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), dibenzyl-ether 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 ALCR, tri-n-octylamine 98 % (TNO) from Acros, silver nitrate 99 % (AgNO₃) and oleylamine 70 % (OAA) from Fluka. All chemicals were used without further purification.
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 (AgNO₃) 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 Ag⁰ by electron transfer from the ligands L.

\[ Ag^+ + L^- \rightarrow Ag^0 + L \]

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 \( a = 10,000 \) g for \( t = 20 \) min at \( T = 20 \) °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.
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 \( h_r = 3 \text{ K/min} \) and allowed to reflux for \( t = 60 \text{ min} \) not only at \( T = 200 \text{ °C} \) but also at the respective boiling point of the solvents as given in Table 1.

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

Analysis of the mean particle size \( \bar{\phi}_m \) and size distribution \( \sigma \) indicates that \( \bar{\phi}_m \) slightly increases with increasing molar weight of the solvent, whereas higher temperature does not seem to effect particle size. Concerning the size distribution \( \sigma \), for solvents with low molar weight \( \sigma \) 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.
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 polydisperse. To verify this, we synthesised particles using DBE as the solvent with \( T = 200 \, ^\circ\text{C} \) and \( t = 60 \, \text{min} \) and varied the heating rate with \( \text{h.r.} = 3, 5, 10, 20 \) and \( 40 \, \text{K/min} \), respectively. As predicted, the particle size increases with \( \text{h.r.} \) and the size distribution broadens (Fig. 3 f). It must be noted, that the broad size distribution for \( \text{h.r.} = 10 \, \text{K/min} \) 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 \( \text{h.r.} = 3 \, \text{K/min} \) with DBE as the solvent by varying the dwelling time at \( T = 200 \, ^\circ\text{C} \) from \( t = 0, 30, 60 \) and \( 720 \, \text{min} \), 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 primarily 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.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>CAS</th>
<th>M [g/mol]</th>
<th>bp [°C]</th>
<th>d [g/ml] at 25°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diphenylether (DPE)</td>
<td>101-84-8</td>
<td>170.21</td>
<td>259</td>
<td>0.073</td>
</tr>
<tr>
<td>Dibenzylerher (DBE)</td>
<td>103-50-4</td>
<td>198.26</td>
<td>298</td>
<td>1.043</td>
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<tr>
<td>Di-n-octylether (DOE)</td>
<td>629-82-3</td>
<td>242.45</td>
<td>287</td>
<td>0.806</td>
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<tr>
<td>1-Hexadecene (1-HD)</td>
<td>629-73-2</td>
<td>224.43</td>
<td>274</td>
<td>0.783</td>
</tr>
<tr>
<td>1-Octadecene (1-OD)</td>
<td>112-88-9</td>
<td>252.48</td>
<td>317</td>
<td>0.798</td>
</tr>
<tr>
<td>1-Eicosene (1-Eic)</td>
<td>3452-07-1</td>
<td>280.54</td>
<td>330</td>
<td>0.7916</td>
</tr>
<tr>
<td>Tri-N-octylamine (TNO)</td>
<td>1116-76-3</td>
<td>353.68</td>
<td>365 - 367</td>
<td>0.809</td>
</tr>
</tbody>
</table>

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.


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)