

A Novel Approach for the Preparation of Silver–silica Nanocomposite

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A novel route for the synthesis of silver–silica nanocomposite has been explored. We have employed dendrimer-protected silver nanoparticles, which act as a template to synthesize silica from its precursor on sol–gel processes. It has been observed that in the composite the nanosize silver particles are homogeneously dispersed in the silica matrix.

Synthesis and characterization of metal nanoparticles are subjects of growing interest from fundamental and applied viewpoints. The application of these nanoparticles introduced a remarkable development in the field of medicine, catalysis, optoelectronics, and many other areas of science and technology.^{1–3} The manufacture of nanoparticles can be achieved through a wide variety of different routes. Colloidal chemistry which belongs to wet chemical processes has been widely used for the preparation of nanoparticles owing to simple experimental procedure and low cost involved. The colloidal solutions in which nanoparticles are capped with suitable chemical agents are useful for spectroscopic and other studies, but they are not convenient for use in the form of prospective devices because of the handling problems, due to evaporation of the liquid host, leading to increase in concentration etc. For such limitations, attempts were made to disperse and confine the nanoparticles in some suitable solid matrixes.^{4–8}

Nanostructured silica materials have drawn considerable attraction because of their potential applications in ceramics, magnetic recording, semiconductor, and antibacterial materials. The morphology of the silica particles plays a vital role in these products. Thus many researches have been devoted to achieve the desired morphology of silica particles.^{9,10}

It has been successfully shown that poly(amido amine) (PAMAM) dendrimers, nearly perfect monodisperse macromolecules with regular and highly branched 3-D structures of a few nanometer size,¹¹ can be used as a structure-directing reagent for the synthesis of composite materials.¹² Synthesis of silica–dendrimer nanocomposite with different morphologies has been recently performed in our laboratory.¹³ On the other hand, dendrimer-coated stable metal nanoparticles have been reported by many researchers.^{14,15}

By exploiting the idea of the preparation of two composites using dendrimer mentioned above, we have synthesized silver–silica nanocomposite, which has been presented in this communication. The as-synthesized samples were characterized by transmission electron microscope (TEM) and infrared (IR) and UV–vis absorption spectra.

Silver nitrate (AgNO₃, 99.99%), sodium borohydride (NaBH₄, 99%) and a methanol solution of amine-terminated fourth generation (G4) PAMAM dendrimer (lot no.11427JO) were purchased from Aldrich Chemical Co. Methanol (99.8%) was purchased from Wako Chemical Co. All of these chemicals were used without modification. Double distilled water was used

throughout all experiments. Tetraethyl orthosilicate (TEOS) (purchased from TCI) was used as a silica source.

Dendrimer-protected silver nanoparticle was synthesized according to the procedure described in the literature.¹⁴ Silver–silica nanocomposite materials with various silver contents were prepared using a sol–gel technique by reacting a dendrimer-passivated silver nanoparticle sol with silica precursor, TEOS: A desired amount of TEOS was slowly introduced into the aqueous colloidal solution of dendrimer–silver nanoparticles at room temperature under the constant stirring. Yellow precipitates appeared within few minutes but the stirring was continued for 1 h. The final mixture was aged at room temperature for 2 days and the yellow solid product was filtered, washed with water and dried in air (yield 80%).

The TEM images were obtained with Hitachi H-7000 operating at an accelerating voltage of 100 kV. Prior to the TEM measurements, a small amount of nanocomposites was sonicated in methanol/ethanol for 10 min, and then 5×10^{-3} cm³ of the dispersion was dropped onto the carbon-coated copper grid, followed by drying at room temperature. IR spectra were recorded on a Bio-Rad FTS 575C instrument. KBr pellets of nanocomposites were prepared. Optical measurements were carried out on a Shimadzu UV 2200 spectrometer for nanocomposite suspension in paraffin oil on a quartz plate.

A TEM image of the dendrimer-passivated silver nanoparticles without addition of silica precursor is shown in Figure 1a. A random distribution of almost spherical particles with an average diameter of 6 ± 1.5 nm was seen. This indicates that dendrimers in the solution are not ordered in the experimental conditions.

Figures 1b–1d show the TEM images of the composites with different silver contents. The average sizes of particles in silica matrixes were the same with that in solution. The images clearly inferred that silver nanoparticles with almost similar morphologies with particles in Figure 1a are randomly dispersed in the silica matrix. More identified silver distributions were observed for the higher silver content samples (vide Figure 1b–1d).

IR spectra of silver–silica nanocomposite materials were measured. As seen in Figure 2, a broad band with a maximum at 3300 cm⁻¹ was observed. This is assigned to a stretching vibration band of OH groups of the residual water. Strong bands at 1073 and 795 cm⁻¹ are attributed to the Si–O–Si antisymmetric and symmetric stretching vibration modes, respectively. The amide I and II bands were observed at 1651 and 1553 cm⁻¹, respectively, indicating the presence of dendrimer in the composite materials. Similar IR bands were observed for materials with different silver contents.

The silver–silica nanocomposites retain a distinctive bright yellow color, which arises from the plasmon effect of silver particles. The UV–visible spectra of synthesized composites showed a plasmon absorption band around 420 nm as well as a band of nanoparticles in solution. This value is comparable to the reported one of nanosized silver particles prepared previously.¹⁴

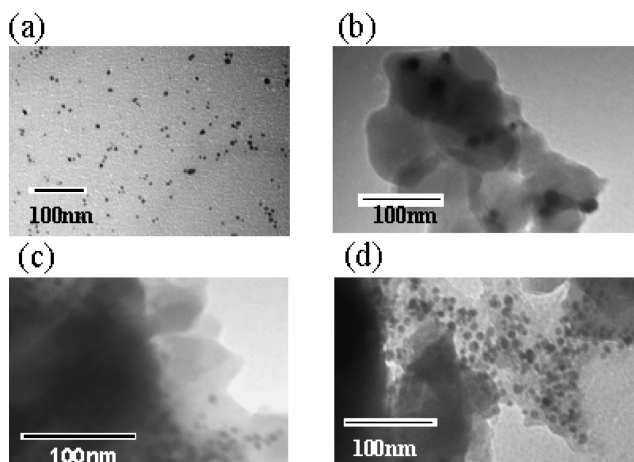


Figure 1. Representative TEM images of (a) PAMAM dendrimer-protected silver nanoparticles and (b)–(d) silver–silica nanocomposites. Silver content : (b) 1 wt %, (c) 2 wt %, (d) 3 wt %.

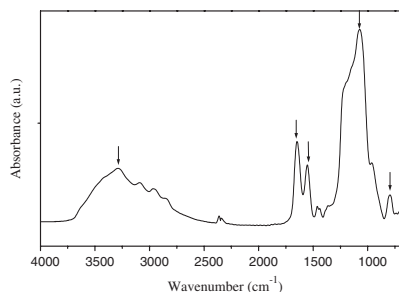


Figure 2. An IR spectrum of silver–silica nanocomposite with silver content of 2 wt %.

In conclusions, we presented a convenient route for the synthesis of silver–silica nanocomposite in which the preformed dendrimer-passivated silver nanoparticles can be homogeneously dispersed into the 3-D silica network. Then the dendrimer interacts through the hydrogen bonding or electrostatic interaction with silica. These silver–silica nanocomposites showed the characteristic plasmon absorption band of silver nanoparticles in UV–vis region.

Using this method, a variety of nanocomposites with various metal nanoparticles and solid host materials could be synthesized using poly(amido amine) dendrimer as a template. Since the synthesis procedure of these metal–silica composite has achieved by very simple and convenient sol–gel process, materials may be readily cast as a variety of forms (e.g., thin film, coating etc.) having potential applications.

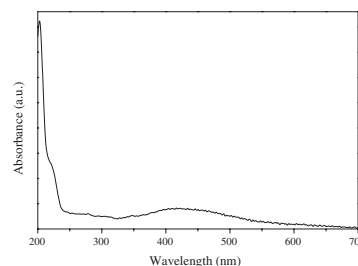


Figure 3. An UV–vis absorption spectrum of silver–silica nanocomposite with silver content of 2 wt %.

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