Synthesis and Characterisation of Silver Nanoparticles using High Electrical Charge Density and High Viscosity Organic Polymer

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Abstract

In this study, we present a facile and cost-effective method for the synthesis of silver nanoparticles (Ag-NPs) using an organic polymer, hydroxyethyl cellulose (HEC). On the introduction of 0.1% HEC (degree of polymerisation 500) into the reaction mixture, colour changes are observed at different temperatures (30°C-90°C). The prepared samples were characterised using a scanning electron microscope, SEM (Type: JOEL 30-kV), and an X-ray powder diffractometer (Type: Siemens AXS D5005). The UV – Vis spectra were recorded using a Shimadzu (UV – 1601) spectrometer. The X-ray patterns indicated a product comprising a mixture of silver (Ag) and small amounts of silver(I) oxide (Ag_2O). The UV-Vis spectra indicated peak positions at around 420nm, consistent with the formation of silver nanoclusters, $(Ag)_n$, made up of very low dimensional nanoparticles. SEM images of the samples at 80°C exhibited the existence of very small and uniformly spherical nanoparticles with sizes <30 nm. Owing to the high electrical charge density and large viscosity of the HEC polymer, particle sizes are restricted. Consequently, the product will contain mono-dispersed Ag-NPs. High yields of Ag-NPs were obtained in relatively short periods of time and at low temperatures. The study therefore would provide a simple, adaptable and cost-effective technique of scientific as well as industrial applicability.

Key Words: Silver nanoparticles, hydroxyethyl cellulose polymer, mono-dispersed particles, scanning electron microscopy

Introduction

Nano-sized silver colloids are characterized by excellent electrical, thermal, optical and catalytic properties. As such, they have attracted a considerable degree of attention over the recent past owing to their various potential applications as conductors, catalysts and chemical sensors[1–5]. It has therefore become necessary to attempt to synthesise small-size and narrow-distribution colloidal silver dispersions. Of the various techniques explored to obtain such silver nanoparticles, the wet chemical method has proved to be the most popular due to its relative practical simplicity, affordability and high percentage yield. One limitation, however, is the nature of the protective agent used to obtain uniform nanoparticle dispersion. A number of other synthetic methods for achieving controlled production of silver (Ag) and gold (Au) nanoparticles have been proposed[6–11]. Silver nanoparticles, for example, have been synthesised using a simple surfactant-assisted aqueous solution approach, based on the conventional Tollen's reaction. The Ag-NP morphologies strongly depended on the temperature adopted during the synthesis[12].

Methods commonly employed to generate silver nanoparticles are also highly time-dependent. Known methods of production are generally of slow kinetics[13-16]. For example, reaction times of 20 hours or more at rather elevated temperatures of 60–80°C are not uncommon. This often results in an undesirably large particle size distribution and relatively low conversion rates. As a result, the techniques are rendered costly and cumbersome. In the present study, we introduce a new technique that utilises hydroxyethyl cellulose (HEC) as an organic polymer for the synthesis of silver nanoparticles. This was prompted by the unusually high electrical charge density and high viscosity properties of the polymer, both of which affect particle size that often results in monodispersed Ag particles.

Material and Methods

Reagents and Instruments: All the reagents in this investigation were of analytical grade, and used as received. Distilled deionised water was utilised throughout. The prepared samples were characterised by a scanning electron microscope, SEM (Type: JEOL 30-kV) and an X-ray powder diffractometer (Type: Siemens AXS D5005). The UV–Vis spectra of the colloidal solutions were taken on a Shimadzu (Type: UV–1601) spectrometer.

Synthesis and Characterisation of Silver Nanoparticles: Test silver nitrate solution (0.2 M) was prepared by dissolving the required amount in 1:1 aqueous ammonia. Equimolar formaldehyde (methanal, HCHO) in *dry* ethanol and 0.1% HEC (degree of polymerisation 500) in water solutions were prepared. With continuous stirring in a clean dry beaker, 5 ml of the HEC solution was added dropwise to 1 ml of the silver nitrate solution for 5 minutes. To this mixture, 1 ml of the formaldehyde solution was added. The resultant solution was heated for 10 minutes on a water-bath maintained at a temperature of 50°C. The initially yellow solutions finally turned brownish black after a period of 30 minutes. No perceptible change in colour was observed at higher temperatures (≤90°C) and on further ageing.

Results and Discussion

Normally, in the absence of HEC, injection of silver nitrate causes an instant pitch black precipitate of amorphous metallic silver. However, on the introduction of HEC to the system, the colour changes from light yellow, persisting for some time before finally changing to dark brown. Analysis of the residual solutions revealed the presence of 3.8% Ag^+ at 20°C, dropping down to 1.6 % at 90°C.

X-ray Powder Diffraction Pattern: After a 10-fold dilution of the solution and collecting the silver nanoparticles by super high speed centrifuge, X-ray diffraction (XRD) was performed to ascertain the identity of the final products. The result is displayed in Fig. 1. The four diffraction peaks, obtained at angles 2θ of 39.98°, 44.28°, 64.46° and 77.32°, respectively, are attributed solely to the face-centred cubic (fcc) crystalline silver content of the sample. The low intensity diffraction peak at $2\theta = 31.94°$ is accounted for by the presence of silver (I) oxide (Ag_2O) in the sample. The diffraction pattern therefore confirmed that the products were a mixture of metallic silver and small amounts of silver(I) oxide.
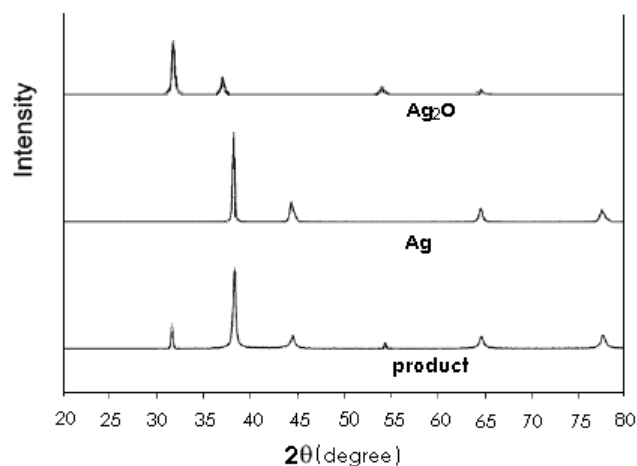
Figure-1: XRD patterns of powders of Ag_2O and Ag; the product in the test case is a mixture of Ag_2O and Ag

UV–Vis spectroscopic studies: Figure 2 shows the UV–Vis spectra of the sample solutions prepared at temperatures of 20, 50 and 90℃. It is noted that there is almost no shift in the peak position and the maxima occur at around 420 nm. This wavelength is consistent with the formation of silver nanoclusters $(Ag)_n$ comprising very low dimensional nanoparticles. This ties up well with previous reports on silver clusters[17]. There was however no observed increase in intensity with temperature. This can be inferred on the assumption that almost all of the silver ions are converted to the colloidal nanoparticle state at temperatures >50℃. High yields of silver nanoparticles with sizes <30 nm diameter are achieved in the 50^oC temperature range within 30 minutes and at as low concentrations of HEC as 0.1%.
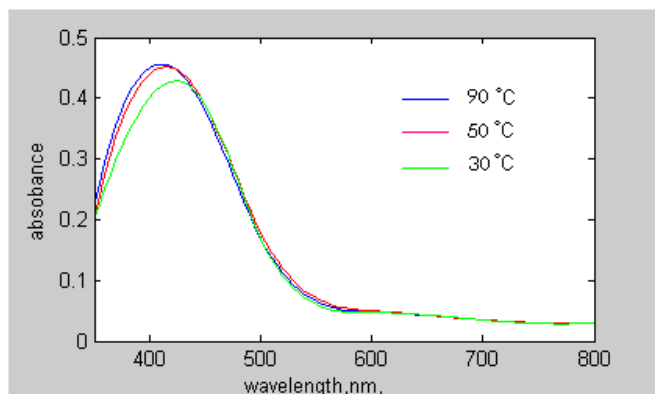

Figure-2: UV–Vis spectra for colloidal solutions at various temperatures

Scanning Electron Microscope (SEM) analysis: Figure 3 is the SEM images of the samples obtained from the colloidal Ag solutions prepared at 80℃. It confirms the existence of very small and uniformly spherical nanoparticles. Particle size and distribution from a chemical synthesis are dependent upon the relative rates of nucleation and growth processes, as well as the extent of agglomeration. Despite this, it is difficult to control these rates and, consequently, size distribution. In present case, it is thought that the hydroxethyl cellulose polymer, possessing a high electrical charge density coupled with a high viscosity, arrests the microscopic motions of the silver ions which in turn inhibits colloidal silver

formation. As a result, the product consists mainly of mono dispersed silver particles.
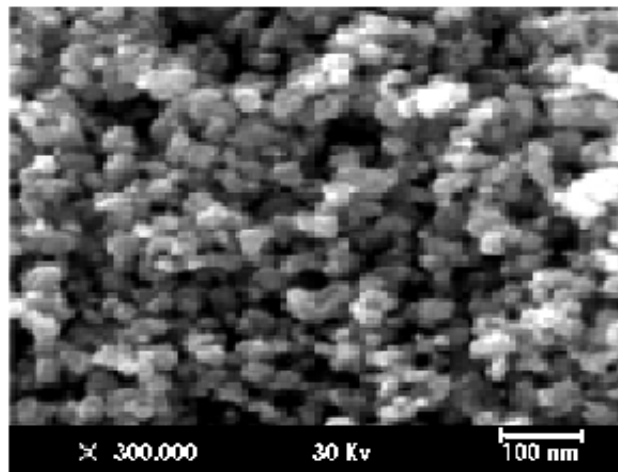
Figure-3: SEM micrographs of silver nanoparticles synthesised at 80℃.

Conclusions

A facile, high conversion and cost-effective method for the synthesis of silver nanoparticles with sizes <30 nm has been developed using hydroxyethyl cellulose. Our results show that although the final product may contain traces of silver(I) oxide, the organic polymer exhibits effective restriction on particle growth.

Acknowledgement

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