

In-Situ Incorporation of Gold Nanoparticles of Desired Sizes into Three-Dimensional Macroporous Matrixes

Shaohua Ding, Weiping Qian,* Yong Tan, and Yi Wang

State Key Laboratory of Bioelectronics, Department of Biological Science and Medical Engineering, Southeast University, Nanjing 210096, PR China

Received January 27, 2006. In Final Form: June 9, 2006

We present here a facile route to the incorporation of gold nanoparticles (GNPs) with desired sizes into three-dimensionally ordered macroporous (3DOM) matrixes. Our route combined the first attachment of small GNPs to the silica colloidal crystal templates as precursors and their subsequent controlled growth by the in-situ chemical reduction method. The desired enlargement of GNPs was acquired via their alternating and repeated exposure to solutions of auric salts and reducing agent NH_3OH . Such gold-decorated silica templates were also converted into self-sustained polystyrene (PS) macroporous films with GNPs embedded in their wall structures. The growth of gold seeds can be easily followed by their UV–vis absorbance spectra. The route provides an alternative way to incorporate GNPs with predetermined sizes into 3DOM matrixes without destroying their ordered structures. A highlight of our approach is that it obviates the need for the preformation of various-sized GNPs, which is an indispensable step in many other approaches.

Introduction

Metal nanoparticles have been studied extensively with respect to their unique optical and electrical properties,^{1–3} which have a wide range of applications in catalysis,^{4,5} sensing,^{6–8} and surface-enhanced Raman scattering (SERS).^{9–11} In recent years, there has been great interest in incorporating metal nanoparticles into a variety of matrixes to form so-called nanocomposite films.^{12–20} Combining the nanoparticles with suitable host matrixes may provide the possibility to control the physical and chemical properties of the film materials, which will extend their utility in many areas. Three-dimensionally ordered macroporous (3DOM) materials, because of their inherently high surface area-to-volume ratios and optical stop-bands from their periodical structures, are favored as host matrixes for the immobilization of nanoparticles. Considerable work has been devoted to the preparation of metal-coated 3DOM materials, and applications

of such composite films as chemical sensors and SERS substrates were demonstrated.^{17–20}

Because the size of metal nanoparticles is one of the key factors that affect their sensitivity in analytical applications,^{5,21,22} it is of paramount importance to fabricate 3DOM materials loaded with metal nanoparticles of desired sizes for versatile use. A feature of the most commonly used approaches would imply the preparation of designer-specified metal nanoparticles before they are incorporated into the matrix. In this letter, we present an alternative route to incorporate gold nanoparticles (GNPs) with desired sizes into the 3DOM matrix, viz., silica colloidal crystal templates and PS inverse opal films in our system. The route combined the first attachment of small GNPs as precursors and their further controlled enlargement by in-situ chemical reduction, thereby obviating the need for the preformation of GNPs of different sizes, which was an indispensable step in many other approaches. Scanning electrical microscopy (SEM) was used to investigate the microstructures of the samples, and UV–vis spectrophotometry was employed to obtain their optical absorption spectra and to verify the growth of GNPs in the matrixes.

Experimental Section

Materials. Silica colloidal spheres (~190 nm) were obtained from Nissan Chemical Ind., Ltd., Japan. Hydrogen tetrachloroaurate(III) hydrate (HAuCl_4), sodium borohydride (NaBH_4), potassium carbonate (K_2CO_3), hydroxylamine hydrochloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$, 99%), and hydrofluoric acid (HF, 40%) were all purchased from Nanjing Sunshine Biotechnology Ltd., China. 3-(Aminopropyl)-triethoxysilane (APTES, 98%) was purchased from Sigma. All reagents were used as received.

Fabrication and Self-Assembly of APTES-Functionalized Silica Colloidal Spheres. First, silica colloidal spheres were purified by centrifuging and redispersing in ethanol at least three times. Then 0.5 mL of APTES was added to 30 mL of the silica colloidal sphere suspension. After the mixture was vigorously stirred for 6 h, APTES groups covalently bonded to the surfaces of silica spheres, extending their amine groups outward as a new termination of the silica surface. To remove excess reactants from the reaction mixture, the APTES-functionalized silica spheres were purified by centrifuging and

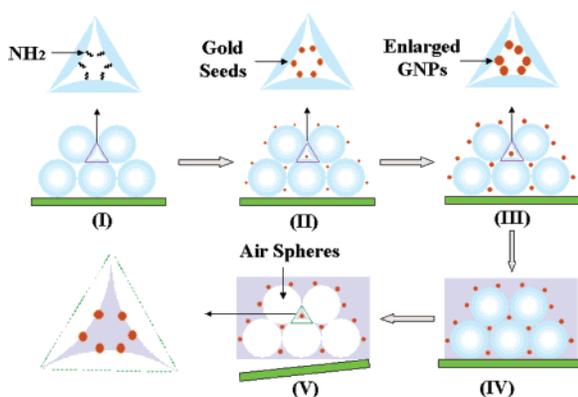
* To whom correspondence should be addressed. E-mail: wqian@seu.edu.cn. Tel: +8625-83795719. Fax: +862583795719.

- (1) Daniel, M. C.; Astruc, D. *Chem. Rev.* **2004**, *104*, 293–346.
- (2) Alivisatos, P. *Nat. Biotechnol.* **2004**, *22*, 47–52.
- (3) Hutter, E.; Fendler, J. H. *Adv. Mater.* **2004**, *16*, 1685–1706.
- (4) Sau, T. K.; Pal, A.; Pal, T. *J. Phys. Chem. B* **2001**, *105*, 9266–9272.
- (5) Wakayama, H.; Setoyama, N.; Fukushima, Y. *Adv. Mater.* **2003**, *15*, 742–745.
- (6) Zhu, Y. F.; Shi, J. J.; Zhang, Z. Y.; Zhang, C.; Zhang, X. R. *Anal. Chem.* **2002**, *74*, 120–124.
- (7) Ma, Z. F.; Sui, S. F. *Angew. Chem., Int. Ed.* **2002**, *41*, 2176–2179.
- (8) Riboh, J. C.; Haes, A. J.; McFarland, A. D.; Yonzon, C. R.; Van Duyne, R. P. *J. Phys. Chem. B* **2003**, *107*, 1772–1780.
- (9) Krug, J. T.; Wang, G. D.; Emory, S. R.; Nie, S. M. *J. Am. Chem. Soc.* **1999**, *121*, 9208–9214.
- (10) Tessier, P. M.; Velez, O. D.; Kalambur, A. T.; Rabolt, J. F.; Lenhoff, A. M.; Kaler, E. W. *J. Am. Chem. Soc.* **2000**, *122*, 9554–9555.
- (11) Larsson, M.; Lu, J.; Lindgren, J. *J. Raman Spectrosc.* **2004**, *35*, 826–834.
- (12) Hsu, S. H.; Chou, C. W.; Tseng, S. M. *Macromol. Mater. Eng.* **2004**, *289*, 1096–1101.
- (13) dos Santos, D. S.; Goulet, P. J. G.; Pieczonka, N. P. W.; Oliveira, O. N.; Aroca, R. F. *Langmuir* **2004**, *20*, 10273–10277.
- (14) Evanoff, D. D.; Chumanov, G. *ChemPhysChem* **2005**, *6*, 1221–1231.
- (15) Vossmeier, T.; Guse, B.; Besnard, I.; Bauer, R. E.; Mullen, K.; Yasuda, A. *Adv. Mater.* **2002**, *14*, 238–242.
- (16) Baumann, T. F.; Satcher, J. H. *Chem. Mater.* **2003**, *15*, 3745–3747.
- (17) Liang, Z. J.; Susha, A. S.; Caruso, F. *Adv. Mater.* **2002**, *14*, 1160–1164.
- (18) Rodriguez-Gonzalez, B.; Salgueirino-Maceira, V.; Garcia-Santamaria, F.; Liz-Marzan, L. M. *Nano Lett.* **2002**, *2*, 471–473.
- (19) Gu, Z. Z.; Horie, R.; Kubo, S.; Yamada, Y.; Fujishima, A.; Sato, O. *Angew. Chem., Int. Ed.* **2002**, *41*, 1153–1156.
- (20) Kubo, S.; Gu, Z. Z.; Tryk, D. A.; Ohko, Y.; Sato, O.; Fujishima, A. *Langmuir* **2002**, *18*, 5043–5046.

(21) Nath, N.; Chilkoti, A. *Anal. Chem.* **2004**, *76*, 5370–5378.

(22) Suzuki, M.; Niidome, Y.; Kuwahara, Y.; Terasaki, N.; Inoue, K.; Yamada, S. *J. Phys. Chem. B* **2004**, *108*, 11660–11665.

Scheme 1. Schematic Illustration of the Fabrication of GNP-Embedded 3DOM Materials^a



^a (I) Modification of silica colloidal spheres with APTES, (II) adsorption of gold seeds onto silica spheres, (III) enlargement of gold seeds by in-situ reduction, (IV) infiltration of PS solutions, and (V) dissolution of silica spheres by HF.

redispersing in ethanol at least five times. Then the amino-functionalized silica spheres were packed into the templates with three-dimensionally ordered arrays on glass substrates by the vertical deposition method.²³ The templates were dried at ambient temperature before use.

Synthesis of GNPs. GNPs (2–5 nm) were prepared by the reduction of chloroauric acid with sodium borohydride according to literature procedures with some modifications.²⁴ Typically, 3 mL of 1% HAuCl₄ was mixed with 200 mL of triply distilled water with vigorous stirring, followed by the addition of 1 mL of an aqueous solution of K₂CO₃ (0.2 M). Afterwards, 9 mL of NaBH₄ (0.5 mg/mL) was quickly added to the mixture. The wine-red solution was stored at 4 °C until use.

Adsorption of Gold Seeds and Their Controlled Growth in the Silica Templates. The silica sphere templates were fixed in a test tube containing gold seeds, and the tube was immobilized in an oscillator with gentle shaking overnight. Then the templates were rinsed to remove the unattached GNPs and dried in air. To initiate the growth of the attached GNPs, the composite templates were exposed alternately and repeatedly to solutions of auric salts and the reducing agent NH₂OH. Between each enlargement cycle, the templates were thoroughly rinsed with distilled water and dried for characterization.

GNP-Embedded Polystyrene Inverse Opal Films. After several cycles of the reduction reaction, a toluene solution of PS was used to infiltrate the vacant space of the templates. After 2 to 3 days, the PS film together with the template was spontaneously removed from the glass substrate. Then the template was removed by treatment with 4% hydrofluoric acid, producing a self-sustained, gold-embedded PS film with three-dimensional ordering of pores.²³

Characterization. A JEM2000EX transmission electron microscope (TEM) was used to image the growth of GNPs on the surface of silica spheres at different stages of the process. Scanning electron microscopy (SEM) was carried out on a LEO 1530 VP microscope. Prior to the SEM measurements, the samples were coated with a gold film to improve electrical conductivity. UV–vis spectra were recorded with a Shimadzu UV3150 UV–vis spectrophotometer in transmission mode. All transmission measurements were performed in the same regions.

Results and Discussion

Scheme 1 shows a schematic illustration of the fabrication of gold-infiltrated 3DOM materials. First, silica spheres were modified with APTES to present the surfaces of silica spheres

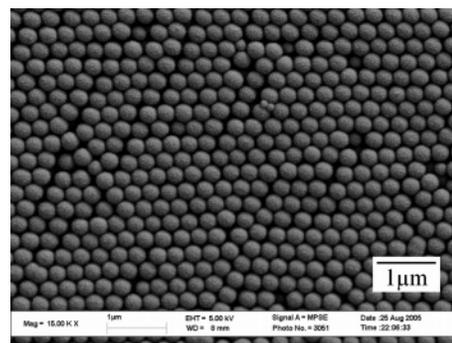


Figure 1. SEM image of the silica colloidal crystal template infiltrated with gold seeds.

with positively charged amino groups. Then the modified spheres formed closely packed arrays on glass substrates by the vertical deposition method.²³ We simultaneously prepared silica colloidal crystal templates of the same quality. Afterwards, the silica templates were dipped into a test tube of aqueous GNPs with gentle shaking. During this process, the negatively charged GNPs attached to the amino groups on the modified silica sphere surfaces by electrostatic interactions.²⁵ The small size of the GNPs and the constant shaking of the test tube facilitated the gold seeds to access the interstitial spaces of the templates. Subsequently, the gold-infiltrated templates were soaked in a solution containing AuCl₄⁻. After 15 min of immersion, the templates were switched to a solution of the reduction agent to increase the sizes of the gold seeds. In this step, the preadsorbed nanoparticles served as nucleation sites for electroless metal deposition. To avoid gold deposition at places other than the preadsorbed gold seeds, a weak reduction agent, NH₂OH, was used as reported in the literature.^{26,27} Simply by the repeated alternating exposure of the template to solutions of auric salts and NH₂OH, the gold seeds in the templates were structurally enlarged in a controlled manner. During each cycle of the reduction process, the templates were thoroughly rinsed and dried, and their optical absorbance spectra were recorded to evaluate the growth of GNPs in the templates. To obtain a gold-decorated PS inverse film, the vacant space of the resulting templates was infiltrated with a toluene solution of PS followed by the dissolution of silica spheres with HF, leaving behind the PS macroporous matrixes with GNPs embedded in the wall structures in a free-standing form.

Figure 1 shows a typical SEM image of the silica template infiltrated with gold seeds. It is clear from Figure 1 that the composite template maintains the hexagonally ordered structures of the bare colloidal crystal template. However, because all of the samples in our system for SEM characterization must be coated with a thin gold layer to improve their conductivity and because of the limit of resolution of the SEM, the primarily adsorbed gold seeds cannot be distinguished from the SEM image. To carry out the TEM measurements of GNPs on the silica surface, the samples of free-standing silica spheres were obtained by making a careful fine scratch on the boundary of the silica multilayers produced by a steel needle at different stages of the reduction process. The released silica spheres were redispersed in distilled water through a brief sonication for TEM observations. Figure 2 illustrates the growth progression of GNPs on the surface of silica spheres. When the reduction process was initiated, the

(23) Qian, W. P.; Gu, Z. Z.; Fujishima, A.; Sato, O. *Langmuir* **2002**, *18*, 4526–4529.

(24) Phadtare, S.; Kumar, A.; Vinod, V. P.; Dash, C.; Palaskar, D. V.; Rao, M.; Shukla, P. G.; Sivaram, S.; Sastry, M. *Chem. Mater.* **2003**, *15*, 1944–1949.

(25) (a) Oldenburg, S. J.; Averitt, R. D.; Westcott, S. L.; Halas, N. J. *Chem. Phys. Lett.* **1998**, *288*, 243–247. (b) Westcott, S. L.; Oldenburg, S. J.; Lee, T. R.; Halas, N. J. *Langmuir* **1998**, *14*, 5396–5401. (c) Pham, T.; Jackson, J. B.; Halas, N. J.; Lee, T. R. *Langmuir* **2002**, *18*, 4915–4920.

(26) Brown, K. R.; Natan, M. J. *Langmuir* **1998**, *14*, 726–728.

(27) Graf, C.; van Blaaderen, A. *Langmuir* **2002**, *18*, 524–534.

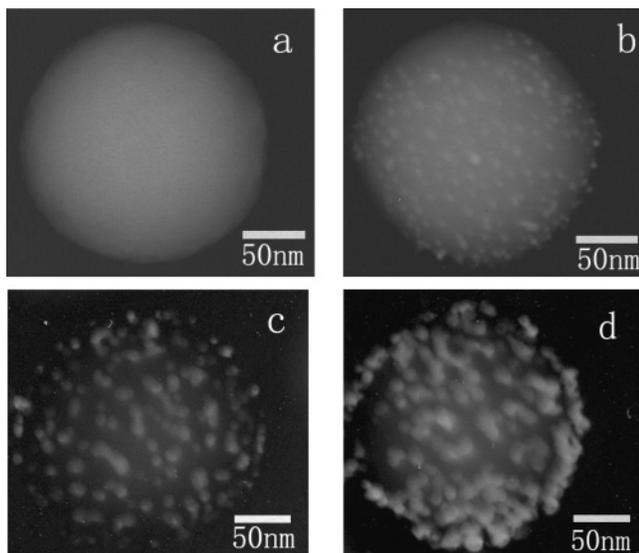


Figure 2. TEM images showing the growth progression of GNPs on the surface of silica spheres: (a) silica sphere modified with APTES prior to the addition of GNPs, (b) adsorbed GNPs as nucleation sites, and (c, d) gradually enlarged GNPs as reduction ensues.

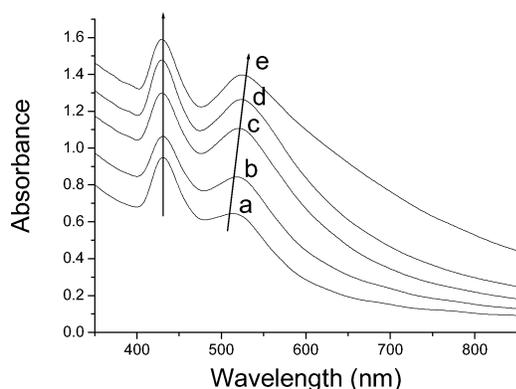


Figure 3. Sequence of UV-vis absorbance spectra recorded from gold-infiltrated silica templates during five cycles of the reduction process.

adsorbed GNPs (Figure 2b) were used as nucleation sites for the subsequent reduction, leading to increases in both the size and the coverage of GNPs on the silica surface (Figure 2c and d). We clearly observe the subtle changes in GNPs from these TEM images. Because GNPs have a rich plasmon band, which is a function of their size and shape and the dielectric constant of their surroundings, the variations in GNP dimensions will surely lead to a change in their plasmon band that can be measured by UV-vis spectrophotometry. Therefore, the enlargement of gold seeds in the template could be verified by measuring the variation of their plasmon resonance spectra in our experiments. Compared with the SEM and TEM studies, the optical studies are timesaving and nondestructive to the samples.

The series of UV-vis absorbance spectra shown in Figure 3 clearly exhibits the evolution of optical absorbance of the gold-infiltrated template during five such reduction cycles as depicted above. From each of the five spectra (Figure 3a-e), two peaks can be obviously observed. The peaks centered at about 430 nm originate from the optical stop-band of the ordered silica sphere arrays that are confirmed by the corresponding SEM image in Figure 1. The other peaks that are located at the red side of the spectra can be assigned to the plasmon resonance of the adsorbed GNPs. As the reduction processes go forward, there are visible

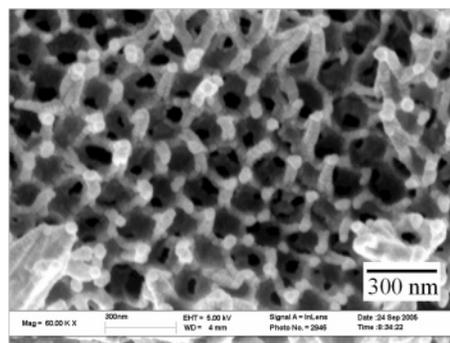


Figure 4. SEM image of a PS film embedded with gold seeds.

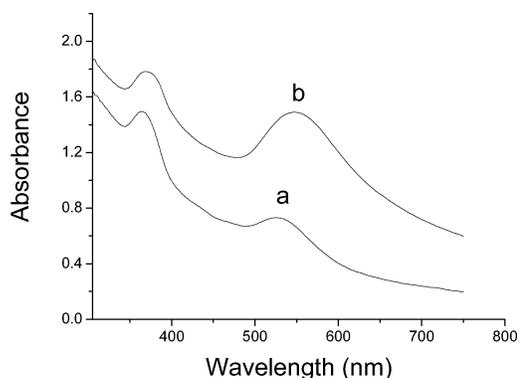


Figure 5. UV-vis absorption spectra of the PS films embedded with (a) gold seeds and (b) enlarged GNPs in air.

changes in the spectra. In terms of the plasmon resonance band of GNPs, we can see a progressive enhancement in its intensity, which indicates the increased content of gold in the template that yields the high absorbance features.²⁸ Furthermore, the maximum of the optical absorbance of gold simultaneously undergoes a red shift of about 12 nm during five such cycles, which can be attributed to the structurally enlarged GNPs caused by the deposition of gold reduced from auric salts. The stepwise growth of GNPs can be achieved by the iterative reduction process. Regarding the photonic band gap from the ordered silica sphere arrays, it possesses an invariant peak position. It is apparent that the electroless plating method can efficiently enlarge the dimensions of preadsorbed GNPs without destroying the crystal-line structure of the template.

Gold-embedded PS inverse opal films were obtained by the template-assisted method. Both silica templates with gold seeds and structurally enlarged GNPs were converted to PS macroporous films. Compared to the gold-infiltrated silica sphere arrays, there are two advantages of the resultant PS films: (1) the PS films are in a free-standing form, so they are flexible and can be easily handled and (2) they possess larger surface areas and pore sizes, which allow larger analyte molecules to freely diffuse throughout the films and thus support the efficient uptake of analyte species.¹⁵ Figure 4 shows a typical SEM image of the PS film decorated with small gold seeds. Honeycomb-like structures can be easily observed. However the GNPs are indiscernible from the SEM image for the same reason as discussed above. The UV-vis absorbance spectra of PS films with gold seeds and enlarged GNPs are shown in Figure 5. Both spectra possess two separate peaks. The peaks that are located at shorter wavelengths in the spectra originate from the ordered pore structures of the PS films, and the other peaks that are situated on the red side can be attributed to the plasmon resonance absorption of GNPs. In

(28) Zayats, M.; Baron, R.; Popov, I.; Willner, I. *Nano Lett.* **2005**, *5*, 21–25.

contrast with that in silica templates, the peaks of the absorption of gold seeds and enlarged GNPs shift to longer wavelengths, which can be attributed to the noticeable change in the dielectric constant around the GNPs. The reasonable difference between the maximum in the plasmon resonance of GNPs before and after transference indicated that the initial arrangement of GNPs in silica templates was preserved.

Conclusions

We have shown the feasibility of our route to incorporate various-sized GNPs into 3DOM materials, viz., colloidal crystal templates and polymer inverse opal films in our system. GNPs of predetermined size were primarily obtained through the stepwise enlargement of adsorbed small gold seeds in the template. GNP-embedded PS films were also acquired by the template-

assisted method. The proposed route was demonstrated to be an alternative approach to infiltrate 3DOM materials with large GNPs without destroying the ordered structures of the films. The efficiency and facility make the method a promising candidate for incorporating other metal nanoparticles into various 3DOM matrixes.

Acknowledgment. This research is supported by the National Nature Science Foundation of China (nos. 20475009, 30370312, and 60121101), the Ministry of Education, the Nature Science Foundation from Jiangsu province, and the Foundation for the Author of National Excellent Doctoral Dissertation of PR China (no. 200252).

LA060273T