Synthesis and deposition of silver nanoparticles

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Introduction

Nanoparticles are particles usually within the size of 1-100 nanometres, where a large fraction of the atoms are located at or near the surface. Therefore, their properties are strongly dependent on the particle size, shape, surface chemistry and inter-particle spacing. For silver nanoparticles this means that the aforementioned factors must be controlled during synthesis as well as during deposition onto solid substrates.

Aim

This project aimed to set up procedures for synthesis and deposition of nanoparticles on glass substrate.

It specifically focuses on:

- Synthesis of highly monodisperse silver nanoparticles
- Characterization of particle size and shape using dynamic light scattering and electron microscopy
- Preparing stable organic nanoparticle dispersions for Langmuir-Blodgett deposition

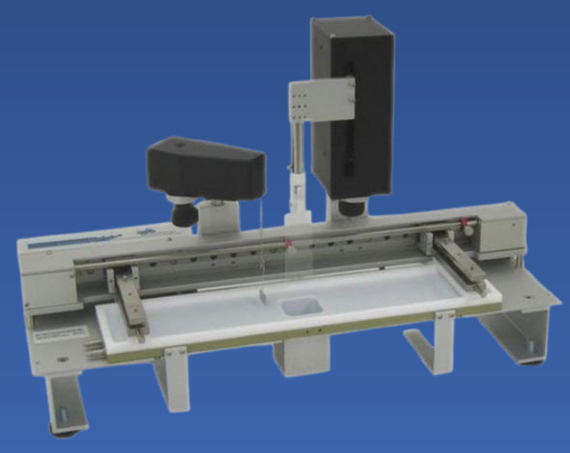
Easymax 102

Synthesis

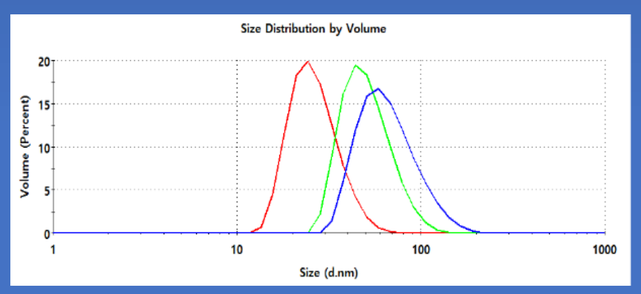
Silver nanoparticles were synthesized using a seeded growth method via citrate and tannic acid reduction of $AgNO_3$.[1] The synthesis was done in an EasyMax 102 reactor, which allows controlled heating and stirring during the initial seed formation and in the latter growth steps. First the seed particles were synthesized in milli-q water from sodium citrate and tannic acid, then addition of $AgNO_3$. The particles were then grown through several generations by addition of sequential $AgNO_3$, sodium citrate and tannic acid. Here three different sizes were synthesized (Seed, generation 7 and generation 12) to be characterized and used for deposition. These were centrifuged and redispersed in both citrate and water to remove access tannic acid and water for characterization with electron microscope and DLS.

Deposition

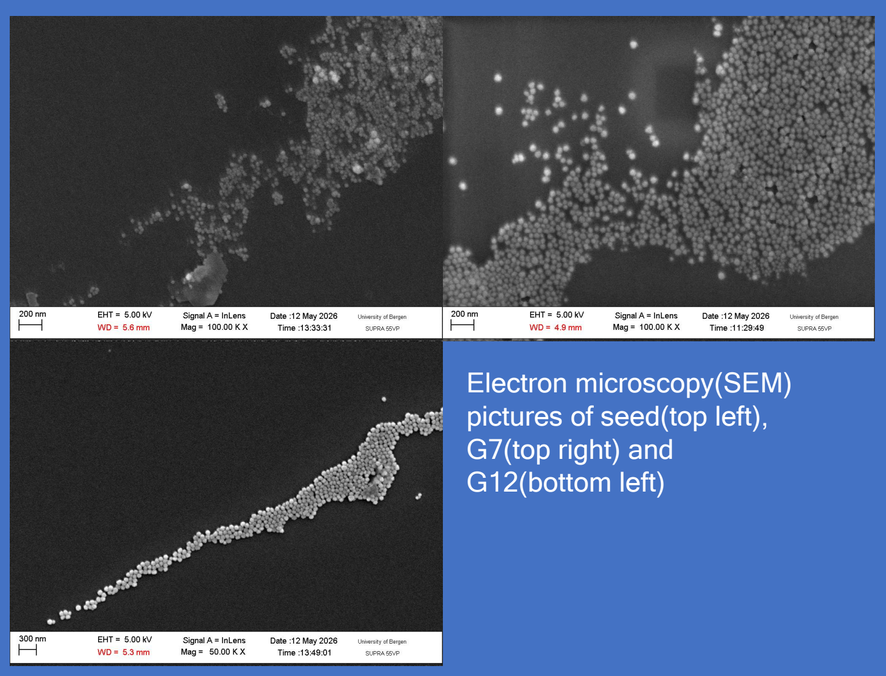
The aim of the deposition work was to produce silver nanoparticle layers onto glass substrates. Dip coating was initially tested on glass plates. The glass plates were cleaned by sonication in a soap solution, followed by sonication in isopropanol and treatment with hydrogen peroxide. The same glass cleaning procedure will be used later when testing Langmuir-Blodgett deposition. The Langmuir-Blodgett method involves spreading the nanoparticle dispersion at the air-water interface, compressing the nanoparticle layer to control how densely the particles are packed, and then transferring it onto the glass substrate by dipping.[3] This will be done with a KSV LB-trough.[4] For the this, the aqueous silver nanoparticles need to be transferred to an organic solvent. Because the synthesized AgNPs are stabilized in water by citrate and tannic acid, they cannot be transferred directly into nonpolar solvents without changing the surface chemistry. Dodecanethiol is therefore being used for a hydrophobic ligand for phase transfer.[2] The thiol group can bind to the silver surface through Ag-S interactions. Toluene is being used as a solvent for the transfer, and after the transfer they will be resuspended in hexane for the deposition.



KSV LB-trough



Volume-weighted DLS size distributions of seed(red), G7(green) and G12(blue) silver nanoparticles



Electron microscopy(SEM) pictures of seed(top left), G7(top right) and G12(bottom left)

Results and discussion

Silver nanoparticles were successfully synthesized and grown through a couple of generations. DLS showed an increase in average hydrodynamic size of the particles from the seed particles and to G7 and G12. The seed particles had a Z-average of 39.7 ± 4.7 nm, G7 and G12 had 56.9 ± 2.0 nm and 74.1 ± 1.4 nm. The PdI values were low for all samples, with average values around 0.12-0.15. This indicates that the particle dispersions were relatively monodisperse after resuspension in citrate solution. The main intensity peaks also increased from 34.1 nm for the seed particles to 65.0 nm for G7 and 84.8 nm for G12. Most measurements have only one main particle size distribution, but a seed measurement has a small high-size contribution. This is due to some aggregation as also seen in the electron microscopy(SEM) pictures. Electron microscopy samples were prepared by first resuspending the particles in water. They were then dripped onto silica plates before they were covered in a thin layer of carbon and gold/palladium for electron microscopy. The microscopy images show that the particles are spherical and can form dense deposited regions on the substrate. The phase-transfer experiments indicated that transferring the particles from water to an organic phase remains a big challenge. The colored interfacial layer is an indication of partial transfer or partial surface modification with ligand, while precipitation is a sign that the particles are not yet fully modified in the organic phase. The next part will be to improve the dodecanethiol exchange before Langmuir-Blodgett deposition is tested.

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References

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