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Controlled synthesis of one-dimensional Au−Ag porous nanostructures

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Abstract: The fabrication of a new type of one-dimensional Au−Ag porous nanotube (NPT) structure was presented based on a facile combination of nanocrystal growth and surface modification. Ag nanowires with various diameters were firstly served as the chemical plating templates via a polyol-process. Then, one-dimensional (1D) Au−Ag porous nanostructures with tailored structural features could be prepared by controlling the individual steps involved in this process, such as nanowire growth, surface modification, thermal diffusion, and dealloying. Structural characterizations reveal these Au−Ag porous nanotubes, non-porous nanotubes and porous nanowires possess novel nano-architectures with multimodal open porosity and excellent structural continuity and integrity, which make them particularly desirable as novel 1D nanocarriers for biomedical, drug delivery and sensing applications.
Key words: one-dimension; Ag alloy; thermal diffusion; dealloying; porous nanostructure; nanotube

1 Introduction

One-dimensional (1D) nanostructures as a kind of important nanomaterials [1−5], have stimulated great and increasing interest due to their various potential applications, such as catalysis, optics, biomedicine, surface enhanced Raman scattering (SERS), and sensors [6−12]. A number of synthesis methods have been developed for the construction of 1D nanostructures (nanorods, nanowires and nanotubes), such as chemical vapor deposition (CVD) [13], lithography [14], template-directed synthesis [15], solvothermal synthesis [16], and surfactant assisted chemical synthesis [17].

Among these techniques, template-based synthesis is considered a facile and effective method to synthesize 1D noble metal nanomaterials [18−22]. For example, Ag nanowires can also be used as chemical templates to synthesize nanowires of other metals, such as, Au/Ag, Pd/Ag, and Pt/Ag alloys, through galvanic replacement reactions between the Ag nanowires with appropriate precursors [23]. In our previous study, Ag nanowires were served as "physical templates" followed a dealloying process to fabricate Au porous nanotubes (Au−PNTs) [24]. Later, we systematically investigated the effects of the reaction parameters on the growth of Au−Ag nanostructures, such as reaction temperature, species, concentration and molar ratios of precursors.

Herein, we present a detailed investigation on the controlled synthesis of 1D Au−Ag porous nanotubes (PNTs). The preparation and structural modulation process of 1D nanotubular structures is clearly shown in Scheme 1. Ag nanowires are used as "seeds"/templates to fabricate alloy composite nanowires. Then, with the modulation of various parameters, alloy nanotubes with smooth exterior and interior surfaces, gradient porous nanotubes with thicker exterior inert metal layer, 3D porous nanotubes, 3D porous nanowires (F) are readily produced. Au−Ag PNTs maintain the original 1D structure and dimension of the Ag nanowires and their walls are composed of interweaved ligaments and pores. Resemble to the nanoporous gold (NPG) structure prepared from dealloying bulk Au/Ag alloys [25], the PNTs show a bicontinuous structure and the ligaments

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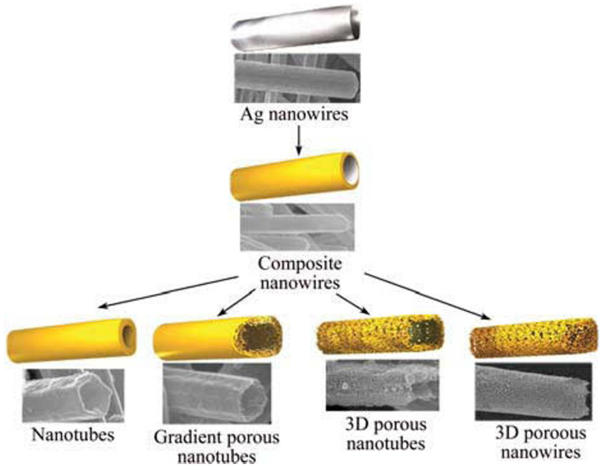

Scheme 1 Schematic illustration of preparation process of 1D hierarchical nanotubes

are not made of nanoparticles but rather adopt a locally single crystalline structure with continuous lattice spanning from one ligament to the other. Based on their high surface area-to-volume ratio, PNTs can be exploited as an excellent candidate platform for the applications in optics, catalysis, sensing and electronics.

2 Experimental

2.1 Materials

$AgNO_3$ (AR), ethylene glycol (EG, AR), $HAuCl_4·4H_2O$ (AR), ascorbic acid (AR), cetyltrimethyl-ammonium bromide (CTAB; AR), concentrated nitric acid (HNO_3; 67%, AR), C_2H_5OH (AR) and NaOH (AR) were purchased from Shanghai Sinopharm Chemical Reagent Co., Ltd., China Polyvinylpyrrolidone (PVP, 55000) was purchased from Sigma-Aldrich. All chemicals were used without further purification.

2.2 Synthesis of Ag nanowires

Ag nanowires were synthesized via a modified polyol process in our previous study [24]. In a typical experiment, 10 mL of ethylene glycol (EG) was first placed in a three-neck flask, and heated at 160 °C for 15 min. Then, 6 mL of an EG solution of $AgNO_3$ (0.5 mol/L) and 6 mL of an EG solution of PVP (0.75 mol/L) were simultaneously added through a two-channel syringe pump at a rate of 0.375 mL/min to the flask, and kept in the oil bath for another 4 h. The final products (Ag nanowires) were thoroughly washed with ethanol several times, then collected by centrifugation, and finally re-dispersed in ultrapure water for further use.

2.3 Fabrication of Au−Ag alloy composite nanowires

In a typical synthesis process, 1 mL solution of the as-prepared Ag wires (0.02 mol/L) was dispersed in 17 mL mixed water solution containing 25 mmol/L CTAB and 6 mmol/L ascorbic acid (AA for short) under magnetic stirring, and heated at 40 °C for 10 min. Then 2 or 4 mL of 1 mmol/L $HAuCl_4$ solution was added to the vial. The solution was kept stirring for another 40 min until the solution color became stable. The samples were washed with ultrapure water and centrifuged to remove excess Cl^-, CTAB and ascorbic acid.

2.4 Preparation of hierarchical Au−Ag porous nanotubes

In a typical synthesis process, the Au−Ag composite nanowire samples were re-dispersed in 10 mL of ultrapure water, then transferred to a 20 mL autoclave, sealed and maintained at 400 °C for 2 h. After the thermal treatment, the products were etched with specific amount of concentrated HNO_3 for 15 min, and finally washed with ultrapure water and $NH_3·H_2O$ before characterization. For example, the 3D Au−Ag porous nanotubes can be synthesized by using Au−Ag composite nanowires fabricated from 2 mL of $HAuCl_4$ as raw materials, followed with a thermal treatment at 450 °C and a dealloying process. Various kinds of hierarchical Au−Ag porous nanotubes could be obtained by tuning the amount of $HAuCl_4$ and the thermal treatment temperature. Detailed results were described in the results and discussion.

2.5 Characterizations

Scanning electron microscopy (SEM) images were taken using a JEOL JSM−6700F field-emission scanning electron microscope operated at an accelerating voltage of 10 kV. Composition measurements were conducted with an Oxford INCA x-sight energy dispersive X-ray spectrometer (EDS) attached to the same microscope. Transmission electron microscopy (TEM) images and selected-area electron diffraction (SAED) patterns were taken using a JEOL JEM−2100 high-resolution transmission electron microscope (HRTEM) operated at an accelerating voltage of 200 kV. The UV-vis spectra were recorded using a Shimadzu UV−1700 UV-vis spectrophotometer.

3 Results and discussion

3.1 Synthesis of Ag nanowires

By adjusting both the concentrations and ratio of Ag precursor salt and PVP, Ag nanowires were synthesized with a series of diameters from 50 to 500 nm (Fig. 1). It was reported that at the initial stage of the process, small Ag seeds formed with the slow injection of new precursor, and heterogeneous nucleation occurred by enclosing a mixture of {111} and {100} facets to lower the total interfacial free energy. And Ag nanowires (or

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