Thin Films of Ag Nanoparticles Prepared from the Reduction of AgI Nanoparticles in Self-Assembled Films

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A novel method for the preparation of thin films of Ag nanoparticles is reported. Using mercaptoacetic acid as the stabilizing agent, AgI nanoparticles were prepared in aqueous solution. And based on electrostatic interactions, the thiol-passivated AgI nanoparticles were assembled in a self-assembled film by alternative deposition with a cationic polyelectrolyte. Then the AgI nanoparticles in the composite film were reduced by NaBH₄, which resulted in the formation of a thin film of Ag nanoparticles. UV-visible spectra and X-ray photoelectron spectroscopy data confirmed the transformation from AgI to Ag. Atomic force microscopy (AFM) showed that the formed Ag nanoparticles distributed on the film homogeneously. Surface-enhanced Raman spectroscopy (SERS) measurement indicated that the prepared thin films could be used as effective SERS substrates. The reduction process was also carried out by UV light at selective surface regions, which resulted in the formation of patterned nanoparticle arrays.

Key Words: Ag nanoparticles; self-assembled film; polyelectrolyte; SERS; patterned nanoparticle arrays.

INTRODUCTION

Metal nanoparticles are attracting increasing attention as functional building blocks for the construction of nanostructured materials. They represent significant fundamental and commercial interest with a wide range of applications (1–4). Currently, nanostructured materials from metal nanoparticles are mostly used in the form of thin films, which have various potential applications in advanced optics (5), electronics (6), sensors (7), and catalysis (8).

Colloidal silver nanoparticles have been investigated broadly, and thin films of silver nanoparticles are of great importance in catalysis and surface-enhanced Raman scattering (SERS) (9–13). A variety of methods have been proposed for the preparation of uniform films of Ag nanoparticles, such as physical deposition (14), electrochemical deposition (15, 16), the Langmir–Blodgett technique (17), and the layer-by-layer self-assembly method (18–23). In addition, in applications of microelectronics or microsensors, patterned assembly of nanoparticles is of paramount importance (4). Several methods for the fabrication of patterned nanoparticle arrays have been developed, such as lithography, microcontact printing, and physical engineering (24–27).

Within these techniques, the use of preformed particles is common, as well as the use of a bifunctional substance to promote the attachment of the particles onto the surface. In this paper, we report a novel method for the fabrication of thin films of Ag nanoparticles, in which the Ag nanoparticles are produced from either wet chemical or photochemical reduction of AgI nanoparticles in preformed self-assembled films. The AgI nanoparticles were prepared with thiolates as the stabilizer agent, which make the nanoparticles negatively charged in aqueous solution. And based on electrostatic interactions, monolayers of AgI nanoparticles could be deposited in self-assembled films using the layer-by-layer (LBL) method. After the deposition process, the AgI nanoparticles in the self-assembled films could be reduced by NaBH₄, which resulted in the formation of thin films of Ag nanoparticles. SERS measurements indicate that the films prepared by this method may be a new candidate for SERS substrates. Reduction of AgI nanoparticles could also be carried out by light. Selective reduction of AgI nanoparticles was performed by masking the substrate with a patterned microchip mask during light irradiation, and patterned Ag nanoparticle arrays were obtained on the surface of the substrate. In both cases, the reduction processes were carried out on the surface of the substrate, which is simpler and more easily controlled compared with colloid methods.

EXPERIMENTAL SECTION

Preparation of AgI Nanoparticles

AgI nanoparticles were prepared as followed: To 150 ml of deionized water, 5.0 ml of a AgNO₃ solution (0.01 M) and 10.0 ml of a mercaptoacetic acid solution (0.01 M) were added with stirring. After 10 min of mixing, 4.8 ml of a 0.01 M NaI solution was dripped into the mixed solution under vigorous stirring. After 20 min of further reaction, the resulting light yellow solution was dialyzed against deionized water to remove the uncapped mercaptoacetic acid molecules. During all the courses, light was kept away from all the reactants. The colloidal
solution of thiol-passivated AgI nanoparticles was stable for weeks.

**Assembly and Reduction of AgI Nanoparticles**

Typical LBL process was carried out for the fabrication of AgI/PDDA film. A cleaned substrate of silica or silicon slide was dipped into a 1% solution (by weight) of poly(diallyldimethylammonium chloride) (PDDA; Aldrich) for 30 min to deposit one layer of PDDA. After being rinsed with water, the substrate was dipped into the colloidal AgI nanoparticle solution to deposit one layer of AgI nanoparticles. Then the slide was immersed in a freshly prepared NaBH₄ (10⁻³ M) solution for 10 min and thoroughly washed with distilled water.

In case of photoreduction, after deposition of one monolayer of AgI nanoparticles, a silicon substrate was covered with a microchip mask and irradiated with a 1000-W Hg lamp at a distance of 50 cm for 30 min. The slide was then immersed in a solution of 2.5% sodium thiosulfate to remove the unreacted AgI nanoparticles.

**Characterization**

UV-visible transmission spectra were obtained on a Shimadzu 3100 UV-Vis–near-IR recording spectrophotometer. Transmission electron microscopy (TEM) photographs were recorded with a Hitachi 8100 instrument at 200 kV. X-ray photoelectron spectroscopy (XPS) of the self-assembled film on a silicon wafer was performed using a VG ESCALAB MKII spectrometer with an AlKα monochromatized X-ray source. Raman spectra were obtained using a Renishaw Raman System Model 1000 spectrometer equipped with an integral microscope. The 514.5-nm radiation was from a 20-mW air-cooled argon ion laser. An appropriate holographic notch filter was set in the spectrometer, depending on the excitation source. Raman scattering was detected with 180° geometry using a Peltier cooled (−70°C) CCD camera (400 × 600 pixels). The data acquisition time used in the measurement of rhodamine 6G and 1,4-bis(2-(4-pyridyl) ethenyl)-benzene (BPENB) was 10 s, with the output power being 100 and 25 mW, respectively. The spectral resolution was 4 cm⁻¹ with the continuous scanning mode.

**RESULTS AND DISCUSSION**

Colloidal silver halides have been investigated for many years (28), and it has been reported that thiolates are effective stabilizer agents for the preparation of nanometer-sized AgI particles (29). Using mercaptoacetic acid (MAA), a kind of thiolate that has been used in the preparation and assembly of CdS nanoparticles (30), as the stabilizer agent, we prepared AgI nanoparticles in aqueous solution. The MAA molecules combine with AgI nanoparticles through mercapto groups, with carboxylic groups pointing to the solvent (29). A TEM photograph of AgI nanoparticles is shown in Fig. 1. As we can see, the AgI nanoparticles are in the size range of 15–40 nm with an average diameter of ca. 20 nm. An electron diffraction pattern of the sample shows the measured lattice spacing to be 3.968(100), 3.753(002), 3.540(101), 2.268(110), which can be attributed to β-AgI (Wurtzite structure).

After dialysis, the pH value of the colloidal AgI solution was measured to be 6.8. At this pH value, the prepared MAA-capped AgI nanoparticles were negatively charged, and using the LBL method they could be deposited on a preformed positively charged monolayer of PDDA. UV-Vis spectroscopy was used to monitor the deposition process. An absorption shoulder at around 420 nm was found in the UV-Vis spectrum of

![FIG. 1. TEM photograph of AgI nanoparticles.](image1)

![FIG. 2. UV-Vis absorption spectra of one monolayer of AgI nanoparticles before reduction (a) and Ag nanoparticles after reduction (b).](image2)
the self-assembled film, which is the typical absorption of AgI nanoparticles (Fig. 2) (28). The similarity in the UV-Vis spectra between the self-assembled film and the AgI solution shows that AgI nanoparticles were assembled onto the slide successfully. The composition of the self-assembled film was detected by XPS. The XPS data of the self-assembled film of AgI nanoparticles indicate that the molar ratio of Ag: I: S is 1:0.789 : 0.207. The total amount of iodine and sulfur atoms is comparable with that of silver atoms, which confirms the formation of a mercaptoacetic acid coating of AgI nanoparticles.

As is well known, NaBH₄ is a powerful reducing agent. When the thin film of AgI nanoparticles was immersed in the NaBH₄ solution, the AgI nanoparticles in the film were reduced to Ag(0) immediately. In the UV-Vis spectra of the reduced film, the absorption of AgI disappeared, while an absorption band of Ag nanoparticles at around 400 nm appeared (Fig. 2), which indicates that the AgI nanoparticles have changed into Ag nanoparticles (23). In the XPS data of the reduced film, we found that after reduction the peak position of Ag 3d₅/₂ and Ag 3d₃/₂ shifted from 367.9 and 373.9 to 367.7 and 373.7, respectively, which could be attributed to the transformation from Ag(I) to Ag(0). In addition, no iodine was found in the XPS spectra of the reduced film, which confirmed the transformation from AgI to Ag.

The surface morphology of the reduced self-assembled film was investigated by atomic force microscopy (AFM). In the AFM image (Fig. 3), we found that although the main composition changed from AgI to Ag, there is no evident change in the surface morphology in the reduced film. Ag nanoparticles distribute homogeneously in the film with a high particle density the same as that of the AgI nanoparticles. Since all of the AgI nanoparticles were deposited separately in the self-assembled film, no aggregation of Ag could happen during the reduction process, and one AgI nanoparticle was reduced to form one Ag nanoparticle. Thus, the PDDA/AgI nanoparticle film changed into a PDDA/Ag nanoparticle film without evident change in the surface morphology.

Figure 4 shows the SERS spectra of rhodamine 6G and BPENB absorbed on the substrate produced by this method. As we can see, rhodamine 6G and BPENB exhibited strong enhancement on the surface of the silver nanoparticles film, indicating that the substrates prepared by the above method could serve as effective SERS substrates.

As is well known, AgI nanoparticles are highly photosensitive and can be reduced by light irradiation. The reduction of AgI to Ag has been widely applied in photographic processes. In our experiments, the reduction of AgI nanoparticles in the self-assembled films could also be achieved by light irradiation. In order to make the film partly exposed to light, a patterned mask was covered on the substrate during the exposure to light. In the areas exposed to light, AgI nanoparticles were reduced to form Ag nanoparticles, while in the masked areas they remained unchanged. Then the AgI nanoparticles were dissolved by immersion in sodium thiosulfate, and patterned nanoparticle arrays of Ag nanoparticles were obtained on the substrate (Fig. 5).

In summary, reduction of AgI nanoparticles in self-assembled films provides a new method for the assembly of Ag nanoparticles. The reduction process can be carried out either by treatment with a reducing agent or by light irradiation. Thin films of Ag nanoparticles produced by chemical reduction have proven to be effective SERS substrates, while UV light irradiation of AgI nanoparticles at selected surface regions resulted in the
formation of patterned Ag nanoparticle arrays, which may find use in optics, microelectronics, and microsensors.

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REFERENCES