JOURNAL OF MATERIALS SCIENCE **39** (2004) 4459–4463

Polymer stabilized silver nanoparticles: A photochemical synthesis route

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This study describes a novel and convenient way for the preparation of polymer stabilized colloidal silver by an ultra-violet irradiation technique. Methoxypolyethylene glycol (MPEG) generates free radicals in presence of ultra-violet radiation and acts as the reducing agent towards the silver ion. MPEG also serves as a stabilizer of the silver particles formed.

1. Introduction

Colloidal metal particles are of great use in studying the neglected dimension in material research where a transition from bulk and molecular properties takes place [1]. Unique electronic and chemical properties of nanoparticles have drawn the attention of chemists, physicists, biologists and engineers who wish to use them for the development of new generation nanodevices. Part of the reason lies in the fact that these colloidal particles are useful in broad range of areas, such as photography [2, 3], catalysis [4], biological labelling [5], photonics [6, 7], optoelectronics [8] and surface enhanced Raman scattering (SERS) detection [9, 10]. A considerable effort has been devoted to the synthesis and characterization of silver nanoparticles by chemical reduction procedure [11–13], laser ablation [14–16] sonochemical [17], electrochemical method [18] templated by DNA [19], carbon nanotube [20], mesoporous silica [21], polymer [22, 23], organic solvents [24], membrane [25] and surfactant [26].

The dispersions of these nanoparticles usually display a very intense color due to plasmon resonance absorption, which can be attributed to the collective oscillation of conduction electrons, induced by the presence of an electromagnetic field. It has been shown that the size, morphology, stability and properties (chemical and physical) of these nanoparticles have a strong dependence on the specificity of the preparation method and experimental conditions.

Here, we present a simple way of preparing colloidal silver under photo irradiation where silver nitrate is the source of silver particles. We have employed methoxypolyethylene glycol (MPEG) which acts as a reducing agent in the presence of UV-irradiation and also serves as a stabilizing agent of the nano-silver particles. To the best of our knowledge this approach is a first report for the synthesis of nano-sized silver particles under controlled conditions.

2. Experimental

2.1. Reagent

Methoxypolyethylene glycol-5000, (MPEG), and Silver nitrate were purchased form Union Carbide and Aldrich respectively. Ultra pure water (>17 M$\Omega \cdot$cm) was used to prepare the solution of MPEG and silver nitrate. A stock solution of MPEG (2gm of MPEG was dissolved in 100 ml of water) was used in this experiment. Silver nitrate was used having concentration 10^{-2} mol dm^{-3}.

2.2. Instrumentation

Photochemical reactions were carried out under a portable germicidal lamp (15W; G 15 T8 VU-C, Phillips, Holland).

UV-visible spectra were measured in Shimadzu UV-160 digital spectrophotometer (Kyoto, Japan).

Transmission electron microscopy (TEM) study of the particles was carried out at 200 kV using a Philips CM200 TEM equipped with a LaB$_6$ source. An energy dispersive X-ray spectrometer (EDS) attached to the TEM was used to determine the chemical composition of the samples. TEM specimens were prepared by pipetting 2 μL of colloid solution onto a carbon coated copper grid.

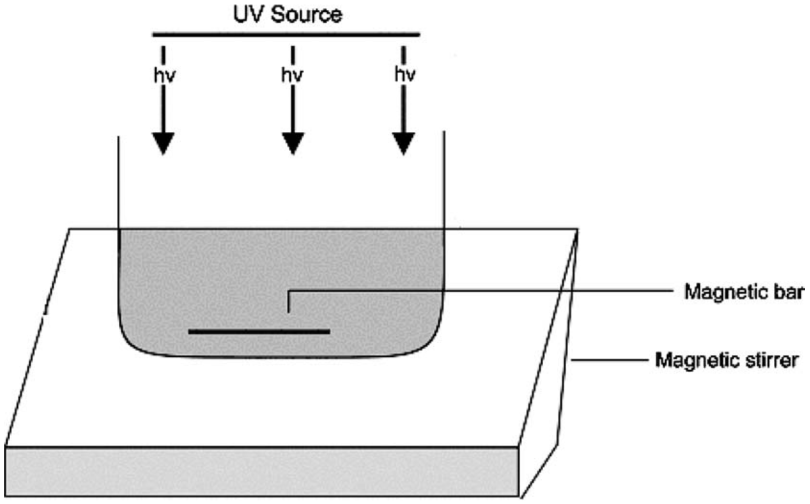


Figure 1 Sketch representation of the experimental arrangement.

2.3. Procedure

In a typical experiment, 10 cc. of MPEG-5000 solution was mixed with 500 μL of $HAuCl_4$ solution. The total solution was then homogeneously mixed in a quartz beaker and purged with nitrogen gas for 15 min in order to remove the dissolved oxygen. The beaker was positioned vertically under UV-source maintained at a distance of 10 cm between the upper surface of the solution and the UV-source (Fig. 1) and placed on a magnetic stirrer with stirring conditions applied. The progress of the reaction was monitored using a spectrophotometer.

3. Result

The homogeneity of the initial mixture of the reactants made it possible to follow the formation and evolution of silver nanoparticles by using UV-visible absorption spectroscopy. The colour of the solution started to change from colourless to yellow after the reaction had proceeded for ~10 min having a $\lambda_{\max}$ value 405 nm (represented as A in Fig. 2). 2 μL of the sample was pipetted out for TEM analysis at this stage. The TEM image indicates the average particle size was 7–15 nm (represented as A in Fig. 3). As the reaction proceeded (15 min), the colour of the solution turned reddish yellow and the absorption peak moved towards higher wavelengths, with $\lambda_{\max}$ at 420 nm (represented as B in Fig. 2). Further, at this stage, one more sample was collected for TEM analysis. The particles were not homogeneous in size and the size ranged between 7–35 nm (represented as B in Fig. 3). After 25 min irradiation, the visible spectra ultimately stabilized at $\lambda_{\max} = 425$ nm (represented as C in Fig. 2). The size of the particles at this stage ranged from 35–60 nm (represented as C in Fig. 3), but the size of majority of the particles ranged between 50–60 nm. Further, irradiation did not result in any considerable change in the spectra or the particle size, which indicates that all the silver ions are reduced and are used for cluster formation. The high magnification TEM image with micro diffraction pattern (Fig. 4) reflects the crystalline character of the particles. Confirmatory EDS analysis was performed on this sample as shown in Fig. 5.

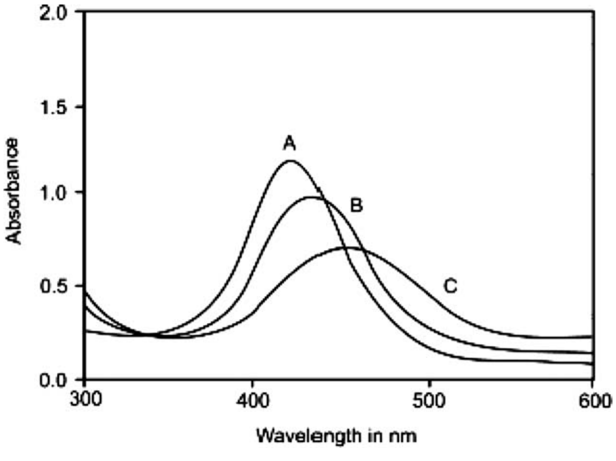


Figure 2 UV-visible spectra of the colloidal silver particle. UV-irradiation applied in the solution, 10 cc of MPEG-5000 (2 gm of MPEG was dissolved in 100 ml of water) and 500 μL of $AgNO_3$ (10^{-2} mol dm^{-3}), for (A) 10 min, (B) 15 min and (C) 25 min.

4. Discussion

4.1. Optical absorption (UV-vis) spectrum

Metal nanoclusters are optically transparent and act as dipoles. Conduction and valence bands of metal nanoclusters lay closely and electron movement occurs quite freely. The potential applications of these systems are mainly associated with the unusual dependence of the optical and electronic properties on the particle size [27–39]. Silver particles having 5–50 nm sizes show a sharp absorption band in the 410–420 nm region [40]. As the particles grow bigger, the absorption band broadens [40].

The sizes of the silver particles prepared by the method currently described depended on the concentration of the ion precursor, the duration of UV-irradiation and the concentration of the polymer. (We would like to note that attempts to produce silver particles in the presence of UV light in the absence of the polymer but with other alcohols present were not successful. Other alcohols used included n-propanol, isoproponol, n-butanol, isobutanol, n-pentanol, isopentanol or allyl alcohol.)

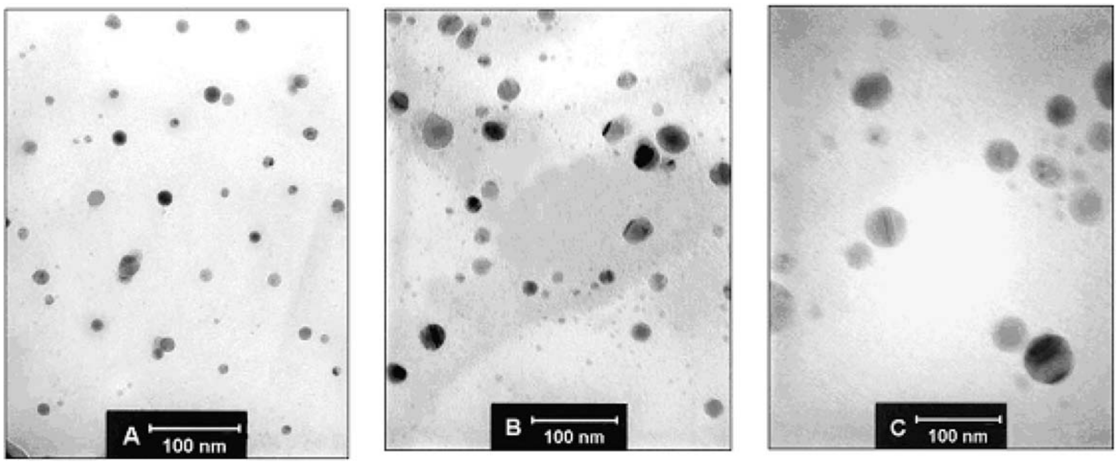


Figure 3 TEM images of the colloidal silver particles. Silver particles are formed by the application of UV-irradiation on the solution, 10 cc of MPEG-5000 (2 gm of MPEG was dissolved in 100 ml of water) and 500 μL of $AgNO_3$ (10^{-2} mol dm^{-3}), for (A) 10 min, (B) 15 min and (C) 25 min.

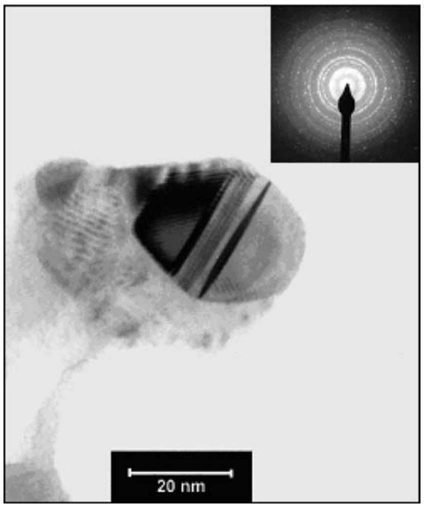


Figure 4 High magnification TEM with micro-diffraction pattern of a single silver particle.

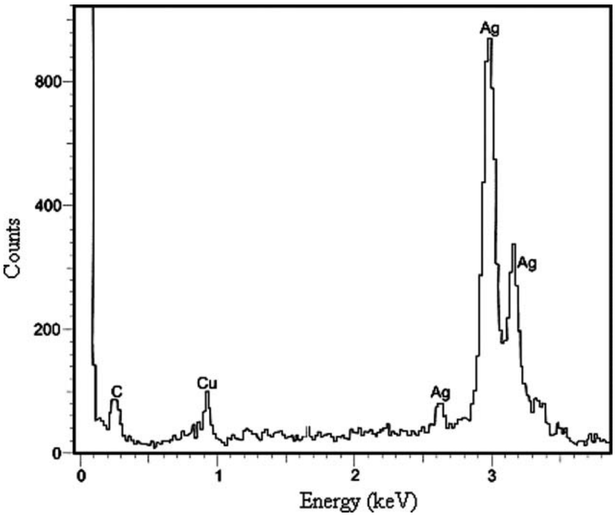


Figure 5 EDS analysis showing the formation of silver nanoparticles. Carbon and copper peak is from the carbon coated copper sample grid.

4.2. Mechanism for the formation of nucleation center and growth of silver particles

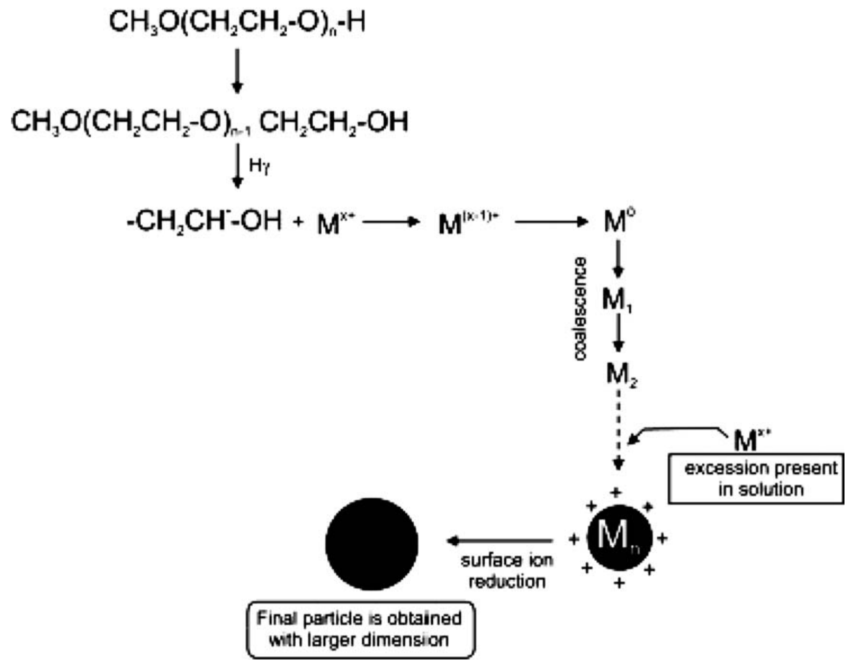
For the synthesis of a particle, the most accepted mechanism suggests a two-step process, i.e., nucleation followed by successive growth of the particles. In the first step, part of the metal ions in solution is reduced by a suitable reducing agent. The atoms thus produced act as nucleation centers and catalyze the reduction of the remaining metal ions present in the bulk solution. The atomic coalescence leads to the formation of metal clusters and can be controlled by ligands, surfactants or polymers. The reduction potential of $\text{metal}_{\text{ion}}/\text{metal}_{\text{atom}}$ and $\text{metal}_{\text{ion}}/\text{metal}_{\text{particle}}$ systems become more negative compared to that corresponding bulk metal. The reduction potential of $\text{Ag}_{\text{ion}}/\text{Ag}_{\text{bulk(aqueous)}}$ system is $+0.79\ \text{V}_{\text{NHE}}$, but for $\text{Ag}_{\text{ion}}/\text{Ag}_{\text{atom(aqueous)}}$ system it is $-1.8\ \text{V}_{\text{NHE}}$ [41] and that for $\text{Ag}_{\text{ion}}/\text{Ag}_{\text{cluster(aqueous)}}$ system, the reduction potential has an intermediate value. This result has great significance in understanding the mechanism of particle synthesis. The formation of metal atoms from the ionic state is difficult because of the large negative potential of the $\text{metal}_{\text{ion(aqueous)}}/\text{metal}_{\text{atom}}$ system. Strong reducing agents are generally used for the formation of the nucleation centers i.e., atoms. Once atoms are formed, it acts as a catalyst for the reduction of the remaining metal ions present in the solution. After their formation, the atoms coalesce which results in cluster formation i.e., particle growth.

4.3. Recommended reaction route

Energy transfer throughout the solution ensures the homogeneous distribution of the photolytic radicals formed by the excitation and ionization of the solvent. However, direct photolysis of water in presence of UV source is as follows:

$$H_2O \xrightarrow{hv} H^{\cdot} + OH^{\cdot} \tag{1}$$

Methoxy polyethylene glycol, $CH_3O(CH_2CH_2O)_n$ -H, *n* indicates the average number of oxyethylene



Scheme 1 Schematic representation for the nucleation and growth for the silver particles.

group i.e., $CH_3O(CH_2CH_2O)_{n-1}$ $CH_2CH_2{-}OH$ is the scavenger of $H^\cdot$ and $OH^\cdot$ radicals, and yields $-CH_2CH^\cdot{-}OH$.

$$-CH_2CH_2{-}OH \xrightarrow{OH^\cdot} -CH_2CH^\cdot{-}OH + H_2O \quad (2)$$

$$-CH_2CH_2{-}OH \xrightarrow{H^\cdot} -CH_2CH^\cdot{-}OH + H_2 \quad (3)$$

$-CH_2CH^\cdot{-}OH$ is a very powerful reducing agent, $E^0_{-CH_2CHO/-CH_2CH^\cdot-OH} = -1.9$ V.

This is able to reduce silver ion as follows:

$$Ag^+ + -CH_2CH^\cdot{-}OH \rightarrow Ag^0 + -CH_2CHO + H^+ \quad (4)$$

The atoms thus formed are homogeneously distributed throughout the solution. The binding energy between two transition metal atoms is higher than the atom-solvent bond energy and as a consequences atoms dimerize or associate with excess ions, which results in the formation of clusters (Scheme 1).

5. Conclusion

- $OH^\cdot$ radicals (Equation 1) can oxidize the ions or the atoms to the higher oxidation state and thus counterbalance the reduction process (Equation 4). For this reason, the solution generally contains a scavenger of $OH^\cdot$ radicals. The preferred choice is solutes whose oxidation by $OH^\cdot$ yields radicals that are unable to oxidize the metal ions but also have strong reducing properties [42]. In this study, MPEG is the scavenger of the $OH^\cdot$ radical (Equation 2).
- Clusters in aqueous solution, in the absence of a stabilizer, undergo further growth leading ultimately to precipitation of the metal. Clusters can be stabilized by their interaction with suitable agents such as surfactants, ligands, polymers etc., and as a result of electrostatic repulsion or steric hindrance, further aggregation is prevented [42].
- When the polymer concentration is effectively low and the amount of ion precursor ($AgNO_3$) is high, then the polymer cannot restrict the size of the particle effectively. In that case particles coalesce and ultimately produce a film like morphology. This work is still in progress and will be reported soon.
- But in the present experimental condition longer irradiation period does not affect the size of the particles because all the silver ions are utilized for atom formation and the atoms ultimately form the colloidal silver particles as discussed earlier.

A simple photochemical method for the preparation of colloidal silver in the presence of MPEG involves the generation of free radicals under UV-irradiation. This free radical has a strong reducing character that facilitates the formation of silver nanoparticles from ionic precursors. MPEG also acts as a stabilizer which restricts the particle growth.

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Received 3 September 2003
and accepted 1 April 2004