



Wet Chemical Syntheses of Ag-Nanoparticles

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Introduction

The synthesis of nanoparticles with well defined size, morphology and crystallinity becomes more and more important to advance in the field of nanotechnology. Especially high-temperature wet-chemical syntheses are very promising to realise the production of particles with narrow

size-distribution and a sufficient yield [1-4]. Beside this goal, for industrial purposes it must be taken into account, that the chemicals costs as well as the expenses for processing are within acceptable limits. In addition, the nanoparticles have to be sufficiently stabilised to ensure their subsequent treatment. In this article, a synthesis-route for silver-nanoparticles is described which fulfils the above mentioned criteria to a large extent. Furthermore, particle size and size-distribution can be varied to some degree by changing the solvent, the heating-rate, the maximum-temperature and the duration of synthesis.

Experimental

Materials

Diphenylether 99 % (DPE), dibenzylether 99 % (DBE), dioctylether 99 % (DOE), 1-hexadecene 92 % (1-HD) and oleic acid 90 % (OA) were purchased from Aldrich, 1-octadecene 90 % (1-OD) from Alfa Aesar, 1-eicosene 85 % (1-Eic) from ABCR, tri-n-octylamine 98 % (TNO) from Acros, silver nitrate 99 % (AgNO_3) and oleylamine 70 % (OAA) from Fluka. All chemicals were used without further purification.

Syntheses

Synthesis route 1

In a typical synthesis, 10 ml solvent (for example DBE) and 8 mmol (2.26 g) OA were mixed in a 100 ml three-necked

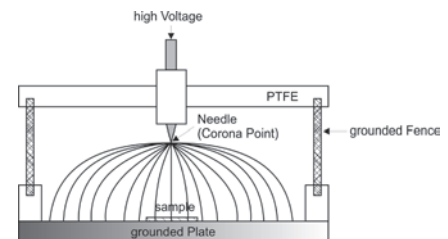


Fig. 12: Polarisation by the corona method

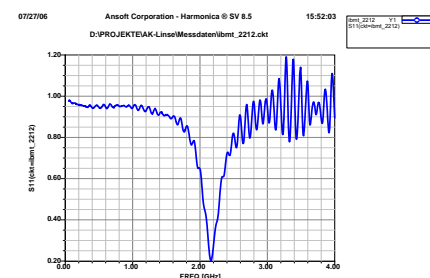


Fig. 13: Dependence of the reflection factor S 11 of various frequencies

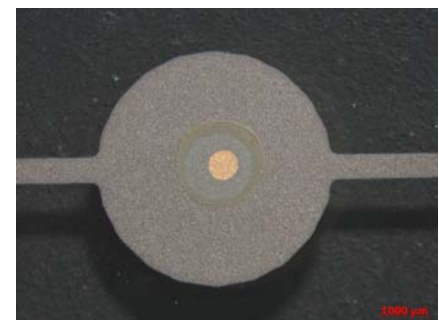


Fig. 14: Completed sensor, image made by light-optical microscope

round-bottom flask and heated under stirring to $T = 200\text{ }^{\circ}\text{C}$ under a nitrogen atmosphere with a predefined heating rate $h.r. = 3\text{ K/min}$. At $T = 140\text{ }^{\circ}\text{C}$, 1 mmol (0.169 g) AgNO_3 was added as a powder, followed by 2 mmol (0.535 g) OAA. Within a few seconds, the formerly colourless solution became first yellow, then brown, indicating the formation of silver particles. After refluxing for 60 minutes, the heating source was removed and the solution was allowed to cool down to room temperature.

Synthesis route 2

In an alternative route, Ag-oleate was prepared similar to a process for Fe-oleate [5] and used as the silver precursor instead of AgNO_3 . 1 mmol Ag-oleate was mixed with 10 ml TNO, 2 mmol OAA and 7 mmol OA to achieve the same concentrations of precursor, surface modifier and solvent as in the synthesis route mentioned before. The mixture was heated to $T = 200\text{ }^{\circ}\text{C}$ with $h.r. = 3\text{ K/min}$ and allowed to reflux at this temperature for $t = 60\text{ min}$ before cooling down to room temperature.

Independent of the synthesis route, the brown product was precipitated by mixing firstly 0.5 g of the particle dispersion with 1 g cyclohexane and then adding 6 g ethanol. This mixture was centrifuged at an acceleration of $a = 10,000\text{ g}$ for $t = 20\text{ min}$ at $T = 20\text{ }^{\circ}\text{C}$ and the yellowish supernatant was discarded. This procedure was repeated once. Finally, the particles were dispersed in 1 g cyclohexane.

Characterisation

To prepare a sample for transmission electron microscopy, one drop of the solution was put onto a carbon coated copper grid. TEM was carried out using a Philips CM 200 FEG high-resolution microscope. To determine the particle-size and size distribution, comparable micrographs of the respective samples were binarised and analysed using the software Digital Micrograph v. 3.8 and ImageJ v. 1.39u.

For revealing the crystallinity of the as prepared silver nanoparticles, X-ray diffraction analyses were carried out. Therefore, the particles were purified four times by a procedure similar to the above mentioned to minimize the amorphous background due to the organic residues.

Results and Discussion

Synthesis

Each synthesis system consists of the following components: silver-precursor, solvent, and organic surfactant. For synthesis route 1, the silver-precursor (AgNO_3) is known to be a salt. Raman and FTIR measurements indicate that this is also the case for Ag-oleate. By heating to a sufficiently high temperature the silver precursor dissociates. Although the reaction mechanism is not yet understood in detail, it is assumed that the Ag^+ -ions are reduced to Ag^0 by electron transfer from the ligands L.

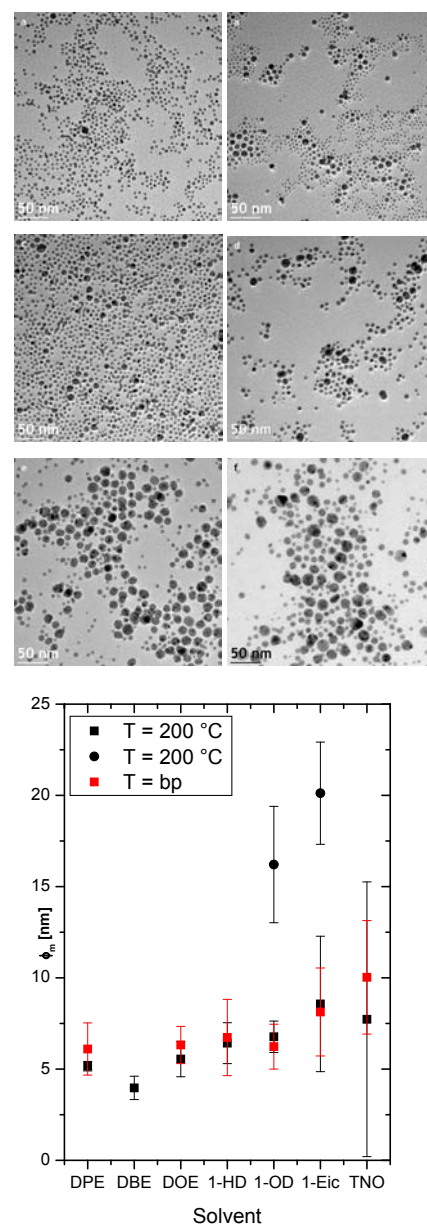
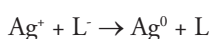


Fig. 1: TEM-micrographs (a-n) of silver particles synthesised with DPE, DBE, DOE, 1-HD, 1-OD, 1-Eic and TNO at $T = 200\text{ }^{\circ}\text{C}$ (a-g) and $T = bp$ [$^{\circ}\text{C}$] (h-n) and the respective size and size distribution (Fig. 1o). Note that for DBE at $T = bp$ [$^{\circ}\text{C}$] (Fig. 1i), no particle size and distribution could be determined because the particles aggregated to clusters of $0.5 - 1\text{ }\mu\text{m}$ in diameter.



Capping of the nuclei with surfactant molecules then promotes the controlled growth [4,6]. As the detailed understanding of the reaction kinetics is crucial for establishing new, advanced synthesis methods, an experimental setup for in situ investigations with mass-spectrometry, FT-infrared spectrometry and UV-Vis spectrometry shall be realised soon.

Influence of the solvent

To investigate the influence of the solvent in the synthesis of silver nanoparticles, we repeated the synthesis based on route 1, using different ether (DPE, DBE, DOE), alkenes (1-HD, 1-OD, 1-Eic) and a tertiary amine (TNO). Mixtures were heated with a constant rate of h.r. = 3 K/min and allowed to reflux for $t = 60$ min not only at $T = 200$ °C but also at the respective boiling point of the solvents as given in Table 1.

The TEM-micrographs show the particles synthesized at $T = 200$ °C in DPE, DBE, DOE, 1-HD and 1-OD as the respective solvent. (fig. 1a-e)

Analysis of the mean particle size \varnothing_m and size distribution σ indicates that \varnothing_m slightly increases with increasing molar weight of the solvent, whereas higher temperature does not seem to effect particle size. Concerning the size distribution σ , for solvents with low molar weight σ increases with temperature while it decreases for solvents of high molar weight. To understand this, different aspects have to be taken into account [1,2,4]. First of all in our case the structure and with

that the sterical hindrance of the solvents used, drastically changes with increasing molar weight leading to a different coordination to the silver nuclei. Secondly, by keeping the solvent volume in the synthesis constant at 10 ml, the molar rate decreases with increasing molar weight. Therefore the number of solvent molecules surrounding each nucleus decreases and during growth, particles become more polydisperse. Thirdly, in the case of TNO, the tertiary amine can compete with the stabilising surface modifiers in coordinating to the silver ions and thus inhibit a controlled nucleation and particle growth. To proof this assumption, we made another particle synthesis with TNO (route 2), using Ag-oleate as the metal precursor. In this case the stabilisation of the nuclei should be much better because a stabilising agent is already introduced in the metal precursor. As assumed, this synthesis route leads to crystalline particles with decreased size and narrowed size distribution (fig. 2).

Influence of the heating rate

Another parameter in particle synthesis is the heating rate. To synthesise nearly monodisperse particles by thermal decomposition it is favourable to have a large gap between the initial temperature for nucleation T_n and particle growth T_g [5]. In an ideal situation one would keep the temperature constant at T_n until nucleation is finished and then jump to T_g to initiate particle growth. The particle size can then be tuned by varying the ratio of solvent, surface modifier and precursor.

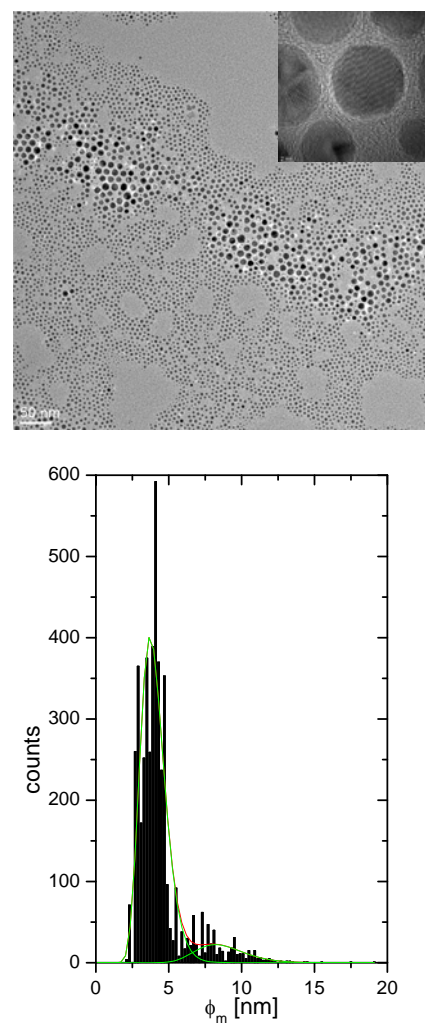


Fig. 2: TEM-micrograph (a) of particles synthesised using Ag-oleate as the metal-precursor. The inset shows an individual particle at high resolution, revealing the crystallinity of the particles. Fig. 2b depicts the particle size and size distribution.

By heating with a constant heating rate, the situation is a little different. Heating too fast, initiates the particle growth before the nucleation has finished and the particles become bigger and more poly-disperse. To verify this, we synthesised particles using DBE as the solvent with $T = 200\text{ }^{\circ}\text{C}$ and $t = 60\text{ min}$ and varied the heating rate with h.r. = 3, 5, 10, 20 and 40 K/min, respectively. As predicted, the particle size increases with h.r. and the size distribution broadens (Fig. 3 f). It must be noted, that the broad size distribution for h.r. = 10 K/min must be ascribed more to problems with particle size analysis due to the formation of a particle bilayer onto the TEM-grid, than on a real effect.

Influence of the dwelling time

The dwelling time at a temperature suitable for particle growth is another parameter that can influence particle size and size distribution [7]. In a first step the particles grow until all of the precursor is decomposed completely. In a second step, small particles dissolve while bigger ones grow. This process is called Ostwald ripening. Therefore we synthesised silver nanoparticles at a constant heating rate of h.r. = 3 K/min with DBE as the solvent by varying the dwelling time at $T = 200\text{ }^{\circ}\text{C}$ from $t = 0, 30, 60$ and 720 min , respectively. As expected, the particle size distribution narrows from $t = 0$ to $t = 60\text{ min}$ but interestingly becomes bimodal for $t = 30\text{ min}$ while the particle size decreases (Fig. 4 a-c). The assumption is, that in this case the final particle size is pri-

marily determined by the ratio of surface modifier to metal precursor. At $t = 0\text{ min}$ the initial particle growth is not completed and the size distribution is therefore broad. At $t = 30\text{ min}$ due to Ostwald ripening, the bigger particles further grow while the smaller ones shrink to a certain size, determined by the amount of surface modifier. In a third step, also the bigger particles shrink to the optimum size determined by the surface modifier. For $t = 720\text{ min}$ it must be noted that due to the continuous flushing of the flask with nitrogen, nearly all of the solvent was carried off although using a reflux cooler and that the surface modifiers (OAA and OA) were already polymerised as can be seen in Fig. 4 d, so that these results are not representative to verify the theory.

XRD measurements were made to determine the crystallinity of the as prepared silver nanoparticles. Although the diffractograms are not suitable to determine the particle size based on the Debye-Scherrer equation, they reveal that the particles are partly (multiply)twinned and crystalline.

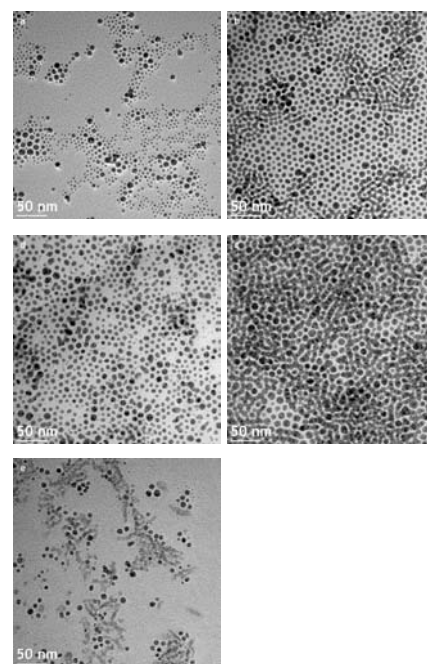


Fig. 3: TEM-micrographs (a-e) of particles synthesised at h.r. = 3, 5, 10, 20 and 40 K/min and the respective size and size distribution (Fig. 3 f)

Chemical	CAS	M [g/mol]	bp [$^{\circ}\text{C}$]	d [g/ml] at $25\text{ }^{\circ}\text{C}$
Diphenylether (DPE)	101-84-8	170.21	259	1.073
Dibenzylether (DBE)	103-50-4	198.26	298	1.043
Di-n-octylether (DOE)	629-82-3	242.45	287	0.806
1-Hexadecene (1-HD)	629-73-2	224.43	274	0.783
1-Octadecene (1-OD)	112-88-9	252.48	317	0.789
1-Eicosene (1-Eic)	3452-07-1	280.54	330	0.7916
Tri-N-octylamine (TNO)	1116-76-3	353.68	365 - 367	0.809

Table 1: Physical and chemical data of the solvents used in the particle synthesis.



Conclusions

We used two different wet chemical routes based on thermal decomposition and reduction to achieve crystalline silver nanoparticles and systematically changed the solvent, temperature, heating rate, and dwelling time to investigate their influence on particle size and size distribution. Most of the results fit well with the theory of nucleation burst, particle growth and Ostwald-ripening.

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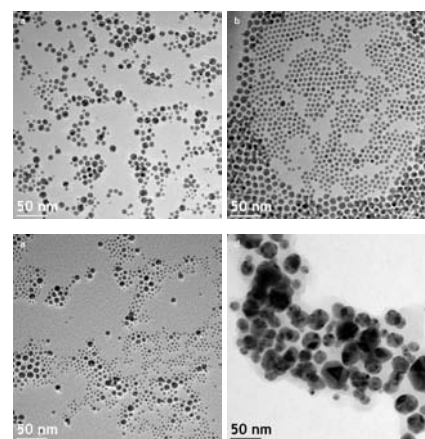


Fig. 4: TEM-micrographs (a-d) of particles synthesised at $t = 0, 30, 60$ and 720 min and the respective size and size distribution (Fig. 4 e)