Effect of TEM grid deposition method on the dispersion of thiol-stabilised silver nanoparticles

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Abstract. Thiol stabilised Ag nanoparticles (NP) in cyclohexane dispersed onto TEM carbon support grids show evidence for agglomeration, whilst the addition of dodecanethiol to the cyclohexane is found to affect the dispersion of the NP which can show highly ordered superlattice formations with close packing, being attributable to the combined effects of convective deposition (coffee ring effect) and the dodecanethiol surfactant.

1. Introduction
Ag nanoparticles (NP) may be regarded as generic building blocks for a range of nanostructured processes [1] and there is particular interest in the control of their size and size distribution, e.g. for optical emission wavelength [2]. Here, we report on the development of Ag NP synthesised using a modified Brust-Schiffrin [3] reduction method, and the effect of dodecanethiol addition on their apparent size distribution, at the sample dispersion stage onto the TEM support grid.

2. Materials and Methods
To a solution of silver nitrate (0.3 mmol) in 30 mL ethanol, a mixture of 50 μL 1-dodecanethiol and 60 μL 1(1H-pyrro-1-yl)undecane-1-thiol was added slowly, followed by vigorous stirring for 15 minutes. To this was added dropwise, a solution of sodium borohydride (saturated) in 60 mL of ethanol and the solution again stirred vigorously for a further 2 h. The product was then precipitated by the addition of 250 mL of ethanol and refrigerated at -15°C for 24 h. After filtration through a 0.2 μm PTFE membrane the product was washed with 10 mL toluene, followed by washing with 200 mL acetone and drying under vacuum to produced mixed thiol stabilised Ag NP (Figure 1a). The product was then dispersed in cyclohexane, with and without dodecanethiol (Figure 1b), and drop cast onto holey carbon / Cu TEM sample grids. Samples were observed using a JEOL 2100F TEM, operating at 200kV, and particle size histograms were generated using ImageJ to appraise the effects of dodecanethiol addition at the sample dispersion stage. Whilst prolonged exposure to an intense electron beam can lead to NP growth, such effects were avoided by minimising irradiation time and intensity.
Figure 1. (a) Mixed thiol stabilisation layer around Ag NP; and (b) Ag NP product dissolved in cyclohexane with and without dodecanethiol.

Figure 2. (a) Thiol stabilised Ag NP dispersed from cyclohexane; (b) Thiol stabilised Ag NP dispersed from cyclohexane in the presence of excess dodecanethiol.

3. Results
Figures 2 (a,b) present conventional bright field, diffraction contrast TEM images of thiol stabilised Ag NP dispersed from cyclohexane, and cyclohexane with 30% dodecanethiol (aka dodecanemercaptan DDM), respectively. It is evident that the final processing step has had a significant effect on the NP size distribution as a consequence of the dispersion. After the drying process on the TEM support grid, Ag NP dispersed from cyclohexane showed a bimodal size distribution (4, 1.5 nm) (Figure 3a) and a random dispersion across the grid. Conversely, samples dispersed from cyclohexane in the presence of excess dodecanethiol showed a much narrower, single size distribution (3, 0.6 nm) and regions of highly ordered superlattice with close packing (Figure 3b), indicative of a surfactant effect.
Particle size histograms were generated using ImageJ, after magnification calibration, individual particles were measured (n = 150) and histograms plotted using Excel.

4. Discussion

The fundamental differences in dispersion of the Ag NP product may be explained in terms of the combined effects of the additional thiol surfactant on the Ag NP in colloidal suspension and solvent drying (convective deposition). It is considered that the Ag NP initial, mixed thiol stabilisation layer used for the synthesis is chemically bonded to the Ag NP and does not influence the processes of self-assembly or agglomeration, as observed here, and does not act as a surfactant in the same way as the dodecanethiol added to the cyclohexane, in advance of the deposition.

It has been reported that aggregate formation in solution may be prevented by the addition of small amounts of a stabilising agent to NP suspended in solution [4]. Accordingly, the self-assembly and separation of dispersed NP may be attributed to the presence of surfactant dodecanethiol molecules [5]. Attention should also be given to the additional ‘coffee ring effect’ consequent from the process of solvent evaporation [6] which may compete with the 2D superlattice formation. If the edge of the solvent is pinned to a surface, flow from the centre results as evaporation proceeds, with the accumulation of particles at the edge driven by capillary flow due to differential evaporation rates, competing with the induced Maragoni flow inside the droplet and the disruptive effect of the added surfactant which reduces the liquid surface tension gradient and further physically separates the dispersed NP upon self-assembly.

By way of illustration, Figures 4 depicts the self-assembly of close packed NP at the liquid-air interface with competing effects of convective flow and the surfactant effect of dodecanethiol addition, leading to very different interpretations of the Ag NP dispersion, once deposited on the TEM grid. In particular, the stabilising surfactant helps to maintain a mono-dispersed particle size in the solvent whilst promoting close packing of the NP on the TEM grid via attraction to the liquid-liquid interface [7]. Nucleation and subsequent development of superlattices occur during the drying process, enhanced by additional drying times associated with the presence of significant quantities of surfactant. In the absence of the stabilising surfactant, the Ag NP are capable of direct interaction leading to the observed variations in NP dispersion. Accordingly, care is needed when dispersing NP in the presence of a surfactant with regard to sample interpretation and the quantification of size and particle distribution.
Figure 4. Schematic depiction of the drop casting process: and (a) the effect of dodecanethiol surfactant to NP in cyclohexane which facilitates partitioning of NP at the liquid-liquid interface and promotes NP superlattice formation. Schematic descriptions of NP product, as observed on the TEM grid: (b) Self-assembled, mono-dispersed Ag NP clusters deposited from cyclohexane with excess dodecanethiol surfactant which acts to prevent particle agglomeration and promotes close packing superlattice formation; and (c) Bimodal agglomerates of Ag NP, as dispersed from cyclohexane.

5. Conclusions
The process of Ag NP dispersion is found to affect the apparent sample particle sizes and distributions. The addition of dodecanethiol to thiol stabilised Ag NP in cyclohexane leads to the deposition of self-assembled, mono-dispersed NP, whilst the absence of the stabilising surfactant appears to lead to the deposition of randomly distributed NP with a bimodal size range. The competing effects of convective deposition and surfactant effects are implicated in these different sample appearances.

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