

Gold Composite- and Macroporous Gold Nanoparticle Films by a Vertical Deposition Method

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ABSTRACT

Composite films have been prepared in one step by a vertical deposition method from the aqueous suspension of gold colloids and polystyrene (PS) microspheres. The composite is formed on a glass substrate by convective assembly from the evaporating meniscus of the suspension. Au-PS composite films appear opalescent and SEM observations have shown that the structure of the composite is partially ordered. The film is “stripe” structured and made of close-packed PS microspheres separated by narrow (around 500 nm) gold filaments. The formation of filaments is accounted for by the strong attractive van der Waals forces between Au particles. The formation of Au filaments is also confirmed by the presence of a plasmon resonance band at 690-736 nm. The non-uniform self-assembly is accounted for by the disrupting effect of the gold nanoparticles. The structure of the composite prepared by the vertical deposition is compared to that of the ready made template infiltrated by gold by a chemical or electrochemical method. A macroporous gold film formed by evenly spaced 500 nm wide filament is obtained from the composite after the removal of PS by dissolution. The fabrication of both composites and macroporous gold films may find a range of applications, such as catalytic and SERS supports and optical coatings.

Keywords: nanostructures, nucleation, surface structure, metals, nanomaterials

1. INTRODUCTION

Porous gold structures containing large internal surface areas have a wide range of potential applications in the field of optoelectronics, catalysis, separation technology and sensing. Two approaches have been used for making macroporous gold films. The first, for the preparation of well-ordered macroporous (pore size > 50 nm) Au films with controlled porosity is colloidal crystal templating. Gold replicas that reflect the structure of the template are generally formed by infiltrating with gold, by chemical or electrochemical means, typically a polystyrene (PS)

or silica template, and subsequently removing the template by calcination or solvent dissolution [1-4].

A different approach to templating is the simultaneous convective assembly of PS microspheres and Au nanoparticles. Based on this idea, Tessier et al. [5] have developed a wet-chemistry route to produce a templated gold structure. By dragging a meniscus with constant velocity along a glass slide containing the concentrated dispersion of Au and PS microspheres, upon drying, the gold nanoparticles aggregate in the void spaces around the microspheres. By the same process and using the same coating apparatus, Prevo et al.[6,7] and Diao et al.[8] recently made pure gold nanoparticle films with controlled thickness and reported on their optical and electronic properties. Template synthesis has also been used to make very large (about 9µm) porous gold microspheres [9]. Less highly ordered structures with pore diameters of 15µm have been prepared by templating biological materials such as the calcium carbonate skeletal plates of echinoids [10].

Our group has prepared and characterized high-quality PS and silica colloidal crystals as well as titania inverted opals synthesized by evaporation induced self-assembly of PS or silica microspheres using a vertical deposition technique [11-14]. Recently, we have used a similar method to grow Au films from unfunctionalized Au nanoparticles prepared by reduction of tetrachloroauric acid with trisodium citrate dehydrate according to Turkevich method [15]. A pre-concentration of Au nanoparticles is made by gentle heating of the as-synthesized colloidal gold solution until its volume is approximately halved. Here, we have attempted the use of the convective assembly method to prepare Au-PS composite films from an aqueous suspension of Au colloids and PS microspheres. The composite film is formed by convective assembly from the evaporating meniscus of the suspension. In certain instances the Au-PS composite film appears strongly opalescent when viewed at small glancing angles showing the presence of a well-ordered material. In other cases and the SEM image has shown that the packing of the PS spheres was random and the resulting structure was only partially

ordered. All the composites prepared by this method exhibit, in addition to the Au plasmon resonance band around 520 nm, a broad band centered around 725 nm due to closely aggregated Au particles. Porous Au films with cylindrical macropores are obtained from the composite after removing the PS microspheres by dissolution. Here we report on a new vertical deposition method to prepare Au-PS composites in one step without any additional equipment.

2. EXPERIMENTAL

The colloidal solution of Au nanoparticles is prepared according to Turkevich's method [15]. A volume of 95 mL of a chloroauric acid (HAuCl_4) solution containing around 5 to 9 mg Au was heated and 5 mL of 1% sodium citrate solution was added to the boiling solution. The reduction of the gold ions by citrate ions is complete after 5 min. The solution is further heated gently until the volume of the solution was approximately halved and then left to cool to room temperature. The carboxylate-stabilized polystyrene microspheres were obtained from Spherotec Inc. as a 5% wt/v aqueous suspension and have an average diameter of 510 nm. For a typical deposition experiment, 2mL of the colloidal Au solution containing around 150 $\mu\text{g/mL}$ were mixed with 0.2 mL (3 drops) of the PS suspension. The substrates were standard 25 X 75 mm glass microscope slides (Fisher Scientific), cleaned by using a standard protocol. The slide was lowered into the mixture and kept at 45°C for 24 hours. The morphology of both the Au and Au composites is studied by scanning electron microscopy (SEM) and the optical properties are measured by UV-VIS-NIR spectroscopy using a specular reflectance accessory. The measurements were carried out in a CARY-5000 double beam spectrophotometer in the range between 300 and 2000 nm. In view of the small size of the samples, a high reflectance mirror was used for reference and the single reflectance values from the samples were recorded.

3. RESULTS AND DISCUSSION

Figure 1 shows the SEM micrographs of a typical Au-PS composite sample (viewed from the top) at different magnifications. The film appears opalescent with predominant red and green colors. The surface coverage is not uniform, the film exhibits a series of uniformly distributed "stripes" that extend the length of meniscus. At lower magnification, the micrographs of the composite (1a and 1b) show a complex, quite regular network of channels that appear as bright wide lines crisscrossing the image. The bright areas correspond to micron-sized flat gold flakes that grow along the empty spaces (cracks) due to the

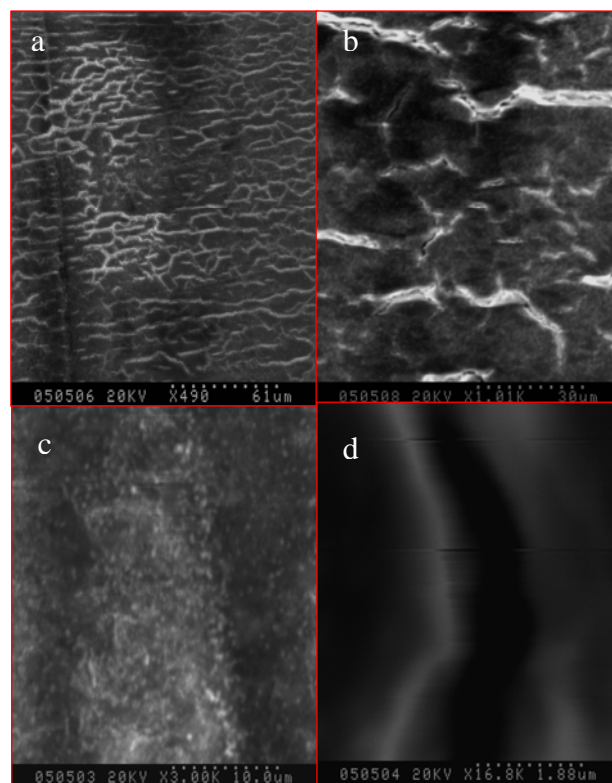


Figure 1: SEM image of a gold-PS composite

shrinkage drying phase. A similar growth pattern of gold has been found by Wijnhoven et al. [16] in the case of electrodeposited gold in PS templates and Coulhard et al. [17] for gold deposited on porous silicon. For p-type silicon substrates, the authors suggested that the preferential deposition of Au near the pores is due to the presence of a large number of surface defects and other high-energy sites available for initial Au nucleation near the fractures. The presence of gold along the sample fractures during the codeposition of Au and PS microspheres as showed in Fig. 1, suggests that Au nanoparticles are driven and accumulate into the drying front and crystallize only after the PS microspheres whose volume fraction is significantly higher in the mixture. In addition to the large flakes, smaller bright dots and patches can be seen upon the entire surface of the sample (Fig. 1b). The enlarged image (Fig. 1d) reveals the presence of Au along one of the cracks and shows gold flakes several microns long and approximately 200-300 nm wide. The large deposits near the fractures are probably formed by the coalescence of smaller clusters of Au. Due to the strong attractive van der Waals interactions, the Au nanoparticles may begin to aggregate before crystallization when accumulated in the drying meniscus. Figure 1b also reveals the presence of PS microspheres in the spaces limited by the fractures. In

some areas they appear closely-packed, while in others, the spheres are spaced. The microspheres assembled in one of the “stripes”, i.e., the areas of higher density, are shown in Fig. 1c. Due to the weak contrast, the presence of Au nanoparticles and aggregates in the film cannot be evidenced directly. The SEM observations on the porous gold structure that results once the microsphere phase has been removed, indirectly reveal the structure of the intermediate composite. It has been noted that the “stripe” structure of the composite is preserved in the gold film. The gold films varied in hue from blue to gray and were moderately absorptive in the visible and near-infrared.

Figure 2 shows the SEM image of the Au films obtained after the dissolution of PS in toluene. When the immersion time was very short, part of the PS microspheres remained in the film (Fig. 2a). This image is interesting because it clearly shows the presence of macroscopic circular voids containing only some isolated clusters. The formation of holes has been recently noted for colloidal crystal films grown by both horizontal [18] and vertical deposition [19] but the mechanism of formation is not elucidated. Fig. 2b shows that the film is highly porous and it is made by a network of narrow Au filaments with quite uniform features. The enlarged image in Fig. 2d reveals that the filaments are evenly spaced (500-600 nm), their width is around 500 nm and that they are several microns long. This microstructure of the porous film can only be accounted for by assuming the growing of Au filaments between the microspheres during the vertical deposition. In certain areas of the film, the growing filaments push away the PS microspheres that tend to form a close-packed structure. This behavior was also found by Kuncicky et al. [19] who suggested that the Au nanoparticles have a disrupting effect during the assembly process. This behavior can be accounted for by the different characteristics of Au nanoparticles compared to that of PS. Indeed, Au colloids are less spherical and less monodisperse than PS microspheres and, because they are protected only with citrate ions, the repulsive interaction between them are weak. The mechanism and the ensuing structure is very different from that formed by infiltrating the voids of a ready-made colloidal crystal template by Au nanoparticles. The growth of micron-sized filaments is probably due to the strong attractive forces between the Au nanoparticles attributed to the large Hamaker constant [20] that results in aggregated structures between the microspheres. However, it can be safely assumed that the crystallographic orientation of the microspheres in the composite is not significantly altered as most of the films appear opalescent. The presence of aggregated Au particles in the film has also been revealed by the reflectance spectra (Fig. 3). In the wavelength range below 900 nm, the reflectance of the Au-PS composites is dominated by two surface plasmon resonances (SPR):

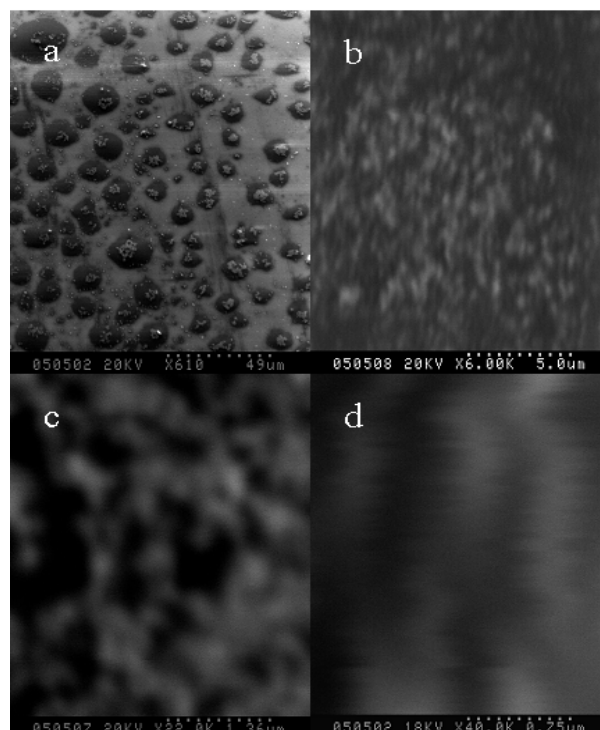


Figure 2: SEM image of gold films the first peak at around 520-530 nm, corresponds to the 10-20 nm isolated spherical particles and a broad band at 690-736 nm, attributed to the closely aggregated Au nanoparticles. The strong 520-530 nm SPR in the reflectance spectra of the composite shows the presence of some periodicity in the composite. This is not the case for the “stripe” structured pure gold film deposited by convective assembly [6], where the reflectance spectra exhibit only a band at 650 nm characteristic to highly aggregated structures.

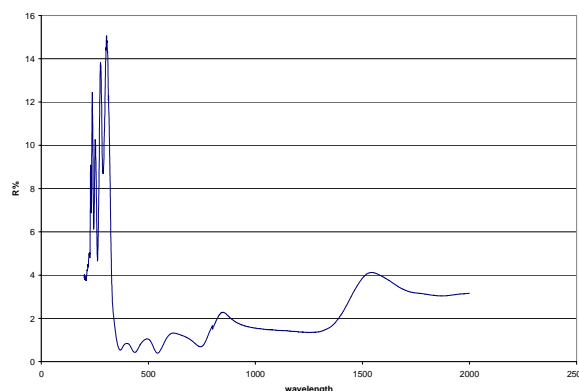


Figure 3: Reflectance spectrum of a gold –PS composite

It has been shown that, for an ensemble of nanoparticles supported on a substrate, the coupled plasmon bands are red-shifted several hundred nanometers [21,22]. The presence of this band in the reflectance spectra of the composites is consistent with the aggregated structure observed via SEM. Our results showed that the band

due to aggregated particles is wider and more red-shifted from that of the individual particles when the concentration of Au in the solution is higher. In addition to the surface plasmon resonance bands, the reflectance spectra of the composites exhibit a broad band in the NIR region, at approximately 1200-1300 nm. This band could be the Bragg stop band corresponding to the 510 nm PS microspheres. It is well known that the photonic band properties scale with the lattice constant of the colloidal crystal, which is proportional to the diameter of the sphere [23]. Miclea et al. [24] has recently shown that in the reflectance spectra of the Au-loaded opals, the diffraction resonance band appears shifted and broadened compared to the bare opal. In order to ascertain the assignment of reflectance bands in the composite, angle-resolved reflectance spectra should be measured. Further studies are also necessary to control the degree of Au aggregation in order to be able to control the optical properties of the coatings. The macroporous Au films prepared as described here may find a range of optical coatings.

4. CONCLUSIONS

In summary, we demonstrate how composite films from Au nanoparticles and PS microspheres can be fabricated in one step on a vertical substrate from the evaporating meniscus of aqueous suspension of their mixture. The composite films made by our method appear opalescent. SEM observations have revealed the presence of close-packed microspheres and of narrow (around 500 nm) gold filaments between them. Dissolution of the PS microspheres resulted in a macroporous gold film formed by evenly spaced 500 nm wide filaments with different lengths. The disrupting effect of gold nanoparticles on the self-assembly of microspheres has been confirmed and it has been accounted for by the strong attractive van der Waals forces between the Au nanoparticles that result in aggregated domains. The presence of the aggregated particles has been ascertained by the reflectance spectra. The structure of composites made by the simultaneous assembly on a vertical substrate is compared to that of infiltrated, ready-made templates.

5. ACKNOWLEDGMENTS

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