 1-butanol was added to microemulsion solution, particles were flocculated to form agglomeration. The separated particles were then washed with ethanol three times, and dried at 150 °C. FTIR specimen was prepared by compacting 20 mg of composite particle with 200 mg of KBr. The obtained FTIR spectra are given in Fig. 32.
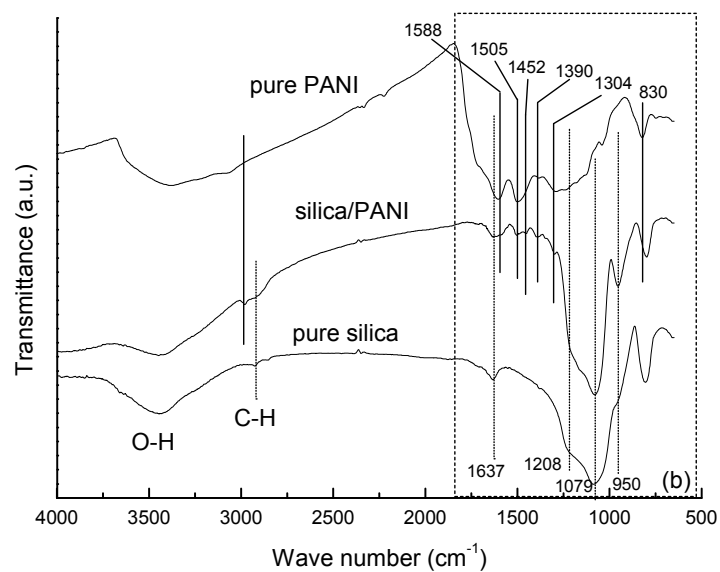
(a)
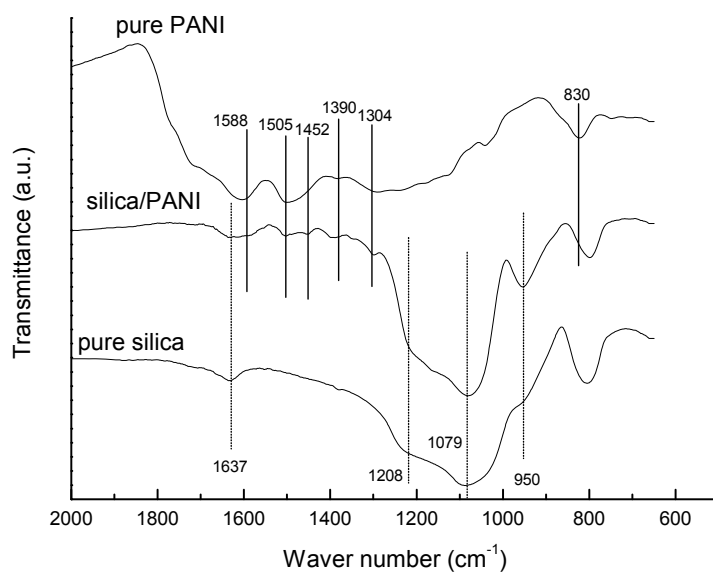


(b)

Fig. 32  FTIR spectra for the pure silica particle and silica / PANI composite particle
obtained from the microemulsion solution (For the composition of the solution
see page 82 and 83, and (b) is magnified view of the dashed box in the
spectrum (a). a.u. of Transmittance axis means arbitrary unit.)

For the comparison between pure silica and silica/polyaniline composite samples, pure polyaniline particle sample was also prepared and was subject to the FTIR spectrum. The polyaniline sample was prepared by the same synthetic method as the silica and composite samples. The pure polyaniline particles were obtained from the microemulsion solution only without the addition of TEOS. The other components for the microemulsion solution were just the same as was given in Table 10.

The characteristic absorption peaks were observed at 1637, 1208, 1079, 950, and 800 $cm^{-1}$, which are assigned to the characteristic absorption stretches for silica. The additional peaks at 1588, 1505, 1452, 1390, and 1304 were observed for the composite sample. These peaks are assigned to the characteristic peaks from polyaniline. The individual assignments of the peaks are given in Table 11.

Table 11    Assignments for IR absorption bands [120-123]

| Wave number ($cm^{-1}$) | Assignment |
| --- | --- |
| 1637 | C-H stretching vibration |
| 1208 | Si-O |
| 1079 | Si-O |
| 950 | Si-OH |
| 800 | Si-O-Si |
| 1588 | Quinonoid ring stretching |
| 1505 | Benzenoid ring stretching |
| 1452 | Benzene ring |
| 1390 | C-C deformation |
| 1304 | Aromatic (C-N) stretching band |
| 830 | C-H vibration in para coupled benzene ring |

The TEM photos and the FTIR spectroscopy results showed that particles with sizes around 10 nm were produced and the particles are either a composite of silica and polyaniline or a mixture of individual silica and polyaniline particle. From the TEM photos, it is not possible to distinguish these two particles or to see any contrast inside the individual particle. It is because of that the atomic number difference for silicon (14)

and carbon (6) is not big enough to have sufficient contrast difference under the TEM. As a composite structure of the particle was intended using microemulsion solution, a characterization method for the composite structure is needed.

### 5.3.2. Structure of the composite particle

Since the TEM investigation results showed no clear evidence that the particle is a composite of silica and polyaniline or separated, a supplementary structural study was done by investigating the surface area change according to a compositional change and to a thermal treatment on the particle. As an indirect investigation method, the surface area change of the particles could give information on the structure of particles. If a composite particle is formed by filling up the pore of porous silica particle with polyaniline, then the specific surface area of the particle would increase as the amount of polyaniline increases. With a same analogy, the surface area could also be changed when the polyaniline is removed from the composite particle by a thermal treatment at an elevated temperature where the polyaniline could possibly be burned out.

The surface area change of composite particle was checked while the concentration of aniline in aqueous phase was changed from 0.01 M to 0.3 M. To see the trend of surface area change seven sets of particle samples were prepared only by changing the content of aniline and the other compositions were the same. The composition of microemulsion was 65.4 wt% cyclohexane, 30.4 wt% surfactant (Triton X-100 : 1-hexanol), 4.2 wt% aqueous phase. The concentration of TEOS in cyclohexane was adjusted to make water-to-TEOS molar ratio as 20. The concentration of APS in the aqueous phase were all 0.2 M, and the pH of the aqueous phase was adjusted to 2 by addition of HCl (Table 10). The surface comparison results are given in Fig. 33.
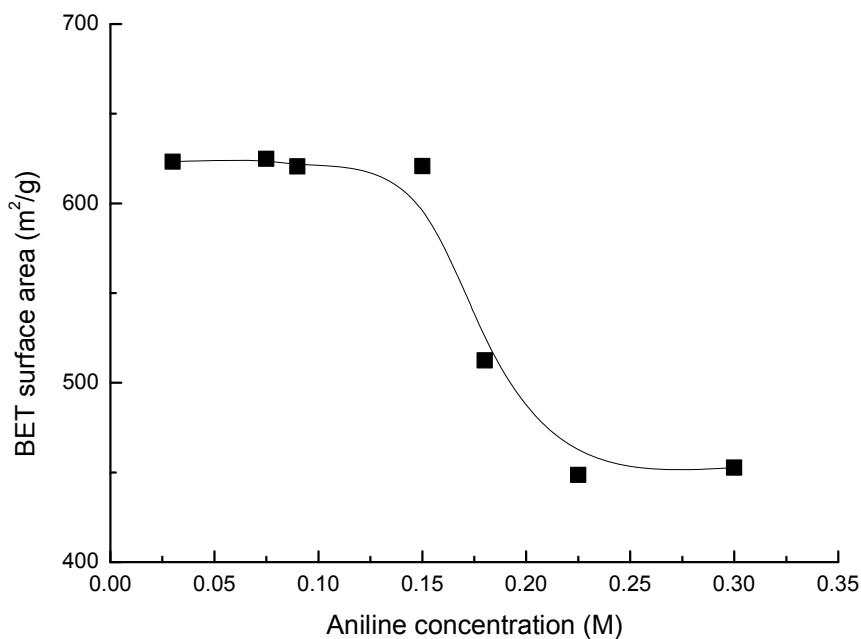
Fig. 33   BET surface area change of the composite particle prepared from the microemulsion solutions according to the aniline concentration in the aqueous micelles. The composition of the microemulsion solution and the TEOS concentration is given in Table 10.

A decrease of surface area was observed when the aniline content is over 0.2 M. At aniline concentrations lower than 0.15 M, the produced composite particles exhibited surface areas around 620 $cm^2/g$, which is almost same as that of pure silica particles from microemulsion. At higher aniline concentrations such as larger than 0.2 M, the surface area of synthesized particles were decreased to around 450 $cm^2/g$.

For a further characterization of the structure, surface area change was also measured after heat treatments at 300 °C and 500 °C in an ambient atmosphere for 2 hrs. This was done with the sample produced with the aniline concentration 0.3 M in the aqueous phase.

The particle samples were extracted from microemulsions and were dried at 150 °C for 2 hrs. The dried particles were put into a furnace and were heated up to 300 °C and 500 °C, respectively in air following the thermal schedule in Fig. 34.
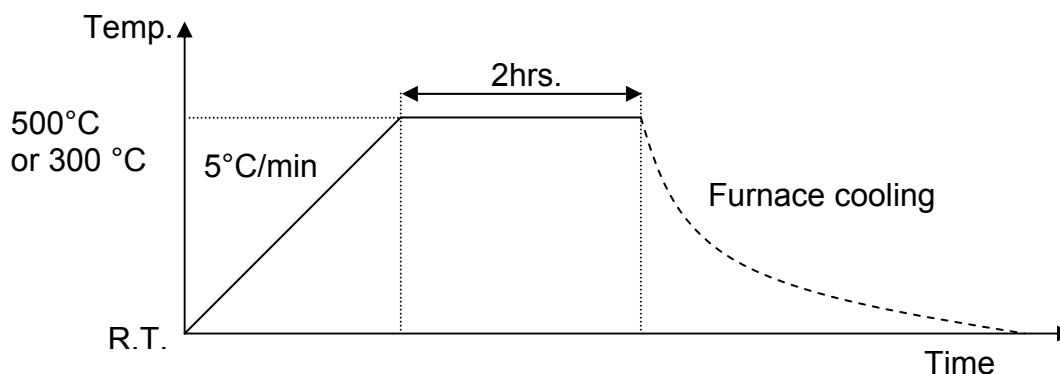
Fig. 34   A thermal schedule for thermal decomposition experiment on the composite particles obtained from the microemulsion solution (For the composition of solution see pages 82 and 83)

The surface area change was also compared with that of pure silica particle. As was shown in Fig. 35, the composite particle shows an increase of surface area as the heat treatment temperature is increased from 450 to 570 cm$^2$/g, while the pure silica particle shows slight decrease of surface area.

After the heat treatments, removal of the polyaniline from the particle could be seen by a color change of particle from dark blue to white after heat treatment. As was shown in Fig. 36, before the heat treatment, composite particles showed dark green or dark blue which are typical color for polyaniline either emeraldine salt or nigraniline, but they showed dark gray and white at 300 °C and 500 °C, respectively. The dark gray color might come from polyaniline pernigraniline, since the pernigraniline phase shows the color [37, 38]. Pernigraniline is most oxidized form of polyaniline. The white color of particles means that all the polyaniline in the composite were removed after heat treatment at 500 °C.
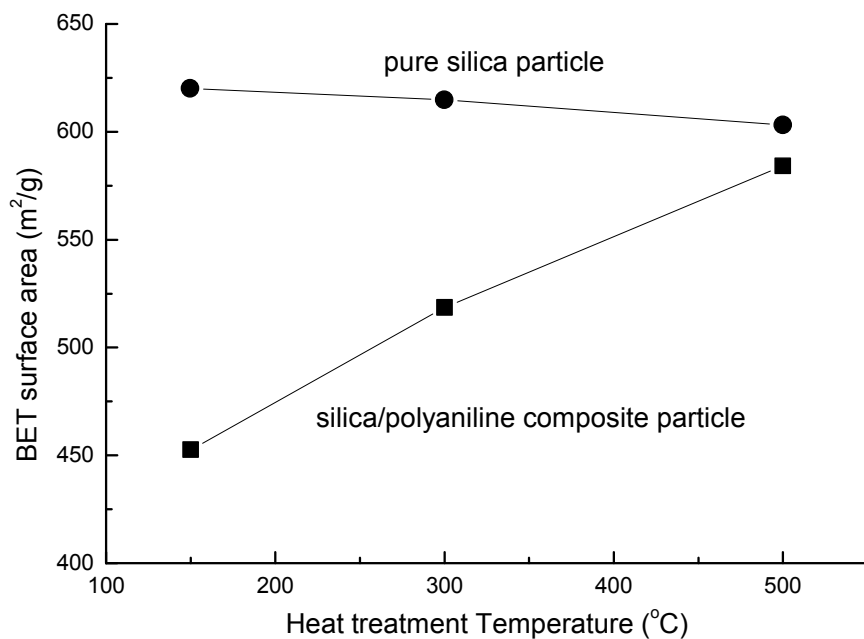
Fig. 35   BET surface area change during the thermal decomposition of polyaniline at 300 °C and 500 °C in air (Silica/polyaniline sample with aniline content 0.3M in Fig. 33)
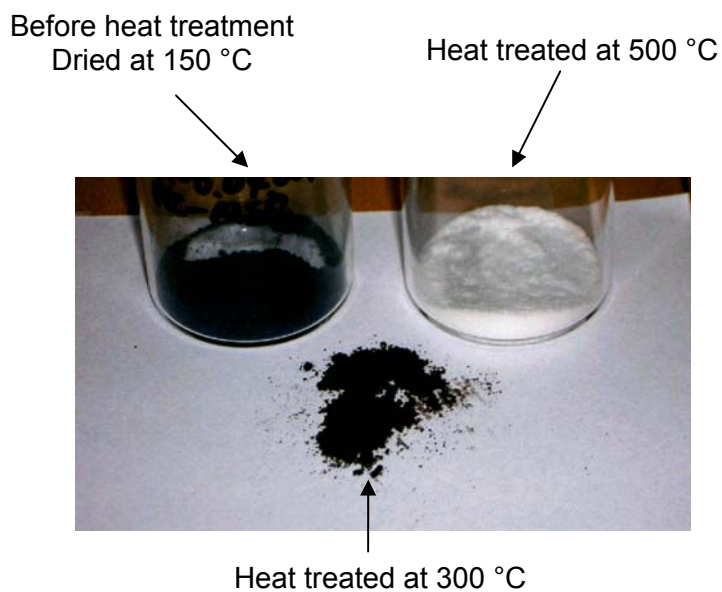


Fig. 36  Color change of the composite particle during the heat treatment

To verify the removal of the polyaniline from the composite particle, the FTIR spectroscopy was done on the heat treated samples. Three sets of sample were collected, 1) after a drying at 150 °C, 2) after a heat treatment at 300 °C, and 3) after a heat treatment at 500 °C. The specimens for FTIR were prepared by compacting particles into pellets with KBr. For each pallet sample, the same amount of silica / polyaniline powder as 20 mg were mixed with the same amount of KBr as 200 mg.

The FTIR spectroscopy results are given in Fig. 37. As shown from the spectra characteristic absorption peaks at 1505, 1455, and 1390 cm$^{-1}$ were vanishing as temperature went up. The peaks were disappeared completely when sample was heated up to 500 °C.
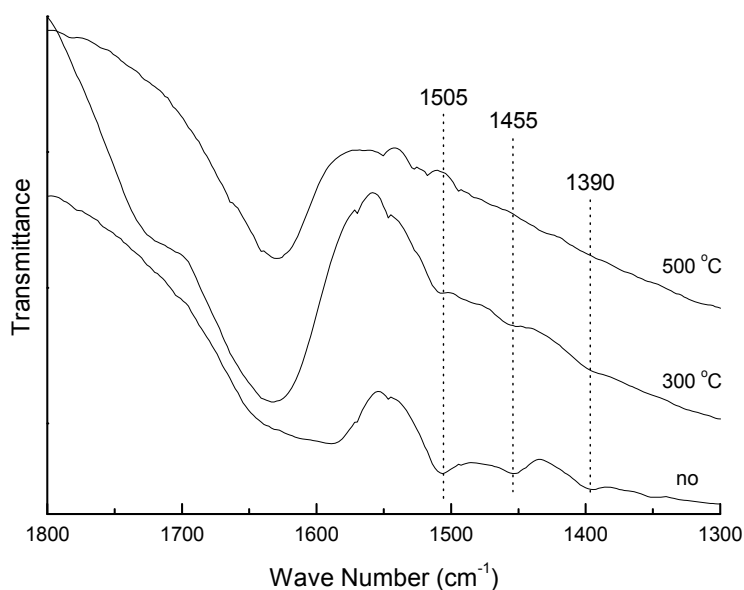


Fig. 37   FTIR spectra of the composite particle from the microemulsion solution heat treated at different temperatures (The concentration of aniline in the aqueous phase was 0.3 M.)

It could be said from the FTIR results that the polyaniline were completely burned out from the particles with the heat treatment at 500 °C in an ambient atmosphere for 2 hrs.

To check the burning out behavior of the material, a thermal analysis was performed on the silica / polyaniline particle. 17 mg of silica / polyaniline powder was collected and put into TG/DTA furnace. Then the sample was heated up to 500 °C at heating rate of 5 °C with an air flow into the furnace. The result of TG/DTA is given in Fig. 38.
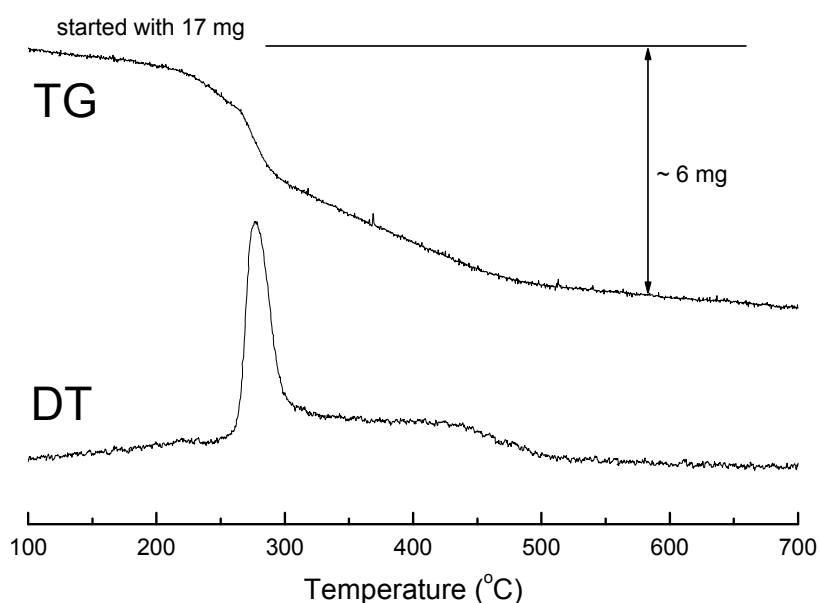


started with 17 mg

TG

~ 6 mg

DT

Fig. 38 TG/DTA curve of composite particle

A mass decrease on the TG curve was observed from around 250 °C. A sharp exothermic peak on the DT curve at around 280 °C was also observed. Another small hill on DT curve was observed at around 430 °C. However, no more peaks on DT curve or no more weight loss on TG curve was found over 500 °C. This means that the burning out of the polymer from the silica / polyaniline particle ended before 500 °C. From the thermal analysis results it could be said that even after a heat treatment at 300 °C noticeable amount of polymer still remains in the powder.

The weight losses of pure silica and silica / polyaniline composite particles during the heat treatment at 500 °C for 2 hrs in ambient atmosphere were measured and

compared. The results are given in Table 12. The composite particle showed larger decrease of weight than pure silica particle.

Table 12   Weight losses of particles after heat treatment up to 500°C.

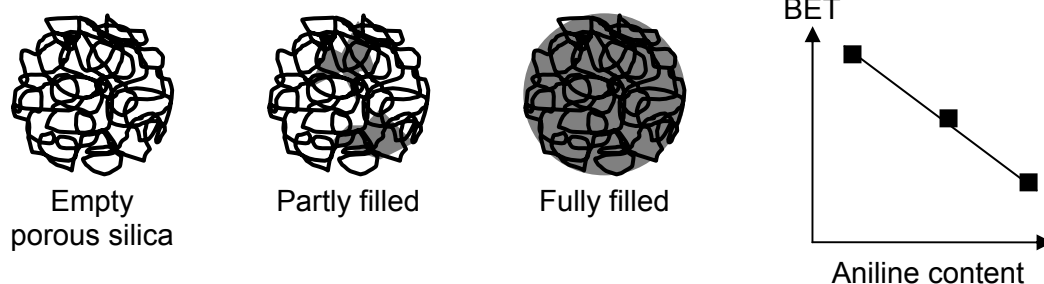|  | Silica / polyaniline particles | Pure silica particles |
|---|---|---|
| Before | 17mg | 17mg |
| After | 11mg | 14mg |
| Weight Loss (rate) | 6 mg (35%) | 3 mg (18%) |

Since the particle samples were dried at 150 °C, where large part of the remaining solvents in the samples were evaporated, the weight losses in Table 12 could be mainly by the removal of polyaniline and capillary condensed solvents into nano-sized pores of particles. The larger weigh loss for composite particles could be ascribed to the removal of polyaniline from particles.

### 5.3.3.  Microstructure model

In this study, production of composite nanoparticle of silica/polyaniline was intended from an inverse microemulsion using TEOS and aniline as precursors. It was proved by the TEM result in Fig. 31 that the sizes of particles obtained from the microemulsion solution are around 10 nm. It is also found from the FTIR spectrum in Fig. 32 that particles are composed of both silica and polyaniline. However, particles are so small that the composite structure of particle can hardly be seen from the TEM image.

As an alternative method to investigate nano structure of particles BET surface area measurements were tried in this study. By changing content of aniline in the aqueous micelles or by decomposing polymer part thermally, surface area changes of the particle were examined. For composite particle, surface area decreases with increasing content of aniline, and surface area increases during heat treatment. These results support that polyaniline could possibly be incorporated into the void space formed by the silica skeleton. For better understanding of the results, a structure model for the composite particle was given as in Fig. 39.

(a) Increase of aniline content
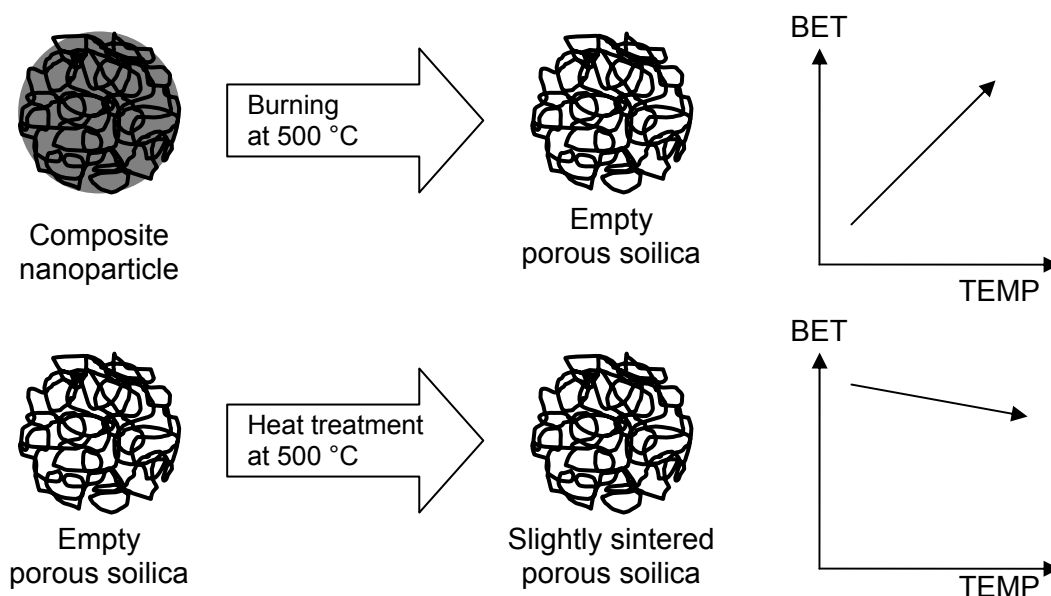


**(b) Thermal decomposition of polymer**



Fig. 39 A model for structures of composite and porous silica particle

As was showed in our previous section, silica particle produced from acidic micelles are porous. If the polyaniline is filling up the void space of porous silica as in Fig. 39 (a), the surface area of the particle would be decreased with increasing content of aniline because of elimination of surface in pores. The actual results of BET surface area measurement in Fig. 33 showed the decrease of the surface area with increasing content of aniline. Therefore we could say that the polyaniline is possibly filling up the pores of silica particle.

If the polymer is incorporated into the pores of silica particle to form composite structure, then surface area would be restored after complete removal of the polymer from particle as shown in Fig. 39 (b). One possible way to remove the polymer from the

composite particle is the heat treatment at temperatures where polymer could be burned out. When particles were heated up to 500 °C, the surface area was increased, as was observed as in Fig. 35. With heat treatments at 300 °C and at 500 °C, we could see gradual increase of surface areas. The removal of the polymer from the composite particle was proved by the FTIR spectra in Fig. 37. After the thermal decomposition at 500 °C there remained no trace of characteristic absorption peaks of polyaniline, which means the complete removal of polymer from particles.

This increase of surface area after heat treatment was not observed for pure silica particles. With the same thermal treatment, pure silica particle showed rather slight decrease of surface area, which could be interpreted as sintering effect as was depicted in Fig. 39 (b).

The observed results are indicating that the obtained particles are in the form of composite nanoparticle. In the composite nanoparticles silica forms the skeleton, and polyaniline was incorporated into the pores of silica skeleton. With these understandings it could be said that composite nanoparticle of silica/polyaniline was synthesized from the aqueous micelles of the inverse (water-in-oil) microemulsion using TEOS and aniline as precursors, HCl as catalyst.

### 5.3.4. Enhancement of stability

The composite structure is made to enhance electrochemical stability of material. The main idea is that silica in the composite structure will protect polyaniline from chemical attacks from outside. As was described from the previous section, composite particles were produced from microemulsion solution using TEOS and aniline. Thus the chemical stability of the obtained material would rather be checked. For the chemical stability check, dissolution of polyaniline from composite particle into an effective solvent for polyaniline was tried and the investigation on the remaining solution and particle were investigated. In this study, formic acid was employed for the effective solvents to dissolve out the polyaniline.

Generally, polyaniline is known with its poor processibility. It's because that polyaniline is non-soluble to almost all organic solvents [81]. However, formic acid is considered as an effective solvent for dissolving polyaniline [69]. Thus in this study, a dissolution of composite material into formic acid was tried. The composite particle

sample for the dissolution experiment was prepared by extracting particles from microemulsion and by a subsequent washing with ethanol and drying at 150 °C.

For a comparison of dissolution behavior, a set of pure polyaniline particle sample was also prepared from microemulsion solution. The microemulsion solution for polyaniline was prepared with the same composition with the composite microemulsion solution only without the addition of TEOS. The solution was kept under mild stirring at room temperature for 24 hrs, and synthesized polyaniline particles were extracted. The extracted particles were also washed with ethanol, and dried at 150 °C for 2 hrs. These were the same treatment for composite particles.

Prepared samples were put into formic acid, and the mixed solutions were kept under ultrasonic agitation for 30 min to induce dissolution. The ultrasonic agitations were done with a laboratory ultrasonic cleaner. After the ultrasonic agitation, samples were kept under mild stirring for 24 hrs to ensure the sufficient time for dissolution. After the stirring, solutions were centrifuged to separate particles which were left from the dissolution. The photo in Fig. 40 showed difference between the two samples, i.e. composite particle and polyaniline.



Fig. 40   Dissolution behaviors for composite particles (left) and polyaniline particles (right) into formic acid.

For the case of composite particle sample, most part of particle precipitates remained after the dissolution. When precipitates were separated, the liquid solution showed a slight tint of green. On the other hand, the pure polyaniline showed almost no precipitate remained after the dissolution, and the liquid solution became homogenous. The color of resulting solution was dark green. It showed that composite particles were not dissolved into formic acid, whereas polyaniline particles were completely dissolved. The slight tint of separated solution for the case of composite particle sample could be understood that a small portion of polyaniline was dissolved out from the particle. After the polymer was successfully incorporated into composite particles, there would have been some portion of polyaniline attached on the surface of particle. There could also have been isolated polyaniline which were not incorporated into the composite particle, while most of the polyaniline was incorporated into composite particles, since they were synthesized in the micelle. During the dissolution, polyaniline on the surface of particles and the isolated polyaniline would be dissolved out into formic acid, and consequently produced the slight tint of green in the solution.

Before and after the dissolution, FTIR spectra were performed and compared for the composite particles. The results are given in Fig. 41.
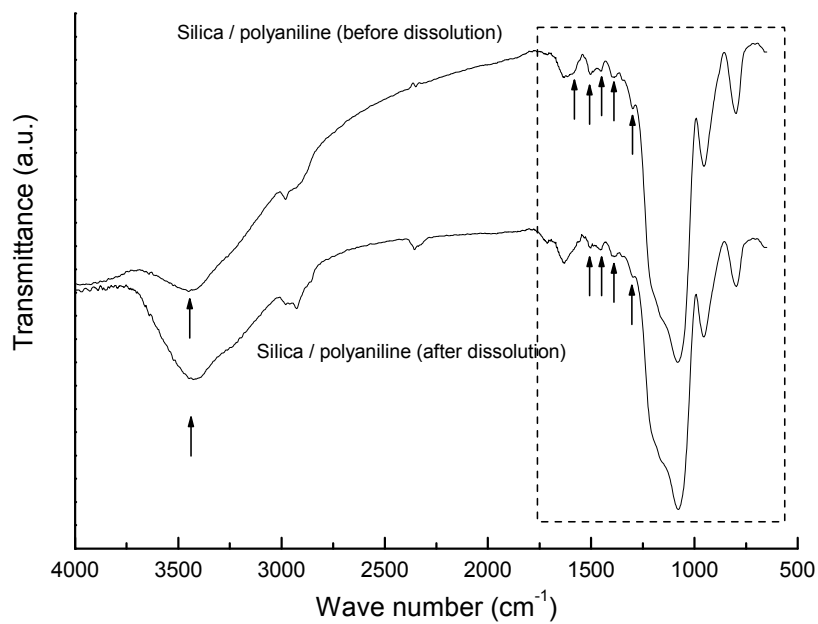
(a)
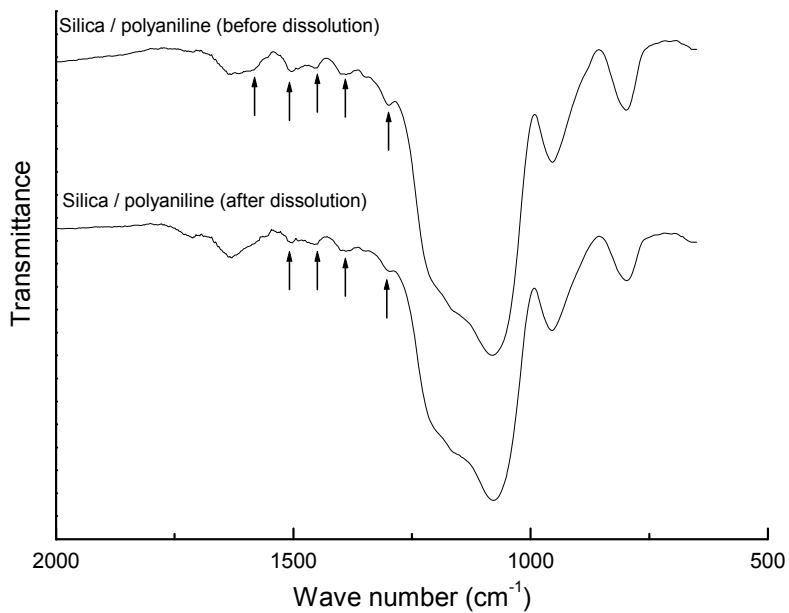


(b)

Fig. 41   FTIR spectra for the composite particle before and after washing with formic
acid (The dashed box from (a) is magnified as (b).)

The characteristic absorption peaks of polyaniline at 1588, 1505, 1452, 1390 and 1304 cm-1 were not affected much after the dissolution trial. This means that majority of polyaniline remained in particles after the dissolution. It can be said that the polymer parts in the composite particle are strongly protected from the chemical attack.

With the results of the BET and the dissolution experiments, it could be said that the individual particles produced from microemulsion using TEOS and aniline has a composite structure. In this composite structure, polyaniline is incorporated in the pores of silica particle rather than attached on the surface or isolated from the particle. As was intended, polyaniline was synthesized inside the pores of silica network which was illustrated in Fig. 39. It could also be said that the composite structure enhances the chemical stability of the material such as resistivity to the dissolution by formic acid; otherwise the pure polyaniline would be completely dissolved.

### 5.4. Electrochromic properties of composite material

Electrochromic behavior is originated by an electrochemically induced oxidation-reduction reaction, and the electrochromic material shows color change in a persistent but reversible manner. High electrochromic efficiency, short response time, long operating life time and reduction of energy consumption are the most important requisites for the electrochromic materials [1-3]. Among these requisites the operation life time of the device is one of the obstacles for display device application. Even though, polymer electrochromic material usually exhibits longer operation life time than inorganic material, but the operation life time of polymers are still not sufficient.

As could be found from the literature review, the electrochemical stability of the polymer is being considered as one of the key factors determining the operating life time [5-7]. In this study, polyaniline was selected as the electrochromic polymer. As Kobayashi et al discussed [46], the electrochemical degradation of polyaniline is observed when sufficiently high anodic potential is applied. The oxidation of polyaniline with the application of potential > 0.8 V could produce positively charged form which is more susceptible to the attack of water or other kinds of nucleophiles from the electrolyte system [124]. Thus, to achieve prolonged operating life time, it is necessary to improve electrochemical stability of the material.

Many efforts could be found to enhance the durability of the polymer electrochromic material. To improve the electrochemical stability, modified polyaniline derivatives could be considered [125, 126]. On the other side, it is widely accepted that the inorganic-organic hybridization is an effective method to improve the mechanical and chemical stability of the polymer material [58, 127]. It has been demonstrated that the electrochemical stability of polymer materials could be improved by forming composites with chemically stable inorganic (i.e. $SiO_2$, $Al_2O_3$) particles or matrixes [47-50]. Fu et al. pointed out, that the strong interaction between the surface group of silica particle and polymer reduces the direct interfacial reaction between polymer and attacking electrolytes. Thus in this study, the inorganic-organic composite structure is being studied, and because of the possibility of application to optical devices the composite is designated in form of nanoparticle.

Up to now it was demonstrated that the silica/polyaniline composite nanoparticle could be obtained from an inverse microemulsion solution using TEOS and aniline as precursors. It was also shown in the previous experiments that the composite structure successfully protects polyaniline from the dissolution attack of formic acid. This could be considered as an enhancement of chemical durability of the material. The next step is to show that the chemical durability could result in an improvement of electrochromic properties. In this section, to investigate the electrochromic properties of the composite material, the silica/polyaniline composite nanoparticle was applied in the electrochromic film. By comparing the electrochromic properties with the polyaniline film which was obtained by conventional chemical polymerization, the enhancement of durability for the composite film was verified.

### 5.4.1.  Preparation electrochromic films

The coating solution was prepared using composite particle synthesized from the microemulsion through the same process as was done in the composite particle production experiment (see page 82). The obtained composite particles were extracted from the microemulsion solution. The extraction of particle was done also by the same method as previous sections in which the excess amount of 1-butanol was added to the microemulsion solution. The precipitates were then separated from the microemulsion solution by a centrifuge at 5000 rpm. The extracted precipitates were shown in Fig. 42.
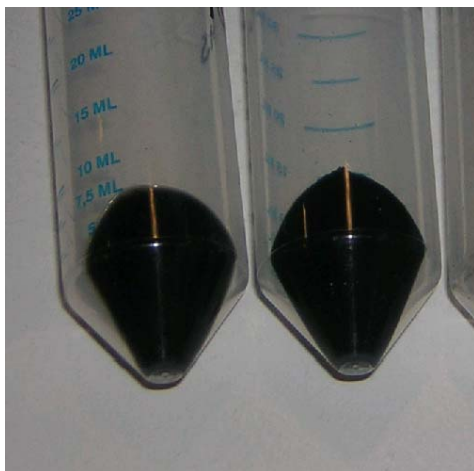
Fig. 42   The composite particles extracted from microemulsion by adding 1-butanol and by a centrifuge at 5000 rpm

The extracted particles were then washed with ethanol five times, and then they were dispersed into ethanol without drying. No other additive was used for the dispersion, since the particles were well dispersed into ethanol. For almost 24 hrs no sedimentation was found. The solution was used as coating solution as it was. The dispersed solution is shown in Fig. 43.
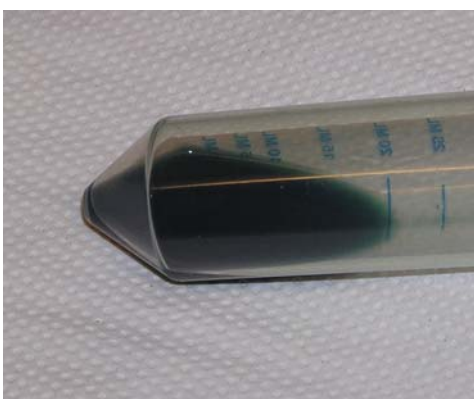


Fig. 43   Coating solution prepared by dispersing the extracted composite particles into ethanol

It could be easily expected that the microstructure of particles were changed after the extraction from the microemulsion solution, since the extraction was done by triggering the flocculation of particle. Before the flocculation the particles were completely dispersed in the microemulsion solution, which was shown in the TEM photo in Fig. 44(a). For the flocculation of the particle, the micelles were broken, and added 1-butanol did that by lowering the critical micelle concentration (CMC) of microemulsion. Once the particles were flocculated, then the dispersion state of the particles could possibly be different when they were redispersed into the ethanol.

The microstructure of extracted composite particle was investigated by a TEM, and compared with the composite particle in the microemulsion solution. A TEM specimen was prepared by dropping the ethanol solution with the dispersed composite particle onto a carbon coated Cu-grid, and drying at room temperature. The TEM photo is given in Fig. 44.
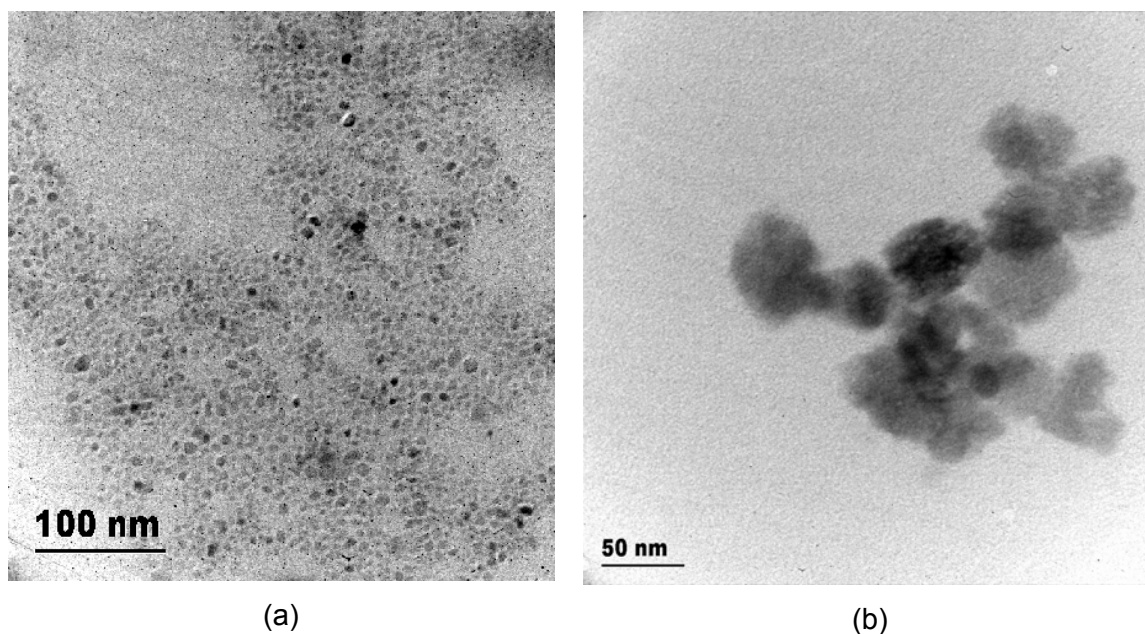


<div align="center">(a)        (b)</div>

Fig. 44   TEM photo of the composite particles: the TEM samples were prepared on the carbon coated Cu grid from a) one drop of microemulsion solution and from b) one drop of ethanol solution dispersed with the extracted particle from the microemulsion

The TEM photo from the ethanol solution showed some big agglomerations with sizes ~ 50 nm (Fig. 44 (b)). The agglomerations are quite obvious when it is compared with the TEM photo from the microemulsion solution (Fig. 44 (a)). In this study, it was not further explored how to break the agglomeration or how to avoid it, but for an application of the material to display device field it seems necessary to find a way. Since the dispersion study itself would be a big topic, in this study, it was left for a future research work.

Using above prepared ethanol solution, composite film was deposited on a fluorine-doped tin oxide (FTO) -coated glass. For the film preparation a spin coating technique was employed. The solution was injected onto the substrate while it was rotating at 2000 rpm under ambient atmosphere. After the injection, the substrate was kept rotating for 30 seconds for further drying of ethanol. To control the film thickness, injection / drying were repeated 10 times. The spin-coated sample was then heat treated in an oven at 150 °C 2 hrs to eliminate remaining solvent.

To see the enhancement of electrochromic properties of the composite film, it is necessary to compare the properties with those of a film which is made of polyaniline itself. The operation life time of a device could be affected not only by the electrochromic film but by the type and kind of electrolyte used also. Therefore, to investigate the improvement effect of the electrochromic properties from the new material, the comparison of the properties before and after the change of materials would rather be indispensable. Then the properties of the electrochromic films could be compared with the other conditions as same.

Polyaniline film was also prepared on the FTO-coated glass. The polyaniline film was deposited through a chemical polymerization coating method. Gospodinova et al [128] showed that polyaniline film could be obtained by a chemical polymerization of aniline in an acidic aqueous solution. In this study, the chemical polymerization of aniline was induced by mixing the two acidic aqueous solutions of aniline and of ammonium peroxodisulfate (APS). Each of the solution was prepared by dissolving monomer aniline and APS into 0.1 M HCl aqueous solutions. Then the two solutions were mixed into one mixed solution. The concentrations of aniline and APS in the mixed solution were set to be 0.1 and 0.1 M, respectively. A FTO-coated glass was then dipped into the mixed solution and kept for 24 hrs. After dark green film was formed, the glass was took out from the solution and washed thoroughly with distilled

water to remove remaining chemicals and solvent. The washed film was then dried in oven at 150 °C for 2 hrs.

As is pointed out above, for the comparison, the other conditions must be controlled in a same range to see clearly the properties differences from the difference of material. In the process of film preparation, it is important to control the thickness of prepared electrochromic film of composite and polyaniline. To check the thickness and to compare the microstructure of the obtained composite and pure polyaniline films the scanning electron microscopy (SEM) was done. The SEM photos of the samples are given in Fig. 45. The thicknesses of the composite film prepared by 10 times spin coating and that of the polyaniline film obtained by 24 hrs chemical polymerization coating were in the same range as 200 – 300 nm.



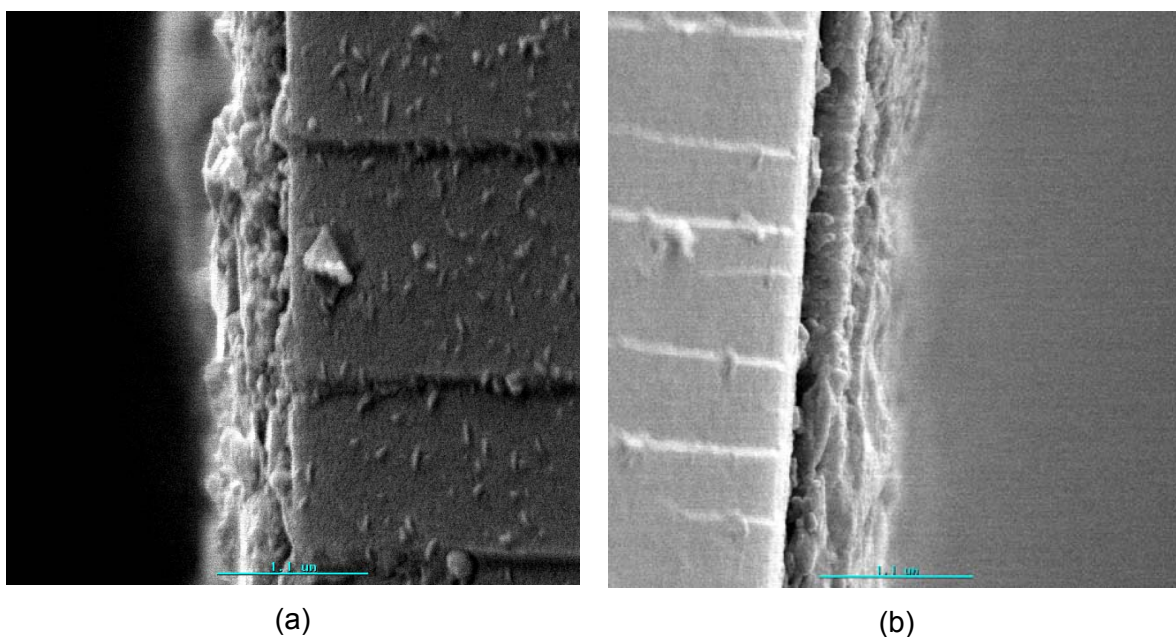(a)                                                      (b)

Fig. 45    SEM photo of coating deposited on the FTO-coated glasses with a) composite material by 10 times spin coating and b) polyaniline by 24 hrs of chemical polymerization coating.

To compare the electrochromic properties of the films, samples with the similar thicknesses were selected. The prepared films on the glass substrate were shown in Fig. 46. The silica/polyaniline composite film exhibits its color as green while the pure polyaniline film shows rather dark blue. This difference seems to be coming from the different oxidation states of polyaniline [37, 38]. The dark blue pure polyaniline film

supposedly represents nigraniline. The green color of composite film represents reduced form as emeraldine phase of polyaniline. This difference of oxidation state could easily be observed when the materials were made following the different preparation processes.
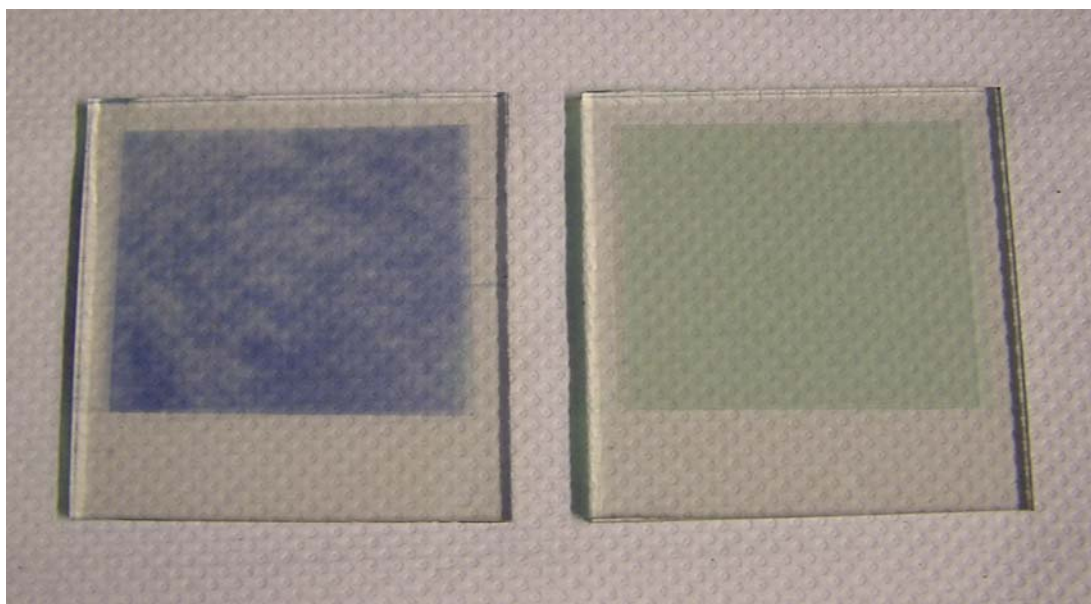


Fig. 46    Electrochromic coatings prepared on the FTO-coated glass; left: polyaniline, right: silica/polyaniline composite

### 5.4.2.  Electrochromic properties

Electrochromic properties of the composite film and polyaniline film were compared by cyclovoltammogram, optical transmittance spectroscopy, and measurement of optical contrast at a fixed wavelength of light.

For the electrochromic properties analyses on the above prepared films, 3-electrode cells were prepared. As was discussed in the "Literature Review" part (see page 13), a 3-electrode cell is useful to see the electrochemical phenomena of the working electrode separately from the counter electrode and reference electrode. The 3-electrode cell is composed of a working electrode, a reference electrode and a counter electrode. From the 3-electrode cell configuration, it is possible to check the electrical current change according to a potential change across the working electrode. The

prepared composite and polyaniline film were placed as the working electrodes for each 3-electrode cell. The reference electrode of the cells was saturated calomel electrode (SCE), and the counter electrode was Pt plate. As the electrolyte, 0.1 M $HClO_4$ aqueous solution was used. The prepared 3-electrode cell in this study is shown in Fig. 47, and the electric circuit is equivalent as the diagram given in Fig. 6 in the "Literature Review" part at page 13.
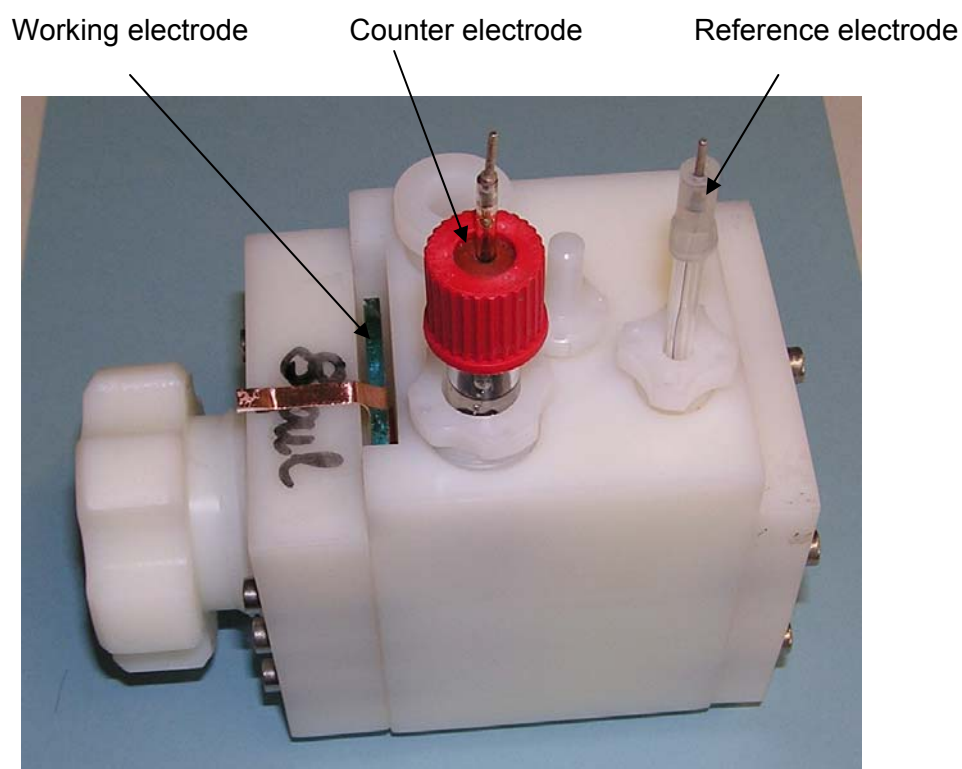


Fig. 47   The 3-electrode cell prepared with the composite film on the FTO-coated glass, Pt counter electrode and calomel reference electrode (The electrolyte solution was 0.1 M $HClO_4$ aqueous solution.)

Utilizing the 3-electrode cell, the comparison of the electrochromic properties of the composite and the polyaniline film was done. The experimental results could be given in the form of cyclovoltammogram, visible transmittance spectrum, the optical contrast variation at a fixed wavelength of light. These experiments were done at room temperature.

The cyclovoltammograms for the composite film and the polyaniline film are given in Fig. 48. The cyclovoltammogram for the samples were done in the potential range from -0.2 to +1 volt with a potential scanning speed 50 mV/s. For the cyclovoltammography, a potentiostat is used. As can be seen from the curves, those two samples showed almost the same shape. Two anodic peaks and two cathodic peaks were observed at the same region of potentials with a difference of peak height for the composite film and the polyaniline film. The peaks positions and heights are compared for the two samples in Table 13.
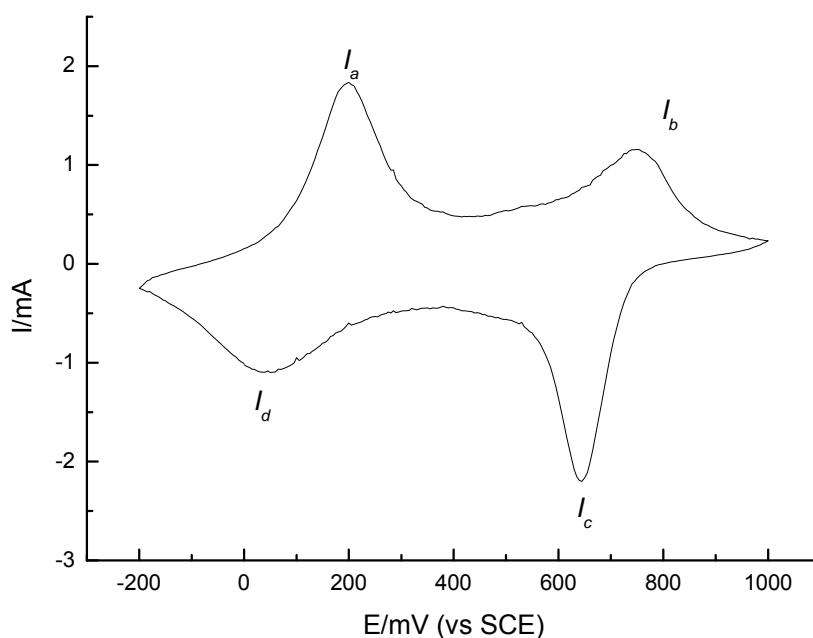


(a)

Fig. 48    Cyclovoltammogram of the prepared cell with the working electrodes made of (a) silica/polyaniline (b) polyaniline at the scan rate 50 mV/s.
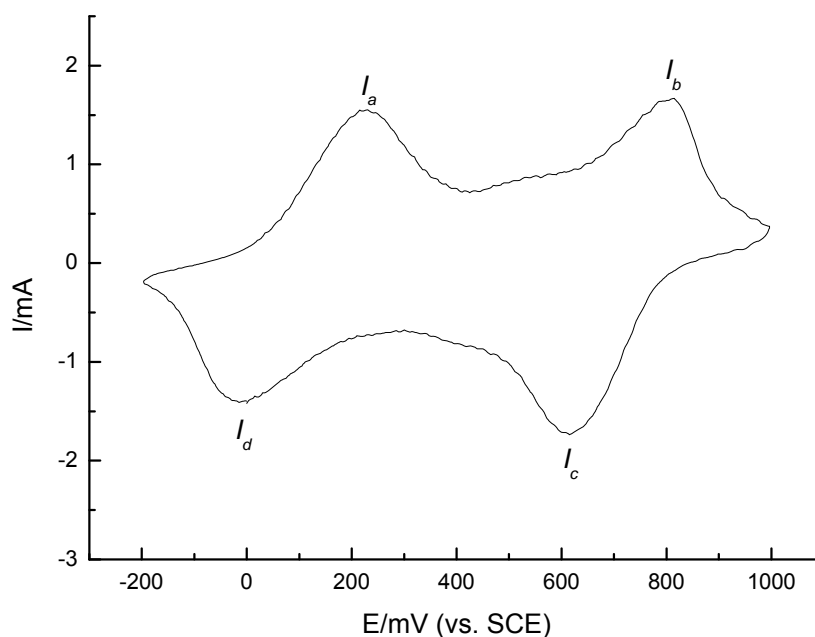
(b)

Fig. 48  continued.

Table 13  The position and current height of the peaks observed from the cyclovoltammograms of composite and polyaniline films in Fig. 48.

|  |  | $I_a$ | $I_b$ | $I_c$ | $I_d$ |
|---|---|---|---|---|---|
| Composite film | Potential Position (mV) | 198.9 | 746.6 | 644.1 | 42.0 |
|  | Current Height (mA) | 1.826 | 1.158 | -2.194 | -1.101 |
| Polyaniline film | Potential Position (mV) | 228.7 | 809.4 | 612.6 | -12.1 |
|  | Current Height (mA) | 1.559 | 1.674 | -1.723 | -1.389 |

When the anodic potential peaks $I_a$ and $I_b$ were compared, the composite film showed higher peak current at lower anodic potential peak $I_a$. However, the polyaniline film showed higher peak at a higher anodic potential peak $I_b$. The peak position of $I_b$ is shifted to a higher potential for the polyaniline film. This observation represents that in the polyaniline film an electrochemical reaction at the higher anodic potential was

stronger compared to the reaction at the lower anodic potential. In the composite film, the reaction at higher anodic potential is weaker than that at lower potential. The potential for the reaction at $I_b$ is lower for the composite film (746.6 mV) than for the polyaniline film (809.4 mV). As was discussed above, the oxidation of polyaniline with the application of potential > 0.8 V could produce positively charged form [124]. And this highly oxidized phase is more susceptible to the attack of corrosive species from the electrolyte solution. According to this, the results of the cyclovoltammetry of the two samples showed that the composite film would be advantageous on the polyaniline film, since in the composite film the weaker phase of polyaniline will be formed less.

If the extent of highly oxidized phase formation is different for the two samples, then the optical transmittance spectra in the visible range would be different, since the polyaniline phases at different extent of oxidation have different colors (see Table 3). The comparison of the visible transmittance spectra for the two samples was done in the wavelength range of 400 – 800 nm, and the results are given in Fig. 49. The 3-electrode cells were put into a UV/VIS spectrometer and the cells have windows so that the incident beam could reach the working electrode passing the electrolyte solution and the transmitted beam could go the spectrometer again.

At the bleached state with the potential -0.2V, the composite film and the polyaniline film showed no color or pale yellow, this is represented by the same shape of curves. When a positive potential, +1.0V applied, the composite film showed its color as dark green while the polyaniline film showed dark blue. This difference of color can also be represented by the different shape of curves below 550 nm. The composite film in a colored state showed higher transmittance than the polyaniline film especially below 550 nm. Normally, the dark blue would be regarded as the color of highly oxidized form of polyaniline as nigraniline or pernigraniline while the dark green for emeraldine. Therefore, from the cyclovoltammogram and the optical transmittance spectra, it could be said that under the same potential range (from -0.2 V to +1.0 V) less amount of highly oxidized phase of polyaniline was formed from the composite film than from the polyaniline film.
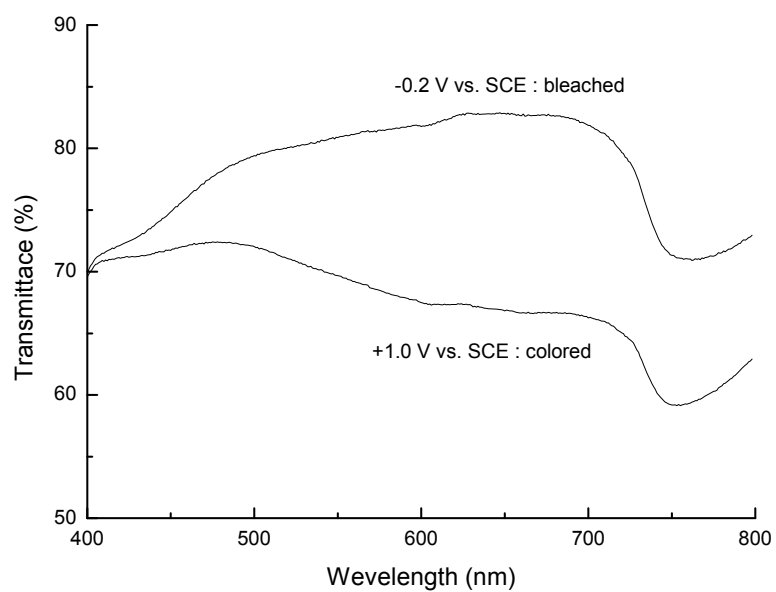
(a)
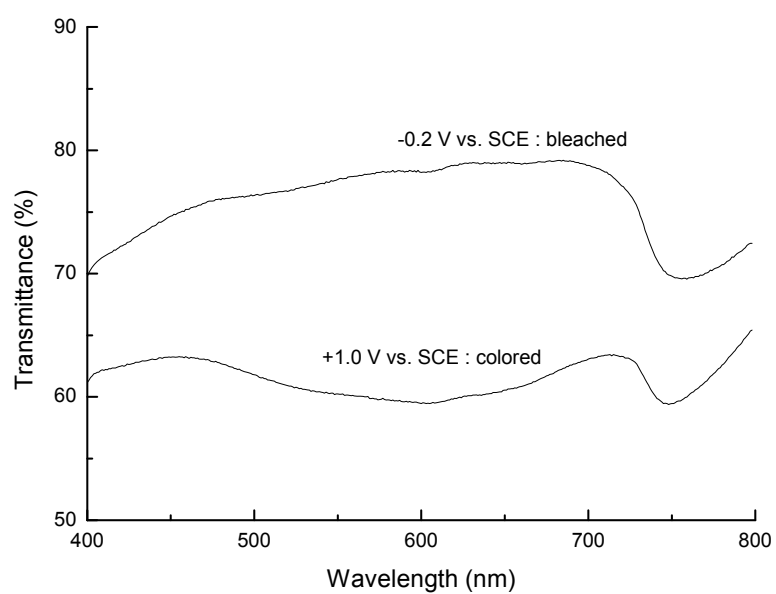


(b)

Fig. 49  Optical transmittance spectra at bleached and colored state of (a) the composite material and (b) the polyaniline in a visible range. The bleaching was done at -0.2 V and the coloration was done at +1.0 V.

The composite structure was intended for a new electrochromic material that the chemically stable silica could protect polyaniline from the attack from electrolyte solution to have better electrochemical durability. However, the composite structure could mean less chance for the polyaniline to form interface with the electrolyte solution from or to where charged species should be transferred for the oxidation and reduction reactions. Therefore, the composite structure could do a disadvantageous effect on the response time of the material. To check the effect, optical response characteristics were investigated and compared.
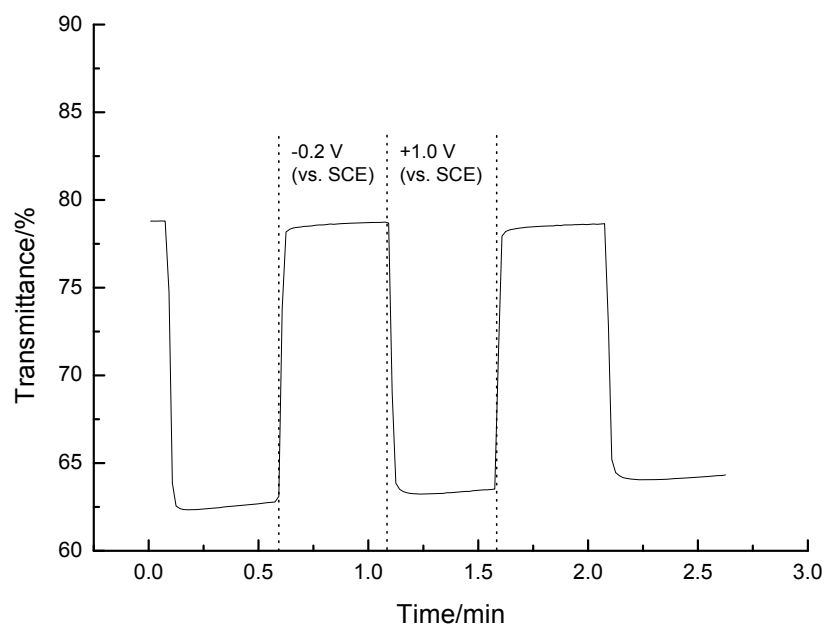
The optical responses of the films were obtained by applying the switching potential of -0.2 V and +1.0 V vs. SCE with 30 seconds delay for each step. During the switching of potential, the optical transmittance change was measured at a fixed wavelength of light. In this study the fixed wavelength was set to 600 nm. The obtained optical response curves of the composite and polyaniline samples were given in Fig. 50. From the response curve,

At the anodic potential (+1.0 V) the polyaniline film showed little faster response than the composite film whereas the responses to the cathodic potential (-0.2 V) for the two samples were almost same. As was expected, the composite structure of electrochromic material did the disadvantageous effect on the response speed of the material.

As was discussed above at page 100, the formation of highly oxidized phase of polyaniline could be a cause of degradation of the electrochromic film. An optical contrast changes were measured and compared for the two samples as in Fig. 51. While applying the switching potential between -0.2 V and +1.0 V with 30 seconds delay, the optical transmittance was monitored at 600 nm. As can be seen from the graphs, the composite film and the polyaniline showed the decrease of optical contrast with the increasing number of switching. The optical contrast (ΔTransmittance%) of the composite film decreased from 12.6 to 6.8 after 80 switchings whereas that of the polyaniline film decreased from 16.5 to 4.4. The optical contrast changes of the two samples (composite film and polyaniline film) were calculated and plotted as in Fig. 52.
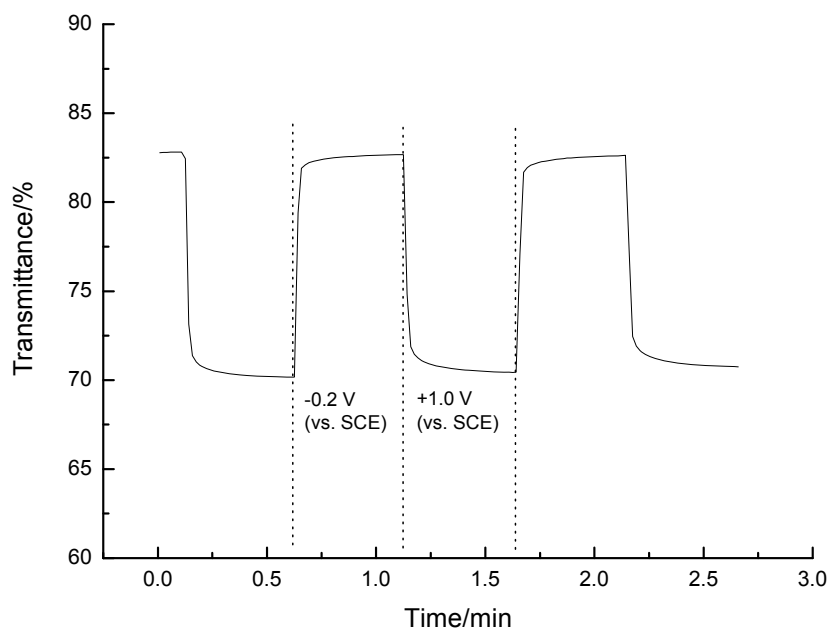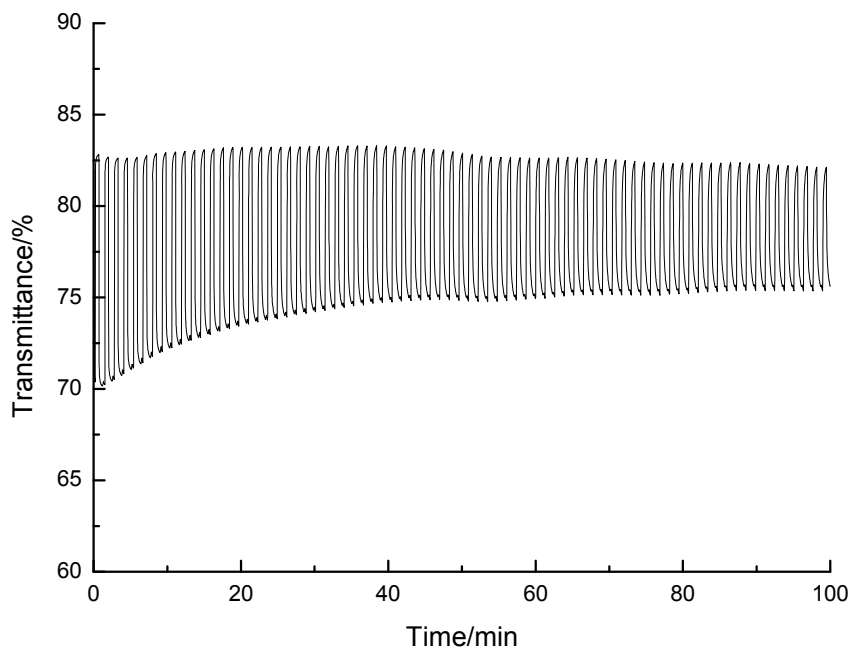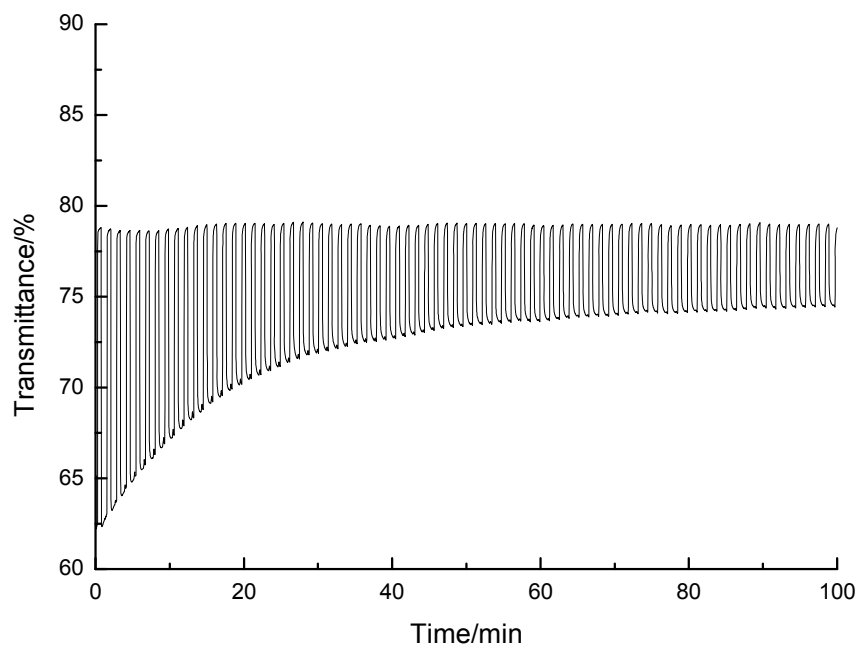
(a)



(b)

Fig. 50  Optical Responses of the films at 600 nm: a) silica/polyaniline composite particle and of b) polyaniline.

(a)



(b)

Fig. 51   Color contrast (at 600 nm) decrease during the potential switching -0.2 V and
+1.0 V for the films: a) silica/polyaniline composite film, b) polyaniline film.
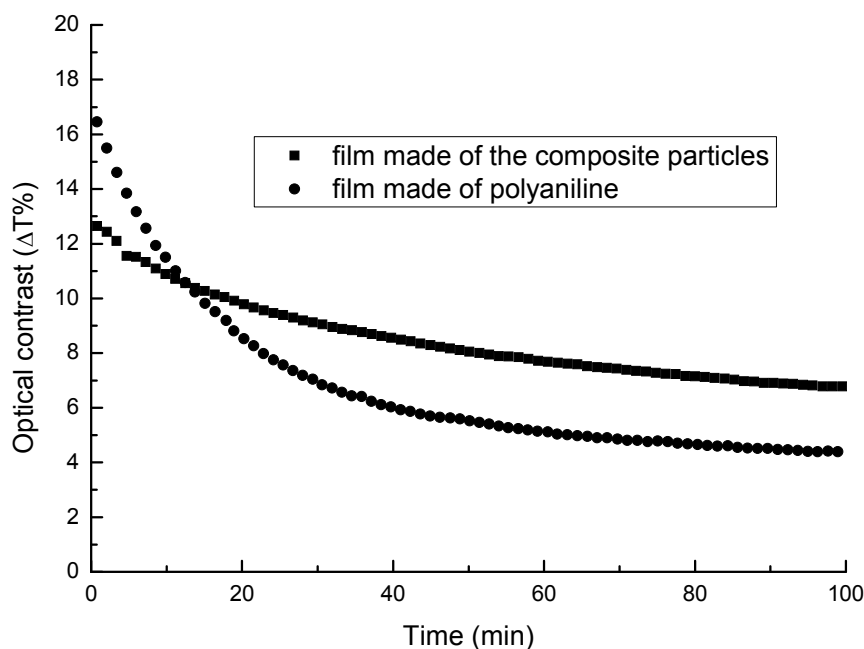
Fig. 52    Comparison of optical contrast change of films made of the composite particle and of polyaniline during the potential switching -0.2 V and +1.0 V (see Fig. 51)

Both of the films showed decrease of optical contrast, but for the composite film the decrease was slower than for the polyaniline film. The polyaniline film showed a rapid decrease of optical contrast at the first 20 switches. At the start of the potential switching the optical contrast of the polyaniline film was larger, but after around 10 times of switching the optical contrast of the polyaniline film became smaller than that of the composite film. This shows the enhancement of the electrochromic operation life time for the film made of composite particle.

The increases of transmittance at anodic potential were observed while at cathodic potential the transmittance was steady. The increase of transmittance at anodic potential was slower for the composite film.

### 5.4.3. Enhancement of electrochromic properties

The main purpose of this study is to see the enhancement of the durability of electrochromic layer by applying the composite structure of silica/polyaniline. In the previous sections, it was demonstrated that the silica/polyaniline composite nanoparticle could be obtained from the inverse microemulsion solution. As chemically stable silica is protecting polyaniline (Fig. 53), the composite particle would exhibit enhanced electrochemical stability than the single component of polyaniline. With the enhanced electrochemical stability of the material, the degradation of the polymer will be delayed and hence the durability of the material could be increased.

In this study, the electrochromic properties of the composite film and the polyaniline film deposited on the FTO-coated glasses were compared. The cyclovoltammogram of those two samples showed quite similar pattern as in Fig. 48. This similar pattern of cyclovoltammogram means that the electrochromic characteristics of the composite film are originated from the polyaniline in the composite material.



silica network

silica/polyaniline composite nanoparticle

inorganic-organic hybrid

higher electrochemical stability than single component polyaniline

polyaniline

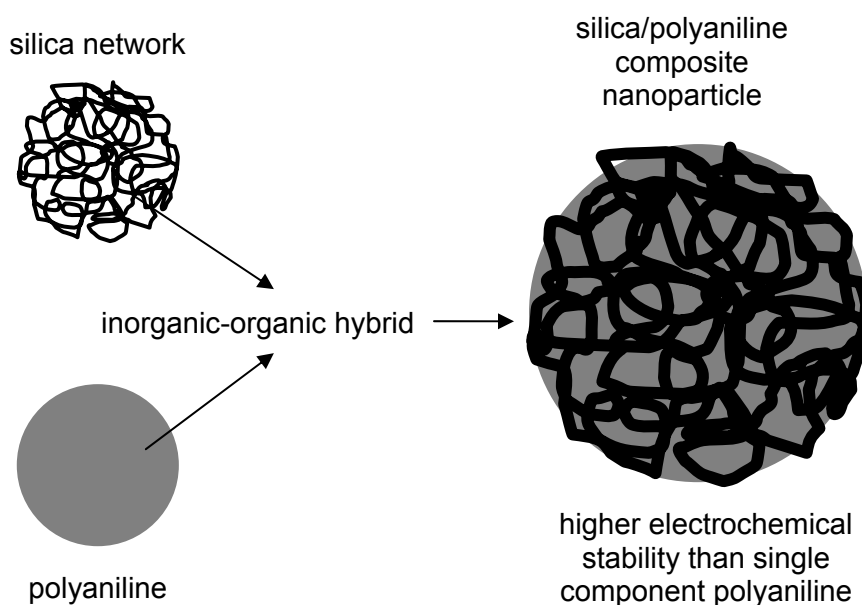Fig. 53  A schematic drawing of the structure of the composite nanoparticle

However the visible spectrum curve showed a little difference at the coloration colored state. The composite film showed a higher transmittance at the coloration state than the polyaniline film in the wavelength region below 550 nm (Fig. 49 (a)). This could be interpreted as the formation of nigraniline rather than the pernigraniline.

Nigraniline phase of polyaniline usually exhibits dark blue color whereas pernigraniline shows dark gray or black. For the polyaniline film (Fig. 49 (b)), the lower transmittance below 550 nm could be caused by the formation of pernigraniline. These different behaviors of the two samples could be observed with bare eyes as the different colors at the oxidized state such as blue color for the composite film and dark gray color for the polyaniline film. The preferred formation of pernigraniline for the polyaniline film could also be observed from the cyclovoltammogram in Fig. 48. In the cyclovoltammogram the composite film showed lower peak at higher anodic potential ($I_b$) than at lower anodic potential ($I_a$) while the polyaniline film showed higher peak at higher potential. The peaks at higher anodic potential represent the oxidation reaction to form nigraniline and pernigraniline [129]. Therefore, it could be said that in the composite film the pernigraniline formation was depressed as compared with the polyaniline film. The highly oxidized form of polyaniline which would be formed at high anodic potential is generally weak against the chemical attack from the electrolyte and is the main cause of the electrochemical degradation of polyaniline [124]. The composite film of this study would be said to be helpful to reduce the formation of the highly oxidized form of polyaniline.

The difference of the coloration response speed could also be attributed to the structure difference of the two samples. The coloration phenomena can be explained by the doping reaction as in Eq. 4. The emeraldine base is doped to transform to nigraniline or pernigraniline salt at the high anodic potential (+1.0 V). For the doping of $Cl^-$ ion, the large cation should be intercalated into the polymer network. When the polyaniline is protected by the silica which is the case of composite film (Fig. 53), the intercalation of the cation would take longer time than the single component polyaniline film. The longer time of the intercalation of cation was shown as the slower response to the potential switching as in Fig. 50.

$$\text{Emeraldine base} + m\,Cl_4^- \leftrightarrow \underset{\text{Pernigraniline Salt}}{\text{Emeraldine base}^{m+}\left(Cl_4^-\right)_m} + m\,e^-$$
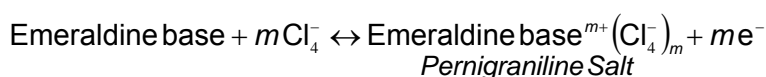
Eq. 4

Since the formation of pernigraniline was reduced in the composite film, it could be expected that the degradation will be slower than in the polyaniline film. The degree of degradation was checked by measuring the optical contrast change with the number of

potential switching. As can be seen from Fig. 51, composite film maintained larger optical contrast (Fig. 51 (a)) than the polyaniline film (Fig. 51 (b)) after the same number of switching. This means the degradation of composite film was slower than the polyaniline film.

With the optical transmittance and the optical contrast measurement results, it could be said that the composite film has higher durability than the single component polyaniline film probably because of the less formation of highly oxidized form at high anodic potential.

In this study, we demonstrated an electrochromic property enhancement of the film made of silica/polyaniline composite nanoparticle. The composite particles which were synthesized from an inverse microemulsion solution were applied as a film on the FTO-coated glass. From the comparison of the electrochromic properties with the chemical polymerization deposited polyaniline, the composite film showed a durability increase. This stability enhancement was interpreted as that the formation of highly oxidized form of polyaniline was suppressed by the protective effect of the composite structure of the nanoparticle.

### 5.4.4.  4-layer structure electrochromic cell

A layer structure cell was assembled to demonstrate the electrochromic behavior of the composite film. Ram et al [130] showed that 4-layer electrochromic cell could be built rather than a 5-layer cell. The 4-layer cell is composed of transparent conducting electrode / electrochromic layer / electrolyte / transparent conducting electrode as was illustrated in Fig. 54.

FTO / polyaniline / Electrolyte / WO$_3$ / FTO

FTO / polyaniline / Electrolyte / FTO

(a)

(b)
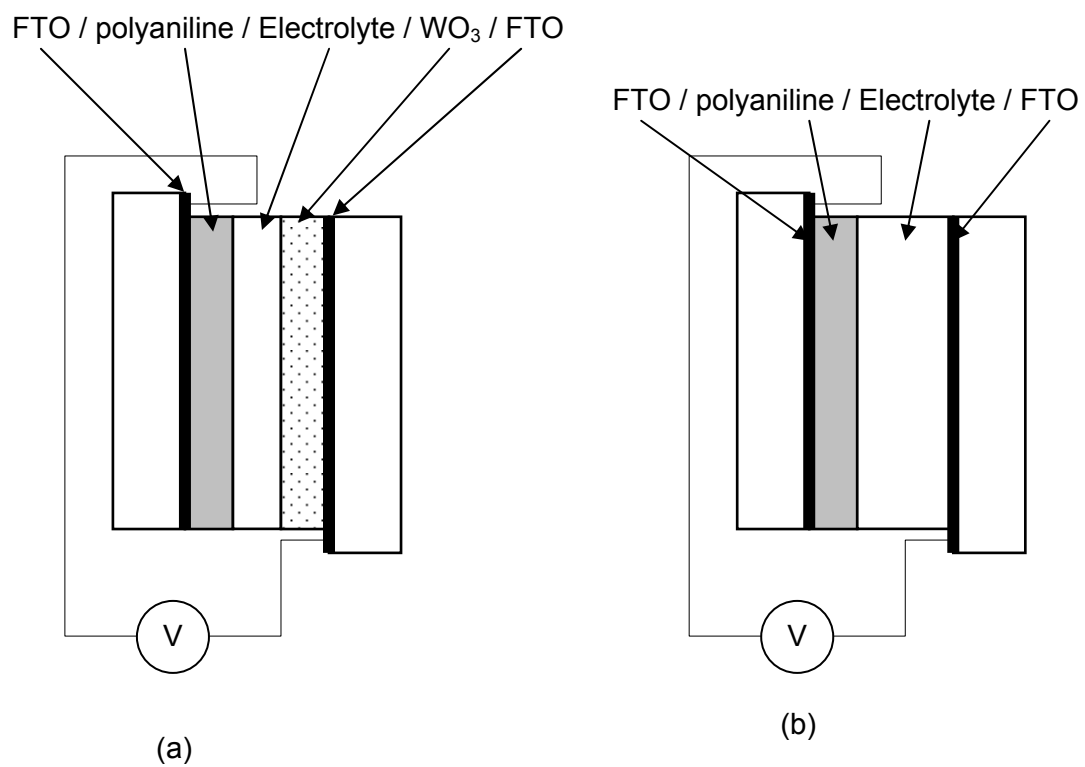
Fig. 54 A comparison of a) 5-layer cell [44] and b) 4-layer cell [130]

In the 4-electrode cell the counter electrode is omitted. For a simple demonstration in this study the 4-layer electrochromic cell was built. The device built in this study is shown in Fig. 55. The electrochromic layer in this case was the composite film deposited by a spin coating.

(a)



(b)

Fig. 55   Color change of 3-layer cell from (a) yellow at -2.1 volt to (b) dark gray at +3.2 volt.

When a positive potential of +3.2 volt was applied on the composite film the color has changed to dark blue from light yellow and when a negative potential of -2.1 volt was applied on the film, then the color has changed to light yellow reversibly.

For a more quantitative view of the electrochromic phenomena of the composite film, a cyclovoltammogram was also performed with the prepared 4-layer cell. The result is given in Fig. 56.
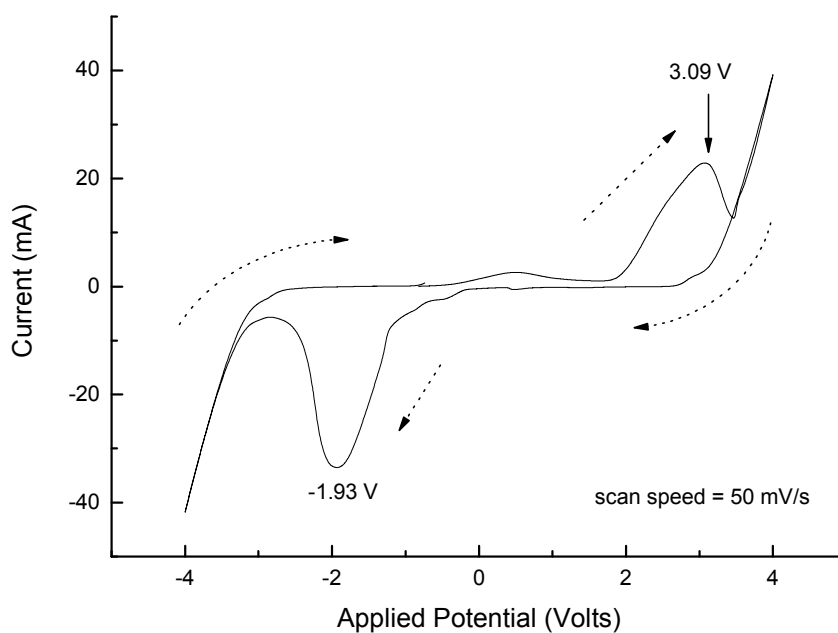


Fig. 56  Cyclovoltammogram of 4-layer cell built with the composite material

At a positive potential of 3.09 volt there appeared a current peak representing an oxidation of polyaniline. This corresponds to a color change from light yellow to dark blue. At a negative potential at -1.93 volt, another current peak was observed, and it represents a reduction of polyaniline. This corresponds to a color change from dark blue to light yellow.

## 5.5.  Evaluation of the results

From the literature survey, it was discussed that the electrochromic device has not been materialized yet mainly because of the limited operation life time of the electrochromic film. One of the possible reasons for the limited operation life time is a weak chemical durability of the electrochromic material. Therefore, it was intended, in

this study, to enhance the chemical durability of a conductive polymer as an electrochromic material by forming a composite with a chemically stable inorganic counterpart.

In this study, the conductive polymer was selected as polyaniline which has been studied by many researchers that the electrical (and/or electrochromic) properties were well explored. The inorganic counterpart was silica which has high chemical durability compared to polymer material and would have no interference to the electrochromic properties of polyaniline. The possibility of the material's application to an optical device required that the composite would rather be made in form of nanoparticle. In this respect, the silica/polyaniline composite was prepared as nanoparticles for which an inverse microemulsion synthetic method was employed. Actually, a simultaneous synthesis of silica and polyaniline was intended in the dispersed aqueous micelles.

An inverse microemulsion with a composition of cyclohexane / Triton X-100 : 1-hexanol / aqueous phase was selected for the particle synthesis. The micelle size study showed that it is suitable for the composite particle preparation, since the micelle sizes were less than 100 nm all through the pH range of dispersed aqueous phase from 2 to 12 (see Fig. 20, Fig. 21 and Fig. 22). This is required so that the composite particle sizes should also be suppressed under 100 nm to avoid optical scattering for the application of the material in optical devices. From the composition selection and micelle size measurement experiments on the microemulsion solutions, it was concluded that the selected microemulsion as 65.4 wt% cyclohexane, 30.4 wt% surfactant (Triton X-100 : 1-hexanol), 4.2 wt% aqueous phase is suitable for the composite nanoparticle production.

With the given microemulsion composition, a synthesis of porous silica particle was tried to see the possibility of silica particle formation in an acidic condition of aqueous phase. As was pointed out in the "Literature Review" part at page 26, the production of silica nanoparticle has been doing usually under basic conditions. However, in this study, it was conducted in an acidic condition since the polymerization of aniline inevitably requires the acidic condition. As can be seen in TEM pictures of silica particle from the microemulsion (Fig. 23) and in the BET specific surface area measurement results (Table 9), highly porous silica particles were obtained from the acidic microemulsion. Thus it was also demonstrated that the microemulsion solution with acidic aqueous dispersion is useful reaction environment for producing porous silica particle. The porosity of silica showed the possibility of silica/polyaniline composite

nanoparticle production as long as both silica and polyaniline could be synthesized in a same micelle simultaneously. The sufficient pores within silica particle could provide enough space to keep solvent containing monomer aniline, and at the same time and place the polymerization of aniline would occur.

With the experimental results so far, the synthesis of the composite nanoparticle was performed by dispersing the aqueous phase where the monomer aniline had already been dissolved. The TEM result (see Fig. 31) showed that particles with sizes ~ 10 nm were obtained. The FTIR results (see Fig. 32) showed that the obtained particles are composed of both silica and polyaniline, and the BET surface area measurement experiment result (see Fig. 33) showed that the obtained particle should be a composite of silica and polyaniline and the polyaniline could possibly reside in the pores of silica nanoparticle. This was also backed up by the combination of BET surface area change (see Fig. 35) and FTIR spectra comparison (see Fig. 37) with thermal decompositions at 300 and 500 °C. Therefore, it could be concluded that the silica/polyaniline composite nanoparticle was obtained from the microemulsion solution (65.4 wt% cyclohexane, 30.4 wt% surfactant (Triton X-100 : 1-hexanol), 4.2 wt% aqueous phase) as was intended as the objective of this study.

From the result of formic acid dissolution experiment (see Fig. 40 and Fig. 41) for the obtained silica/polyaniline composite particles, it was demonstrated that the chemical stability of polyaniline was enhanced with the composite structure. The chemical stability enhancement could well be ascribed to the composite structure of the particle. Since the polymer part of the composite particle is protected by the chemically inert silica, it could be understood as a property improvement which is frequently observed for the inorganic-organic hybrid materials. As Fu et al [49] discussed, the composite nanoparticle structure could reduce possibility of interfacial reaction between polymer and solvent. Therefore, it could be concluded the composite structure of silica/polyaniline which was produced from the inverse microemulsion solution was proved to be helpful for the enhancement of chemical stability of the polymer material.

From the beginning of this study, it was expected that the improved chemical (or electrochemical) durability could also increase the electrochromic operation life time of the material. The electrochromic properties comparison between pure polyaniline and above prepared silica/polyaniline composite material showed that the chemical stability has some effect. A cyclovoltammetry showed that the composite film showed almost same pattern of cyclovoltammogram with the polyaniline film (see Fig. 48), which could

be easily expected, since the electrochromic properties of the composite material is still coming from the polyaniline part. However, the result also showed that the formation of highly oxidized form of polyaniline was suppressed for the case of composite film. As Novak et al [124] reported the highly oxidized form of polyaniline pernigraniline is believed to cause the electrochromic properties degradation of material. The less pernigraniline formation resulted in the enhancement of operation life time of the device, which was demonstrated in the optical contrast change comparison experiment between composite and polyaniline film (see Fig. 51 and Fig. 52).

On the whole, it could be said that the silica/polyaniline composite nanoparticle was produced from an inverse microemulsion (cyclohexane / Triton X-100 : 1-hexanol / aqueous phase), where TEOS was used as the silica precursor and monomer aniline for the source of chemical polymerization to form polyaniline. The electrochromic film made of the composite nanoparticle showed an enhancement of operation life time, which is originally intended from the beginning of this study.

However, there are still a few things which were left as the future works. There were obvious enhancement of operation life time of the material because of the composite structure, but the composite structure cause a little drawback in the response property of the film as was shown from the optical response characteristic in Fig. 50. The response speed of the material is also a very important property for an electrochromic display device. Therefore, to put some supplementary idea into the composite structure would rather be the next work.

At the last part of experiment in this study, a test sample of electrochromic device was made with the obtained composite particles and tested just to show a possibility of an electrochromic device. Since this work has actually been motivated from the application needs for the electrochromic display device, it would also be necessary to study on the other parts of device such as electrolyte and counter electrode. Especially when a flexible electrochromic device is concerned, those components of the device should also facilitate the flexibility. These works are also left as the future works following this study.

## 6. Summary and conclusion

In this study, a composite nanoparticle of silica/polyaniline was synthesized and tested as an electrochromic film. The composite structure is tried to enhance the electrochromic durability of the material. To produce the composite material in form of nanoparticle with a diameter less than 100 nm a microemulsion synthetic method was employed to control the size of the produced particles.

As a starting the compositions for the stable microemulsion system were explored. While changing relative mixing ration of each component as cyclohexane, 1-hexanol : Triton X-100, and the aqueous phase, transparency of the microemulsion solutions were checked and phase diagrams were drawn. From the phase diagram in Fig. 18, a composition of microemulsion was selected as 65.4 wt% cyclohexane, 30.4 wt% surfactant and 4.2 wt% aqueous phase. Hexanol-to-Triton X-100 mixing ratio in weight was selected as 2. This composition gives stable microemulsion at aqueous phase pH of 2, 7, and 12. The sizes of micelles prepared with the given composition were within range of 45 to 55 nm.

It was demonstrated that silica particles with very different microstructures could be obtained from an inverse microemulsion solution using TEOS and various catalysts. The size of the particle obtained from the acidic microemulsion where HCl was used as the catalyst is much smaller as 11.9 nm than that from the basic microemulsion where $NH_3$ was used as 38.3 nm. The particle from the micelles containing HCl has larger surface area as 623 $cm^2$/g than the particles from the micelles containing $NH_3$ as 89 $m^2$/g. By comparing these experimental results with the calculated surface areas, it could be said that porous silica particles were obtained from the acidic microemulsion solution. Since the production of porous silica from a microemulsion solution was demonstrated, it could be extended to the preparation of silica/organic hybrid material where the acidic catalyst would necessarily be involved.

The composite nanoparticle of silica/polyaniline was also synthesized from the microemulsion solution with the same composition with the one for silica production. A simultaneous synthesis of silica and polyaniline was performed in the same micelles. With the produced particles, microstructure analysis such as TEM and BET surface area measurement were performed.

With results of the BET and the dissolution experiments, it could be said that the individual particles produced from microemulsion using TEOS and aniline has a composite structure. In this composite structure, polyaniline is incorporated in the pores of silica particle rather than attached on the surface or isolated from the particle. As was intended, polyaniline was synthesized inside the pores of silica network. This was also explained by a synthetic model for the composite nanoparticle from a microemulsion solution.

It could also be said that the composite structure enhances the chemical stability of the material such as resistivity to the dissolution by formic acid; otherwise the pure polyaniline would be completely dissolved. It was also demonstrated that an electrochromic property enhancement of the film of silica/polyaniline composite nanoparticle. The composite particles which were synthesized from an inverse microemulsion solution were applied as a film on the FTO-coated glass. From the comparison of the electrochromic properties with the chemical polymerization deposited polyaniline, the composite film showed an increased durability. This stability enhancement was interpreted as that the formation of highly oxidized form of polyaniline was suppressed by the protective effect of the composite structure of the nanoparticle.

In this study, the production of silica/polyaniline composite nanoparticle was demonstrated and the enhancement of the electrochromic durability of the material was also proved. The enhancement of durability is believed to come from the enhancement of chemical stability of the composite structure of the material. To explain the stability enhancement of the material, a microstructure model was also proposed. With the model it would be possible to understand the composite structure of the prepared nanoparticle. However for more clear understanding on the structure, the chemical bonding between silica and polyaniline would rather be explored which would be remained as the further works.

For a development of the electrochromic displays it would be also necessary to have gel-type electrolyte. It is especially necessary to build a flexible device. These are remained as the future works also.

# 7. Appendix

## 7.1. Chemicals used

| Chemical name | Synonym | Molecular formula | Supplier |
|---|---|---|---|
| 1-buthanol | n-Butanol<br>Butyl alcohol | $CH_3(CH_2)_3OH$ | Fluka |
| 1-hexanol | Hexyl alcohol | $CH_3(CH_2)_5OH$ | Fluka |
| ammonium persulfate | Ammonium peroxodisulfate<br>Ammonium peroxydisulfate<br>AP<br>APS<br>PER | $(NH_4)_2S_2O_8$ | VWR |
| aniline | | $C_6H_5NH_2$ | VWR |
| Cyclohexane | | C6H12 | Fluka |
| Distilled Water | | $H_2O$ | |
| Ethanol | | C2H5OH | |
| Perchloric acid | | $HClO_4$ | Sigma-Aldrich |
| TEOS | Tetraethoxysilane<br>Orthosilicic acid tetraethyl ester | $Si(OC_2H_5)_4$ | Hüls/Brenntag |
| Triton X-100 | 4-(1,1,3,3-Tetramethylbutyl)phenyl-polyethylene glycol<br>Polyethylene glycol tert-octylphenyl ether<br>t-Octylphenoxypolyethoxyethanol | t-Oct-$C_6H_4$-$(OCH_2CH_2)_xOH$, x= 9-10 | Fluka |

## 7.2.  Instruments and equipments used

| Instrument | suppler and model |
| --- | --- |
| 4-point electrical resistivity measurement | NAPSON corp. RT-70 |
| Box furnace | Nabertherm S27 |
| Dip coater | |
| Electric stirrer | Variomag Multipoint HP6 |
| Fourier transform infrared (FTIR) spectrometer | Bruker IFS 25 |
| Microcentrifuge | Eppendorf Hermle Z380, Z323 |
| Particle size analyzer | Microtrac UPA 150 |
| pH-meter | Metrohm 780 PH meter<br>WTW PH535 multical |
| Photon correlation spectrometer<br>  - Laser goniometer<br>  - He-Ni Laser<br>  - Electronic tube | ALV ALV/SP-125<br>JDS uniphase 1145p-3083<br>Thorn EMI RFI-QL-30F |
| Potentiostat | Princeton Applied Research 273A |
| SEM | JEOL JSM-7000F |
| Spin coater | Convac 1001 |
| Surface Area and Pore Size Analyzer | Quantachrome Autosorb-6B |
| TEM | JEOL JEM-2010 |
| Thermogravimetric/Differential Thermal Analysis TG/DTA | Bähr STA 501 |
| Universal digital timer | |
| UV-Vis-NIR spectrophotometer | Varian CARY 5E |
| Vacuum oven | Heraeus instrument VTR 5022 |

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