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Short communication

Au nanoparticle-built mesoporous films based on co-electrophoresis deposition and selective etching

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ABSTRACT

A simple and facile strategy is presented to fabricate mesoporous Au spherical nanoparticle films based on the combination of co-electrophoresis deposition in the mixed colloidal solutions of Au and Ag and selective etching of the Ag nanoparticles which act as a sacrificial metal. The film is homogeneous in the macroscale but with numerous nanoscaled pores. The film configuration can be easily tuned by the size of Au colloidal nanoparticles and the amount of Ag colloidal solution mixed. Importantly, such structured mesoporous film exhibits strong surface-enhanced Raman scattering activity with good reproducibility and repeatability. Additionally, this study provides a novel method for the controllable construction of other mesoporous films from simple metals to multicomponent hybrids, by using nanoparticles as building blocks.

1. Introduction

Au mesoporous films have received a considerable attention recently owing to their outstanding properties and potential applications in biosensor [1], catalysis [2], fuel cells [3], etc. Especially, they are excellent substrates for surface-enhanced Raman scattering (SERS) sensors by virtue of their good thermal stability and great enhancement ability [4]. The already-used fabrication techniques fall into two categories: chemical processes [5–7] and physical vapor deposition [8–10]. However, both methods have many drawbacks, such as difficulty in reproducible preparation or high cost due to the use of sophisticated lithographic steps. The development of reproducible, cost-effective and easily prepared mesoporous films is still under intense investigation.

Previously, our group fabricated Au/Ag nanochain-built netlike porous films on ITO substrate [11] and Au/Ag nanoparticles-decorated ZnO nanorod arrays [12] based on electrophoretic deposition in the colloidal solutions formed by laser ablation in water. We found that the colloidal nanoparticles of Au and Ag formed under certain experimental conditions may perform co-electrophoresis. Generally, co-electrophoresis deposition is difficult to occur due to the extreme conditions toward different colloidal solutions [13], such as identical zeta potentials and good stability during electrophoresis. Laser ablation in liquids, by which various colloidal solutions can be obtained, can well meet these demands. Here a novel strategy is presented to fabricate Au nanoparticle-built mesoporous films based on co-electrophoresis deposition (C-EPD) in the mixed colloidal solutions of Au and Ag prepared by laser ablation in liquid, and selective etching of the Ag nanoparticles which act as a sacrificial metal, as illustrated in Scheme 1. To our knowledge, this is the first report on fabricating mesoporous films using the strategy of C-EPD and selective etching. Such film is homogeneous in the macroscale but rough and porous in the nanoscale. It exhibits excellent SERS performance due to its unique structure.

2. Experimental section

2.1. Preparation of Au and Ag colloidal solutions

Colloidal solutions were prepared by laser ablation of metal targets in an aqueous solution of 20 mM sodium dodecyl sulfate, $C_{12}H_{25}SO_4Na$ (SDS). Briefly, the targets in 20 mL such solution was irradiated for 20 min by a Nd:YAG pulsed laser (wavelength 1064 nm, frequency 10 Hz, pulse duration 10 ns) with a power of 90 mJ/pulse, vigorously stirring with a magnetic stirrer.

2.2. Co-electrophoresis deposition and selective etching

Two cleaned ITO substrates were used as cathode and anode electrodes, with a distance of 3 cm. C-EPD was performed at a DC voltage of 30 V for 30 min. After C-EPD, the ITO covered with products was immersed into a 70% HNO_3 aqueous solution for 5 min to etch

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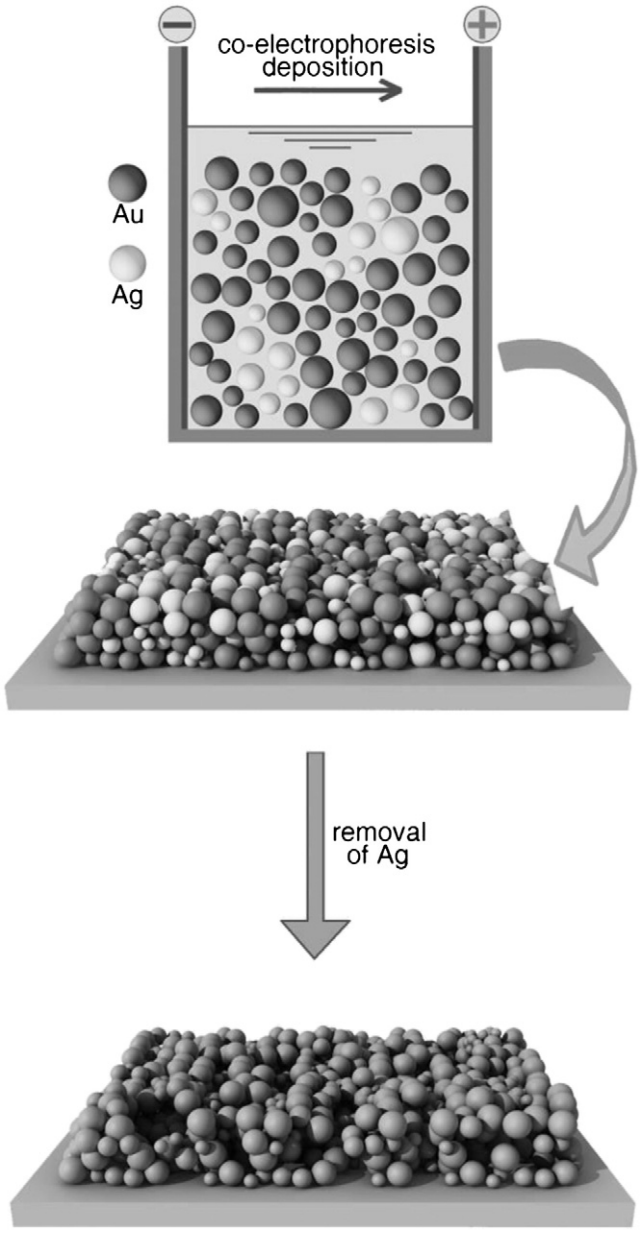

Scheme 1. Schematic illustration of the strategy for fabrication of mesoporous Au spherical nanoparticle films.

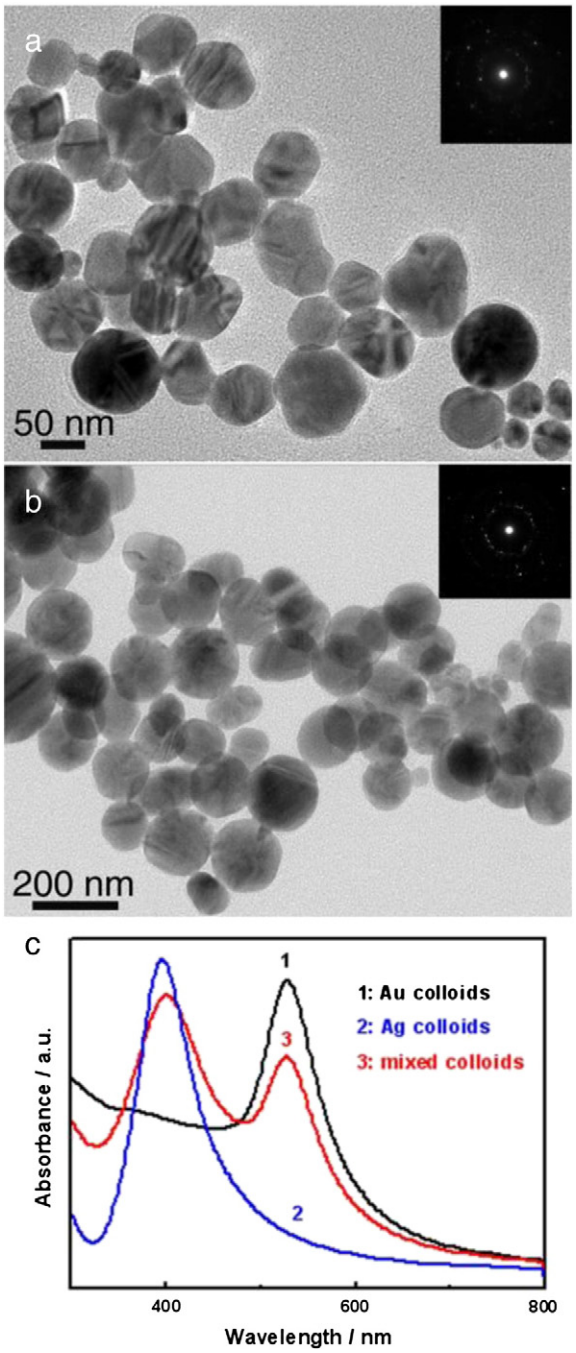

Fig. 1. Morphologies and optical property of colloidal solutions. (a, b) TEM images of the colloidal nanoparticles from ablation of Au and Ag targets in SDS aqueous solution, respectively. Insets: the corresponding SAED patterns. (c) Optical absorption spectra of their mixture.

away the Ag nanoparticles and rinsed softly by deionized water to remove the residual SDS.

2.3. Characterization

The samples were examined by scanning electron microscope (SEM, Sirion 200) and transmission electronic microscope (TEM, JEM-200CX). XRD measurement was conducted on a Philips X'Pert with Cu Kα radiation. Optical absorption spectra were recorded on a spectrophotometer (Cary 5E UV/vis-NIR). Zeta potential was measured by using a Zetasizer 3000 (England, MALVERN). For SERS spectral examination, the samples were immersed in rhodamine 6G (R6G) aqueous solutions with different concentrations for 30 min. Raman spectral measurements were performed on a French LABRAM-HR confocal laser microRaman spectrometer with a laser at 514.5 nm and a beam spot of 10 μm.

3. Results and discussion

Fig. 1a and b presents the TEM images of the colloidal nanoparticles formed by laser ablation of Au and Ag targets, respectively. Nanoparticles in both colloidal solutions are nearly spherical with sizes in the range of 20–100 nm. The SAED patterns show that these nanoparticles are crystallites with fcc structure. Optical absorption spectra of both colloidal solutions as well as their mixture only exhibit the dipole resonance absorption peaks of Au and Ag nanoparticles, around 528 and 400 nm respectively, as illustrated in Fig. 1c, suggesting that the nanoparticles are well dispersed without agglomeration. This is attributed to the used surfactant SDS surrounding each nanoparticle