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Poly(ethylenimine)-stabilized silver nanoparticles assembled into 2-dimensional arrays at water–toluene interface

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ABSTRACT

A one-pot, size-controlled preparation of amine-functionalized silver nanoparticles is possible using poly(ethylenimine) (PEI) as a reducing and a stabilizing agent simultaneously. The PEI-stabilized Ag nanoparticles thus prepared in aqueous phase can further be assembled into 2-dimensional (2-D) arrays at the water–toluene interface by heating. By the addition of benzenethiol (BT) into the toluene, a more robust 2-D film is formed, not only at the interface but also on the inner surface of the sampling bottle. The latter Ag film can also be formed, through brief contact with the mixture, on glass slides and even on dielectric beads and cotton fabrics. These Ag-coated films are highly surface-enhanced Raman scattering (SERS) active and also exhibit a very intense SERS spectrum of 4-aminobenzenethiol (4-ABT) or 4-nitrobenzenethiol (4-NBT) via a place-exchange reaction that takes place between BT and 4-ABT or 4-NBT. In addition, the Ag-coated fabrics would be used as antibacterial gauzes for the treatment of burned skin and also as antistatic mats for the ready dissipation of electrical energy buildup. The present electroless deposition method of Ag is thus expected to serve as a technique in high demand in various fields.

1. Introduction

Metal nanoparticles anchored to surfaces in the form of a film are particularly important because of their potential use in nanodevices [1–5]. Over decades there has, therefore, been a great deal of interest, not only in the synthesis of monodisperse nanoparticles, but also in their self-organization into 2-dimensional (2-D) arrays [6–12]. In general, however, it is difficult to assemble well-ordered 2-D films of metal nanoparticles, without voids, on solid substrates. Large-scale ordered arrays of nanoparticles may be obtained at the air–water interface using the Langmuir–Blodgett method [13–15]. In recent years, the creation of 2-D arrangements of nanoparticles at liquid–liquid interfaces has been in continuous development [16,17]. For instance, Reincke et al. reported that the introduction of ethanol can pull hydrophilic citrate-stabilized Au nanoparticles into a water–heptane interface, leading to a closely packed monolayer [18]. Han et al. showed that C_{60} can induce the self-assembly of gold nanoparticles at water–oil interfaces [19].

Branched poly(ethylenimine) (PEI) has been known to be an efficient agent for the preparation of stabilized Au nanoparticles [20]. Recently, Wang and his colleagues showed that Au nanoparticles can be prepared in a single process which involves only heating an aqueous solution of a metal precursor and polyamine [21–23]. The reductive capability of amines has been known for long time, but the detailed mechanism of how Au nanoparticles are formed by amines has not yet been clarified [24]. We also have discovered recently that PEI-capped Au nanoparticles can be fabricated into a 2-D film by adding toluene into the colloidal solution [20]. In our experiments a homogeneous Au film was formed at the toluene–water interface, as well as at the bottle walls, either by heating the mixture or by adding thiol molecules such as benzenethiol (BT) into the toluene phase at room temperature. The film was able to form on a separate glass substrate immersed in the mixture and could also be transferred to a glass substrate as a Langmuir–Blodgett film. The optical property of the Au films could be controlled by the amount of BT added into the toluene phase. In addition, the Au film was microscopically smooth and shown to be highly surface-enhanced Raman scattering (SERS) active.

In the polyamine-based syntheses of nanoparticles, most of the works have been focused on the preparation of Au nanoparticles [21–23,25]. On the other hand, not many works have been published on the synthesis of Ag nanoparticles using polyamine. Recently, Sun et al. reported one-step preparation of dendrimer-protected Ag nanoclusters by heating $AgNO_3$ and poly(propyleneimine) (PPI) mixtures [26]. In this article, we report that the PEI-stabilized Ag nanoparticles can be prepared by heating an aqueous solution of $AgNO_3$ and PEI, and also homogeneous Ag films can

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be fabricated at the aqueous–toluene interface similarly to Au films. Firstly, Ag nanoparticles were prepared using PEI as the reductant as well as the stabilizer. Then, homogeneous Ag films were formed at the toluene–water interface simply by heating the mixtures or by adding BT into the toluene phase. The plasmon resonance, as well as the associated SERS activity, of the Ag films could be controlled simply by varying the amounts of BT added into the aqueous sol and toluene. In fact, the obtained large area of PEI-stabilized Ag film exhibits strong SERS activity of BT and also exhibits a very intense SERS spectrum of 4-aminobenzenethiol (4-ABT) or 4-nitrobenzenethiol (4-NBT) via a place-exchange reaction that takes place between BT and 4-ABT or 4-NBT. Since the proposed method is cost-effective and is suitable for the mass production of diverse Ag films irrespective of the shapes of the underlying substrates, it is expected to play a significant role especially in the development of surface plasmon-based analytical devices.

2. Materials and methods

Silver nitrate ($AgNO_3$, 99.8%), benzenethiol (BT, 99+%), 4-aminobenzenethiol (4-ABT, 95%), 4-nitrobenzenethiol (4-NBT, 80%), and branched poly(ethylenimine) (PEI, MW ~25 kDa) were purchased from Aldrich, and used as received. Other chemicals, unless specified, were reagent-grade, and highly purified water, with a resistivity greater than 18.0 MΩ cm (Millipore Milli-Q System), was used in preparing aqueous solutions. Silica particles with a mean diameter of 1 μm were prepared using the Stöber–Fink–Bohn method [27]. Bleached and sterilized fabrics made of 100% cotton, purchased from Dong-A Healthcare Company (Seoul, Korea), were used.

The PEI-stabilized Ag nanoparticles were prepared by heating a mixture of 100 mL of 10 mM $AgNO_3$ and 0.5–3 mL of 2% (w/w) PEI for 15 min. The size of the Ag nanoparticles was controlled by the amount of PEI added into the reaction mixture. The reacted mixture was ultracentrifuged and filtered, and the precipitate washed with copious amounts of deionized water. The PEI-stabilized Ag nanoparticles thus obtained were re-dispersed in water. To assemble a 2-D film, toluene was first poured over the aqueous Ag sol. A fairly homogeneous film was formed at the toluene–water interface by adding BT into the toluene phase. A large area of 2-D film was able to form on a separate glass substrate, as well as on silica and polystyrene beads and a cotton fabric, immersed in the mixture.

UV–vis spectra were obtained with a SINCO S-4100 UV–vis absorption spectrometer. Transmission electron microscope (TEM) images were taken on a JEM-200CX transmission electron microscope at 200 kV. Field emission-scanning electron microscope (FE-SEM) images were obtained with a JSM-6700F FE-SEM operated at 5.0 kV. Raman spectra were obtained using a Renishaw Raman system Model 2000 spectrometer. The 514 nm line from a 20 mW Ar^+ laser (Melles–Griot Model 351MA520) or the 632.8 nm line from a 17 mW He/Ne laser (Spectra Physics Model 127) was used as the excitation source. Raman scattering was detected over 180° with a Peltier cooled (−70 °C) charge coupled device (CCD) camera (400 × 600 pixels). The data acquisition time was usually 30 s, and the measured intensity was normalized with respect to that of a silicon wafer at 520 cm^{-1}.

3. Results and discussion

The PEI-stabilized Ag nanoparticles were readily produced when a mixture of PEI and $AgNO_3$ solutions was heated. The size of the Ag nanoparticles was largely dependent on the molar ratio of the PEI and $AgNO_3$. By increasing the molar ratio of PEI, smaller metal particles were produced, and vice versa. In this study, approximately 5–30 nm-sized Ag nanoparticles were prepared, as demonstrated in the TEM images in the upper panels of Fig. 1. The particles are spherical. The lower panels of Fig. 1 show the size histograms; the average sizes are 5 ± 4 nm, 14 ± 6 nm, or 30 ± 10 nm. Clearly, when the concentration of PEI is low, larger particles are formed. In the UV–vis absorption spectra shown in Fig. 2, the surface plasmon resonance (SPR) bands of Ag nanoparticles are observed at 390–408 nm, depending on the ratio of PEI added into the reaction mixture [28,29]. Specifically, the maximum of the SPR bands appears at 390, 398, and 408 nm, respectively, for the Ag sols corresponding to the TEM images in Fig. 1a–c. The distinct appearance of the SPR bands indicates that the PEI-stabilized Ag nanoparticles are present in a well-dispersed state. The gradual

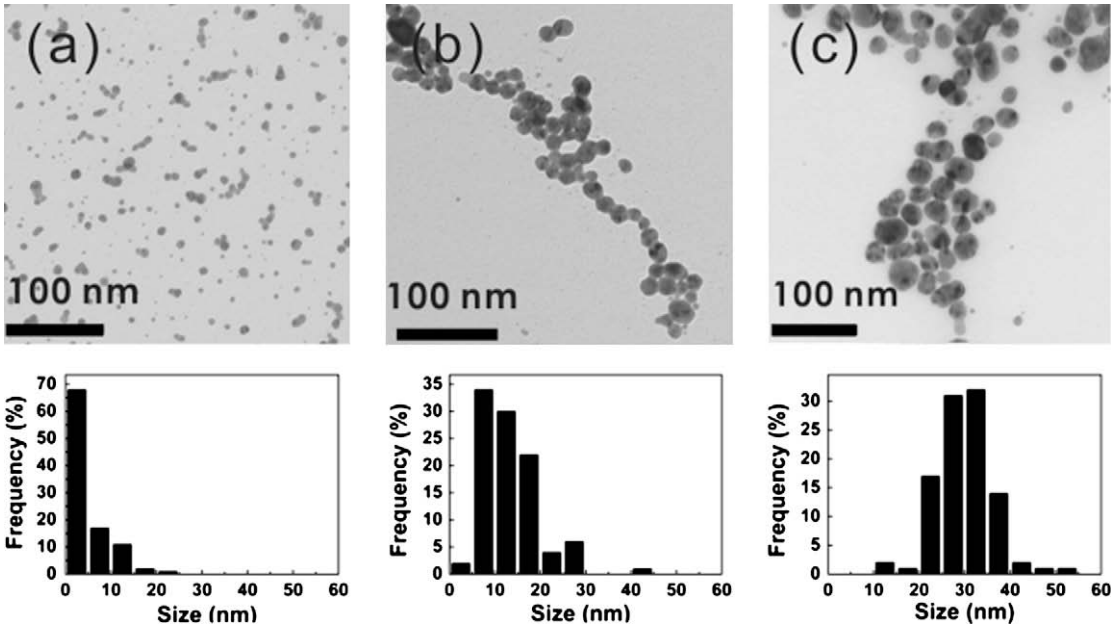

Fig. 1. (Upper panel) TEM images of Ag nanoparticles prepared by heating 100 mL of 10 mM aqueous $AgNO_3$ with (a) 3, (b) 1, and (c) 0.5 mL of a 2% (w/w) aqueous PEI solution for 15 min. (Lower panel) Size histograms of Ag nanoparticles from left to right corresponding to (a)–(c), respectively.