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Hydrothermal Synthesis of Silver Nanoparticles for High Throughput Biosensing Applications

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Abstract

Metallic silver nanoparticles were synthesized using a hydrothermal route for use in high throughput biosensing applications. Particle shape was engineered by varying polyvinyl pyrollidone (PVP) concentration in the precursor mixture, resulting in the emergence of flat triangular shaped nanoparticles with increasing PVP content. The hydrothermal method was found to yield particles with better particle size distribution and longer shelf life relative to polyol synthesis particles.

INTRODUCTION

Several studies have observed the size dependence of properties of NPs such as UV absorbance and reaction sensitivity which consequently result in changes to the capabilities, toxicity and suitability of these NPs for electronic, sensing and biomedical applications [1-3]. In addition to particle size, other factors such as shape also play a significant role in determining NP behaviour [4]. The toxicity of silver in its ionic form is widely acknowledged [5]; however, recent studies have noted that Ag NPs could also have a toxicological response which can be studied in isolation from ionic silver [6], and as is the case with many nanoparticulate materials, this toxicological response is rather dependent on the size and shape of the Ag NPs. [7,8] We present results from investigations into the use of a hydrothermal route (HT) for controlled synthesis of Ag NPs of various shapes and their potential for use in high throughput biosensing applications.

MATERIALS AND METHODS

Silver nitrate (puriss. p.a., ACS reagent, ≥99.8%), ethylene glycol (EMPLURA, ≥99.0%), polyvinyl pyrollidone (MW 40k, Fisher BioReagents) were used as-received for NP synthesis. Precursor mixtures were prepared by dissolving silver nitrate and PVP in ethylene glycol respectively. For polyol synthesis, the precursor (50 ml) was heated for 3 h in a stirred oil bath maintained at 160 ^{o}C. In the case of hydrothermal treatment, 50 ml of precursor mixture was transferred into a 125 ml TEFLON-lined hydrothermal vessel (Parr Instruments, model 4748), heated at 5 °C/min to 160 °C, and held for 2 h. The reaction products were washed with deionised water (MilliQ, 18.5 MΩcm^{-1}), using a centrifugation-sonication sequence prior to characterisation.

Information on particle size distribution was obtained through dynamic light scattering (DLS) performed on a Malvern Instruments Zetasizer Nanoseries ZS, with a PerkinElmer Lambda 25 spectrophotometer and a Nicolet iS10 FT-IR Spectrometer used for UV absorption and FT-IR spectroscopy respectively. Details of particle size and shape were acquired through scanning electron microscopy (Hitachi SU8230 UHR Cold Fe-SEM) and transmission electron microscopy (FEI Tecnai F20 FEG-TEM operated at 200 kV and equipped with a Gatan Orius SC600A CCD camera).

RESULTS & DISCUSSION

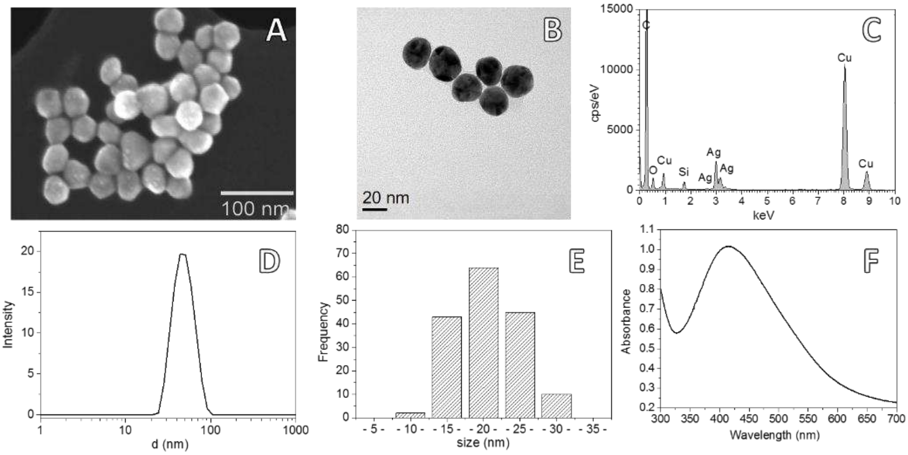

Figure 1: Characterisation results: (A) SEM; (B) TEM micrographs of hydrothermally synthesised Ag NPs, (C) TEM-EDX confirming nanoparticles as Ag, (Cu, Si, O and C are artefacts originating from the TEM grid and instrument), (D) DLS results, (E) size distribution obtained by measuring particles from multiple TEM micrographs, (F) UV-Vis spectrum showing characteristic Ag^0 absorption at ~ 420 nm.

Analysis of particles obtained after hydrothermal treatment of the ethylene glycol based precursor mixture (1:1 PVP to Ag molar ratio), showed synthesis products consisted of equiaxed multifaceted nanoparticles with an average diameter of 23 ± 7 nm obtained from measuring individual NPs in multiple TEM micrographs (Figure 1B). From DLS size measurements, an average hydrodynamic particle size of ~ 45 nm with a PDI of 0.12 was recorded (Figure 1D).

Higher magnification TEM images revealed the presence of an amorphous layer coating the Ag NPs (Figure 2A). FT-IR analysis of this coating showed the presence of hydroxyl group vibration (~3300 cm^{-1}) and amide group vibration (~1640 cm^{-1}) indicative of the presence of bonded PVP (Figure 2B) [9]. Therefore, results from the DLS analysis reflected the hydrodynamic diameters of the Ag NPs occasioned by the surrounding coating of PVP on individual nanoparticles. This indicates that the final synthesis products are PVP coated Ag NPs.

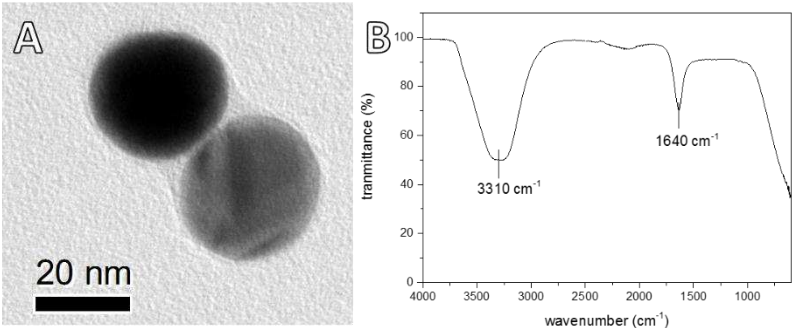

Figure 2: (A) TEM micrograph showing a coating around the Ag NPs (B) FT-IR spectrum confirming particle coating as PVP.

Effect of PVP on particle shape

Experiments were conducted to investigate the effect of varying the amount of PVP in the reaction system on the characteristics of the product NPs by preparing precursor mixtures containing different PVP: Ag molar ratios. Results from the examination of reaction products in the electron microscope showed a gradual transition from equiaxed multifaceted nanoparticles to triangular and polygonal shaped particles with increasing PVP: Ag molar ratios, as shown in SEM micrographs of the hydrothermally prepared Ag NPs (Figure 3). Also, particle size distribution was observed to increasingly vary with higher PVP content (Table 1). PVP can preferentially attach to the {100} facets of silver and encourage growth along the <111> directions resulting in the formation of Ag NPs having shapes such as: pyramids or triangular plates.

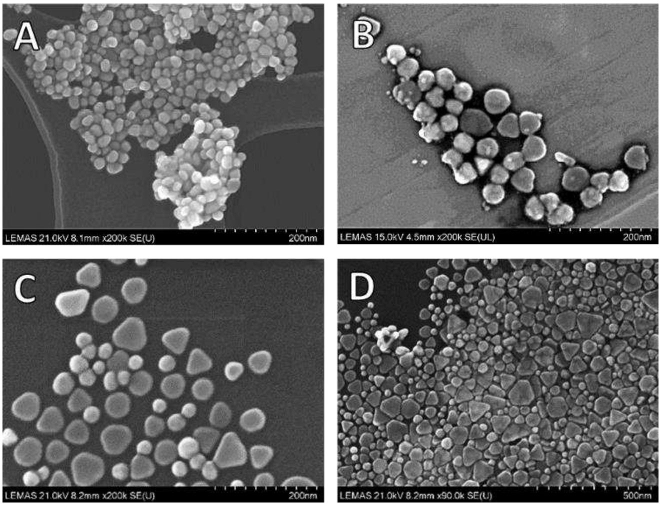

Figure 3: Progressive shape transition as a function of increasing PVP: Ag molar ratio in hydrothermally prepared Ag NPs (A) 1:1 (B) 2:1 (C) 4:1 (D) 6:1.

Comparison of polyol vs HT synthesis

To provide a comparative analysis of the effect of hydrothermal treatment on Ag NPs, particles obtained from our polyol synthesis route were compared with hydrothermally prepared particles. The non-HT material had a broader particle size distribution as well as a lower degree of shape uniformity (Table 1). Analysis of UV-Vis spectral data revealed slight variations in the extinction coefficient of the suspension implying size and shape influenced shifts in UV-absorbance as the molar ratio of PVP relative to Ag increased. Additional absorption peaks were also observed (~ 520 nm) in coincidence with increased presence of polygonal and triangular shaped Ag NPs at higher PVP molar ratios (figure 4).

Table 1: Effect of PVP: Ag molar ratio on characteristics of hydrothermal silver NPs.

PVP :Ag molar ratio	Shape characteristics	Size of HT particles-TEM (nm)	Size of HT particles – DLS (nm)	Size of polyol particles – TEM (nm)	Size of polyol particles – DLS (nm)
1:1	Equiaxed multifaceted	23 ± 7	44.6; PDI 0.12	20 ± 7	54.6; PDI 0.47
2:1	Equiaxed multifaceted, polygonal	30 ± 5	70.9; PDI 0.15	28 ± 8	86.1; PDI 0.27
4:1	Equiaxed multifaceted, polygonal , triangular	35 ± 10	101.2; PDI 0.19	31 ± 5	149.3; PDI 0.22
6:1	multifaceted, triangular	50 ± 15	153.7; PDI 0.22	50 ± 17	162.9; PDI 0.35

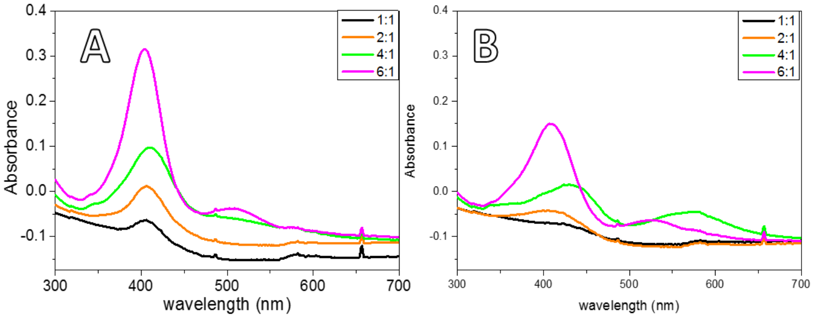

Figure 4: UV-Vis absorption spectra of Ag NPs (A) HT route, (B) polyol route; showing effect of increasing PVP concentration and hydrothermal treatment on suspension characteristics

The stabilities of nanoparticle suspensions from both synthesis routes were compared after storage under identical room temperature, pressure and lighting conditions for 1500 hours. Results showed significant changes to the size and shape of the polyol samples, while the HT samples remained relatively unchanged (Figure 5).

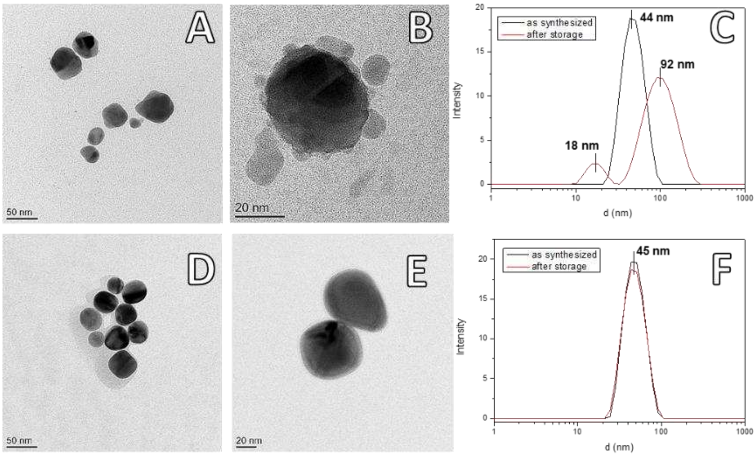

Figure 5: (A,B) TEM micrographs and (C) DLS plot of polyol synthesis, (D,E) TEM micrographs and (F) DLS plot of hydrothermal samples after 1500 hours of aging showing changes in particle characteristics of the polyol synthesis sample.

Thus a suspension containing particles obtained via the hydrothermal synthesis was found to have suffered a lower degree of degradation and particle dissolution relative to the polyol synthesis Ag NPs. This may be due to a higher degree of reaction completion achieved by the hydrothermal route relative to polyol synthesis after the same residence time, such that a lower level of unreacted components (which could change under exposure to light resulting to changes in the nature of suspension while in storage) existed in the HT samples. Continuous evolution of the particles post-synthesis is often undesirable as many nanoparticle suspensions require some form of ageing or incubation before they are used, for example in biological tests. Changes in the characteristics of the nanoparticles due to aging could introduce significant uncertainties in the accuracy of relating the results of such tests to the as-synthesized properties of the particles.

CONCLUSION:

A hydrothermal route has been used to synthesise silver nanoparticles. Changes to particle shape and size were achieved by variation in PVP: Ag molar ratio of the precursor mixture. Hydrothermally synthesized Ag NPs were observed to have a relatively lower sensitivity to environmentally-induced changes to particle characteristics under storage. The results presented in this paper may be of interest to industrial processes that seek to make nanoparticles on a relatively large scale with reduced environmental and human exposure risks.

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