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Temperature controlled synthesis of silver nanostructures of variable morphologies in aqueous methyl cellulose matrix

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Spherical, hexagonal, triangular and bar shaped silver nanostructures have been synthesized at large scale in aqueous media using methyl cellulose (MC) as soft template. Synthesis is based on the reduction of Ag^+ by hydrogen at different temperatures. Morphology of particles is mostly spherical at 60 °C with an average diameter 4–8 nm, whereas hexagonal, triangular and truncated hexagon silver nanostructures are obtained at 80 °C. On the other hand bar shaped silver nanoparticles are formed as the reaction is carried out at 90 °C. Silver nanoparticles are characterized using UV–Vis and TEM study. Formation of silver nanostructures of variable morphologies has been explained in terms of different shaped template formed by MC at different temperature due to its thermogelation properties.

1. Introduction

Chemistry and Physics on the nanometer scale have been experiencing an enormous development in recent time leading to the emergence of new interdisciplinary field of 'nanoscience' [1]. Nanoparticles often exhibit very interesting physical and chemical properties which are both quantitatively and qualitatively different from their bulk materials and also from the discrete atomic or molecular species from which they are derived [2,3]. Among the noble metal nanoparticles silver is perhaps the most widely recognized for its unique optical properties, as manifested by its central role in photography [4]. Study of silver nanoparticles has led to significant advancement in the areas like photonics [5–7], micro-electronics [8,9], photo-catalysis [10–12], lithography [13,14] etc.

Since the last decade a large spectrum of research has been focused to control the size and shape, which is crucial in tuning the physical, chemical and optical properties of nano-materials. A large variety of synthetic approaches have been explored for the preparation of silver nanoparticles with different morphologies, such as hydrothermal synthesis [15,16], microemulsion [17], electrochemical deposition [18,19], photochemical method [20,21], γ-ray irradiation [22] etc. Among these approaches 'hard and soft' templates are commonly used in order to obtain silver nanoparticles with different morphologies. For examples, silver nanowires can be prepared within 'hard' templates, such as porous alumina membranes, carbon nanotubes and block copolymers [23–25]. Alternatively a range of 'soft' templates, such as PVP [15], CTAB [16], bis (p-sulfonatophenyl) phenylphosphine dehydrate dipotassium salt solution [26], SDS [27], unsaturated isomeric dicarboxylate [28] have been used to prepare silver nanobelt, nanocube, nanoprism and nanosphere respectively. On the other hand seed mediated growth process has been extensively used to synthesize silver nanowire [29,30], nanocube [31] and nanorods [32,33]. Though the reports on morphology-controlled synthesis of silver nanoparticles are quite abundant, still there are enough scope for the morphology controlled synthesis of nanoparticles in terms of its purity and monodispersity.

In this paper, we report a simple one step process to synthesize silver nanostructures by heating the aqueous solution of silver nitrate ($AgNO_3$) and methyl cellulose (MC) under hydrogen atmosphere. Here, MC is used as stabilizing agent and hydrogen gas is being used as reducing agent at elevated temperature. The structure of the MC (Scheme 1) shows that there are linear chains with β- (1→4) linkage with one free –OH and two free $–OCH_3$ group per unit. Due to the β-linkage, the methylated glucose unit in MC is flipped over. This enhances the intra and interchain hydrogen bonding, causes the MC chain to be rigid, straight and pack with crystalline arrangement of thick bundles, called micro fibrils. The as-prepared Ag-nanoparticles are adsorbed on the surface of microfibrils. We carry out the present synthesis at three different temperatures i.e. 60 °C, 80 °C and 90 °C. Synthesized particles are small and spherical as the reaction is carried out at 60 °C. Particles having shapes like hexagon, triangle, truncated hexagon, and truncated triangle are obtained at 80 °C. On the other hand mostly bar shaped particles are obtained as the reaction is carried out at 90 °C. Synthesis of these different shaped silver nanoparticles has been explained in terms of different shaped template formed by MC due to its thermogelation properties.

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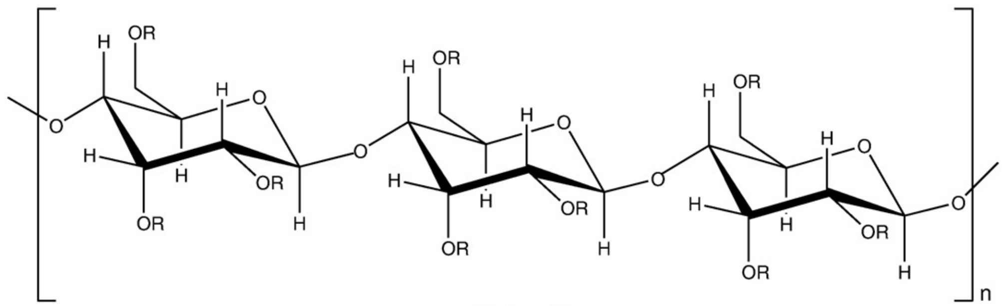

Scheme 1. Chain structure of methyl cellulose.

2. Experimental

Silver nitrate was purchased from Sigma Aldrich Chemical Corp. and methyl cellulose (MC, 4000 cps, viscosity 2% (w/v), water, 20 °C) was purchased from Merck and was used without further purification. All solutions were prepared in triple distilled de-ionized water.

2.1. Preparation of methyl cellulose (MC) solution

85 mg methyl cellulose was taken in a 100 mL round bottom flask. It was heated to 80 °C with distilled water for 1 h. The turbid solution was kept in deep freeze for an hour and clear MC solution was obtained.

2.2. Synthesis of Ag nanoparticle

50 mL aqueous MC (0.085 wt.%) was mixed with 50 mL 2.0×10^{-4} M aqueous $AgNO_3$ in a two necked round bottom flask. Three sets of the above reaction mixture were taken in three different RB flasks and then heated to 60°C, 80 °C and 90 °C respectively under hydrogen atmosphere for 5 h. The solution turned yellow at 60 °C; golden yellow at 80 °C and reddish yellow at 90 °C respectively indicating the formation of silver nanoparticles of different size and shapes.

2.3. Characterization

UV–Vis extinction spectra were measured using Shimadzu UV-1601 spectrophotometer. Morphology and size of silver nanoparticle were investigated using JEOL-JEM-2100 transmission electron microscope (TEM). Samples for TEM study were prepared by placing a drop of silver sol onto a carbon film supported on a 300 mesh size copper grids followed by solvent evaporation under vacuum.

3. Results and discussion

3.1. UV–Vis spectra

UV–Vis spectroscopy is one of the most important tools for characterizing metal nanoparticles. The absorption behaviour arises from Surface Plasmon Resonance (SPR), which originates from coherent oscillations of electrons in the conduction band induced by the electromagnetic field. The size and shape of the particles as well as the dielectric function of the surrounding medium determine the frequency and strength of the resonance [34]. Fig. 1 shows UV–Vis extinction spectra of silver sol obtained in MC matrix at various temperatures. Colour of the silver sol changes from light yellow at 60 °C to golden yellow at 80 °C to reddish yellow at 90 °C. The light yellow coloured silver sol shows SPR absorption peak at 415 nm. The peak is symmetric and there is no obvious absorption in the range of 550 nm, which indicates that little aggregation occurs during the synthesis and the nanoparticles are well dispersed. On the other hand the silver sol obtained at higher temperature (at 80 °C and 90 °C) shows broad and long tail SPR band in the range 550 nm apart from the most intense SPR band at 410 nm (at 80 °C) and 408 nm (at 90 °C) respectively.

Broad and red shifted SPR band at 60 °C (415 nm) compared to the most intense SPR band of silver hydrosol obtained at 80 °C (410 nm) and 90 °C (408 nm) is due to the scattering of visible light by the small nanoparticles (≤5 nm). Link et al. [35] suggested that one major reason for SPR broadening is electron surface scattering, which may be enhanced for very small clusters. In smaller particles, electrons reach the surface faster and scatter quickly, losing the coherence of collective oscillation. Blue shift and decrease of full width at half maxima (FWHM) of the SPR band centered around 400 nm for silver hydrosol synthesized at 80 °C and 90 °C are due to less scattering of visible light from the surface of comparatively larger size particles.

3.2. TEM study

Effect of temperature on the shape, size and dispersity of Ag-nanostructures are truly noticeable from the TEM image. Fig. 2 shows the TEM images of the as synthesized silver nanoparticles at 60 °C. It is obvious from Fig. 2 that most of the particles are spherical in shape with diameter ranging from 4 to 8 nm. Hexagonal and truncated hexagonal silver nano disks were obtained at 80 °C (Fig. 3). Most of

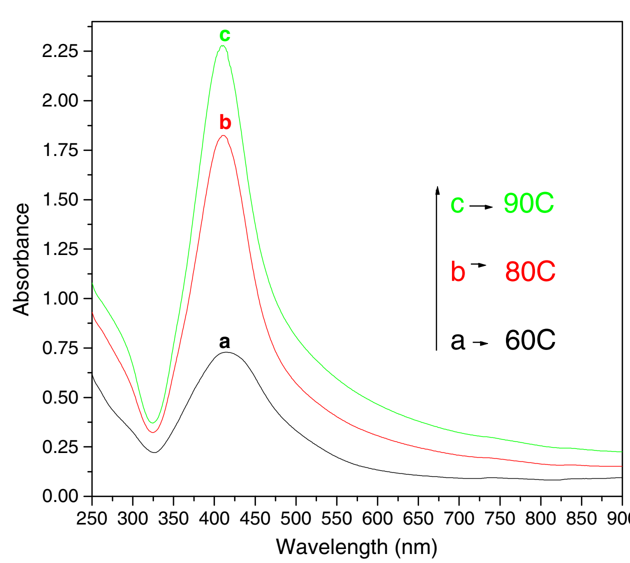

Fig. 1. UV–Vis extinction spectra of the silver hydrosol synthesized from 0.005(M) $AgNO_3$ in MC (0.0425 wt.%) under hydrogen atm. (5 h of heating) at (a) 60 °C, (b) 80 °C and (c) 90 °C.