Facile Synthesis of Narrowly Dispersed Silver Nanoparticles in Hydrogel

Jian Zhang, Xudong Wang,* Baohui Zhao, and Chenxi Li*
Key Laboratory of Functional Polymer Materials (Nankai University), Ministry of Education,
Institute of Polymer Chemistry, Nankai University, 94 Weijin Road, Tianjin 300071, P. R. China

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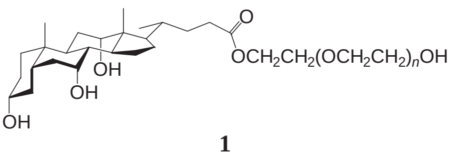
A novel method to prepare narrowly dispersed silver nanoparticles in hydrogel is reported. Gelator, the conjugate of cholic acid and polyethylene glycol 400, was used to form the gel, and it acted not only as the stabilizer preventing the silver particles from further growth and aggregation, but also as a reducing agent. Through this single-step synthesis, narrowly dispersed Ag nanoparticles were obtained in the hydrogel system at ambient temperature. The approach here is simple, economical, and environmentally benign.

Currently, silver nanoparticles are an intense field of research because of their vast number of significant applications, including optics, electronics, catalysis, and data storage.[1] However, both the development of simple and versatile methods for the preparation of monodispersed silver nanoparticles and utilization of environmental friendly chemicals are emerging issues and challenging tasks.[2] Owing to their ease in processability, confined microenvironment and long-term stability, gels have been successfully used to prepare nanomaterials, such as porous silica with tubular structure prepared by using organic gel fibers as a template,[3] dendritic polyaniline nanofibers synthesized in a surfactant gel,[4] and right- and left-handed silver nanohelices obtained in a self-assembled organogel.[5] Thus, it is conceivable that growth in a gel environment allows materials much finer control than growth from solutions, and some of the systems, which influence the nucleation and growth of inorganic crystals, may be important for better understanding biomineralization.[6] In this paper, we report a novel method of single-step synthesis of narrowly dispersed Ag nanoparticles with average size of 9.1 nm by reducing $AgNO_3$ in the presence of natural light in a hydrogel system at ambient temperature.

The conjugate of cholic acid (CA) and polyethylene glycol 400 (PEG400), a novel and facile gelator (**1**, CA–PEG400, Scheme 1), was prepared[7] and aimed to form the matrix of synthesizing silver nanoparticles. Interestingly, Ag^+ ions could be reduced in this hydrogel system without adding any other reductant.

The preparation of narrowly dispersed Ag nanoparticles is described as followings: 0.03 g of CA–PEG400 was dissolved in 1.5 mL of distilled water at $\approx$50 °C. To this cooling solution was added 1.5 mL of $AgNO_3$ solution (1.0 mM) with shaking. After the system was cooled to room temperature under static condition, a transparent gel was formed (Figure 1a). During the reduction process in natural light at ambient temperature, a color change from transparent to orange was observed (Figure 1b). After 4 h, the reduction was completed, and the gel was well maintained.



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Scheme 1.

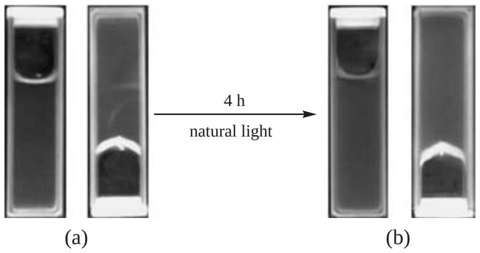

Figure 1. The morphology and color of the gel before (a) and after (b) reduction.

The process of the reduction was measured by UV–vis spectroscopy.[8] An absorption around 470 nm corresponding to the surface plasmon of spherical silver nanoparticles developed with time on the successive spectra (Figure 2).[9] After 4 h, the absorption maximum did not change any more, which means that the reduction had finished. The mechanism of the reaction may be attributed to the reductibility of the terminal hydroxy groups of CA–PEG400 on Ag^+ ions upon radiation.[10]

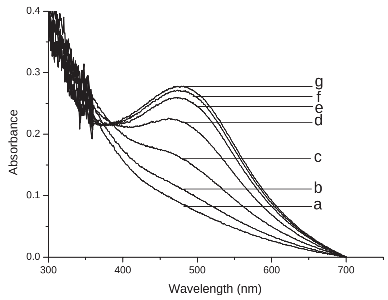

Figure 2. Successive UV–visible spectra of growing Ag particles in the gel: (a) 0, (b) 0.25, (c) 0.5, (d) 1, (e) 2, (f) 3, and (g) 4 h.

The morphologies of Ag nanoparticles were characterized by transmission electron microscopy (TEM).[8] A representative TEM image of narrowly dispersed Ag nanoparticles obtained in the hydrogel and the corresponding size distribution analysis are shown in Figure 3. The diameter size of the nanoparticles ranged from 3.1 to 17.4 nm, and the average diameter and the standard deviation were 9.1 and 3.1 nm, respectively, which indicated their uniformity in size. This should be contributed to the matrix structure of the gel, which prevented the particles from further growing and aggregation.

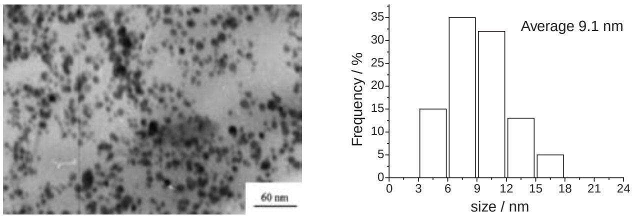

Figure 3. TEM image (left) and size distribution analysis (right) of Ag nanoparticles obtained in gel in natural light.

We used selected-area electron diffraction (SAED) to investigate the crystalline structure of these nanoparticles.[8] The SAED pattern of Ag nanoparticles, in Figure 4, shows diffraction rings from the same crystalline planes of face-centered cubic (fcc) silver (space group *Fm*3*m*). The ED rings, which were indexed to the (111), (200), (220), and (311) planes of fcc silver,[11] were relatively broad because of the small size of the particles and the polycrystalline nature.

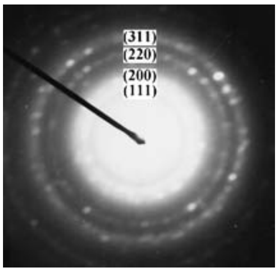

Figure 4. SAED pattern of Ag nanoparticles obtained in gel in natural light.

In conclusion, the present paper has demonstrated a novel method to prepare narrowly dispersed silver nanoparticles in a hydrogel. CA–PEG400 has been used to form the gel, the stabilizer preventing the particles from further growth and aggregation, as well as to be a reducing agent. The approach here is simple, economical, and environmentally benign. The microenvironment provided by the hydrogel influences the nucleation and growth of inorganic crystals, and this may be used to understand biomineralization. The various parameters controlling nanosize and morphologies of Ag particles are being further studied.

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7 The synthesis of CA–PEG400: Cholic acid (10.0 g) was dissolved in PEG400 (150 mL). Concd hydrochloride was added to acidify the reactant to pH 3. The mixture was stirred at 55 °C for 24 h. Brine (100 mL) was added and extracted with ethyl acetate (3×100 mL). The organic layer gathered was dried over anhydrous magnesium sulfate and filtered. After removing the solvent, the product was purified by column chromatography on silica gel (100–200 meshes) with dichloromethane/methanol (20/1, v/v) as eluent, and finally was obtained in 13% yield.

8 UV–visible spectra were measured on a Shimadzu 2010-PC UV–vis spectrometer. TEM and SAED images were obtained on a JEM-100CXII microscope, using an accelerating voltage of 100 kV. The size distributions of the silver nanoparticles synthesized were obtained by measuring the diameter of 200 particles viewed in the micrograph.

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