

Template-directed synthesis of Ag nanowire arrays by a simple paired cell method for SERS*

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The silver (Ag) nanowire arrays with regular and uniform size were successfully fabricated inside the nanochannels of anodic aluminum oxide (AAO) template by a simple paired cell method. X-ray diffraction (XRD) and scanning electron microscopy (SEM) results indicate that the as-synthesized samples are composed of face-centered cubic structure, and the average diameter is about 60–70 nm. Transmission electron microscopy (TEM) and the corresponding fast Fourier transformation (FFT) results show that Ag nanowires have a preferred single-crystal structure. Ultraviolet-visible (UV-vis) spectrum of Ag nanowire arrays exhibits UV emission band at 383 nm which can be attributed to the transverse dipole resonance of Ag nanowire arrays. A good surface-enhanced Raman scattering (SERS) spectrum is observed by excitation with a 514.5 nm laser, and the intensity of the SERS peak is about 23 times higher than that of the normal Raman peak measured from an empty AAO template. The high enhancement factor suggests that this method can be used to fabricate SERS sensor with high efficiency.

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One-dimensional (1D) metal silver (Ag) nanomaterials, such as nanorods, nanotubes and nanowires, have attracted considerable attention due to their novel properties and potential applications^[1-4]. Besides, the surface plasmon of Ag nanoparticles is excited by laser irradiation, and the Raman signal of the molecules adsorbed on the surface of the Ag nanoparticles can be enhanced to extreme levels. This phenomenon is known as surface-enhanced Raman scattering (SERS)^[5]. SERS is emerging as a probing technique for biosensors due to its high sensitivity^[6-11].

Ag nanowires for SERS have been prepared by using various methods^[12-16]. However, it is still a challenge to develop a versatile and cost-effective approach to prepare regular and uniform size 1D metal nanomaterials.

Anodic aluminum oxide (AAO) templates have been widely used in the production of nanostructures due to their relatively uniform pore distribution, as well as their thermal and chemical stability^[17,18]. In this paper, we develop a new method to fabricate an SERS substrate whose Ag nanowire arrays are patterned and nearly joined together. Ag nanowires were synthesized in AAO template by using a simple paired cell method. The surface shows a very high SERS enhancement. The growth mechanism is also discussed.

AAO template was prepared by a two-step anodization

process. The high pure aluminum foil with size of 2 cm×2 cm×0.5 mm was annealed at 500 °C for 5 h, and ultrasonically cleaned for 3 min in acetone, ethanol and deionized water, respectively. The native oxide layer was removed into 2 mol/L NaOH solution at 60 °C for 2 min. Then the aluminum foil was anodized in 0.3 mol/L oxalic acid aqueous solution under a constant voltage (40 V) and a constant temperature (5 °C). After anodization for 4 h, the formed alumina was removed by a mixture solution of phosphoric and chromic acids. Afterwards the foil was anodized for 5 h again in the same condition as the first anodization. The remaining aluminum layers at the bottom of the alumina membranes were removed into a saturated CuCl₂ solution. Finally, a transparent alumina template with through hole was obtained by a subsequent etching treatment in phosphoric acid with mass percent of 5%.

In our experiment, a home-made paired cell as shown in Fig.1 is used to prepare metallic Ag nanowires. The preparation process has been addressed in our previous paper^[19]. Briefly, silver nitrate solution (0.02 mol/L) was poured into one side of template, and sodium borohydride (0.02 mol/L) was poured into the other side. The silver ion and sodium borohydride were transported into the nanochannels of the anodic alumina membranes by diffusing, and reacted to form nucleus. In this case, the

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nanochannel of the AAO template acted as a micro-cell inside which the Ag nanowire grew through chemical reduction reaction. To obtain dense nanowires, the reaction ought to last long enough. After 20 h, the template fully embedded with Ag nanowire was taken out, rinsed for several times with deionized water, and dried in air for 1 h.

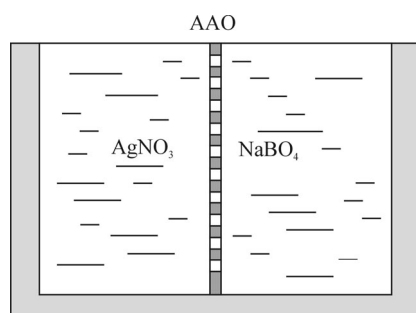


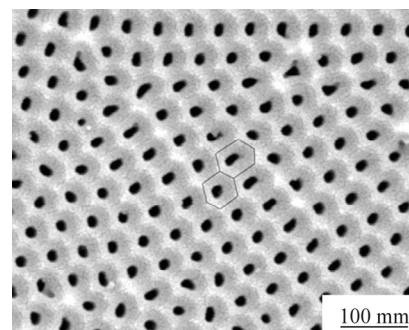
Fig.1 Schematic diagram of the home-made paired cell used in the experiment

The morphologies and compositions of the samples were observed by scanning electron microscope (SEM, Quanta 200 FEG) and X-ray diffraction (XRD) (Japan Mac science). A transmission electron microscopy (TEM) pretreatment process was conducted in 2 mol/L NaOH solution (60 °C) for 5 h to dissolve the alumina template completely. Then, the sample was separated by centrifugal effects and dispersed in 3–5 mL ethanol. Finally, a drop of the sample solution was dripped on a Cu grid for TEM observation. The Ag/AAO sample was dipped into a 20.0 mL ethanol solution of 1.0×10^{-4} mol/L pyridine for 24 h, and then dried for Raman measurement after washing the surface with ethanol. Raman spectra were observed by using a micro-Raman system equipped with a home-made sample stage, monochromator (SPEX 500 M), and charge coupled device (CCD) camera cooled with liquid nitrogen (Roger Scientific 7346-001 Model). SERS and normal Raman spectra were observed by excitation with a 514.5 nm laser. The incident laser power on the sample was approximately 10 μ W, and the acquisition time was 1 s. The ultraviolet-visible (UV-vis) spectra were recorded with a model UV-3310 PC spectrophotometer (Hitachi, Tokyo, Japan).

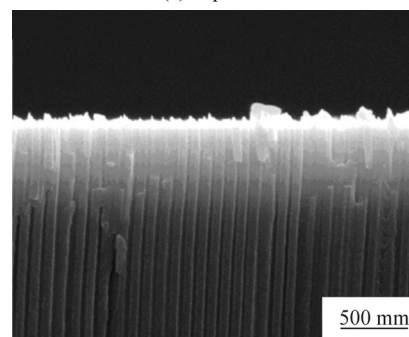
Fig.2 shows SEM images of the ordered AAO template. Fig.2(a) shows that the honeycomb-like template is highly ordered with circular holes and hexagonal structure cell. The pore diameter and pore density are approximately 60 nm and 1×10^{10} cm⁻², respectively. Fig.2(b) indicates that the pore channels are smooth and parallel to each other.

Fig.3(a) shows the cross-section SEM image of Ag/AAO sample. It can be seen that large-area Ag nanowires were successfully synthesized into the AAO channels. The length of nanowires ranges from 1 000 nm to 2 000 nm, and the diameter is about 70–80 nm. The inset of Fig.3(a) shows the energy dispersive spectrometry (EDS) analysis of nanowires, which indicates clearly

that the nanowire is composed of silver. Fig.3(b) shows XRD pattern of the sample. The diffraction peaks are indexed as (111), (200), and (311) planes of face-centered cubic Ag (JCPDS 04-0783, $a=0.409$ nm), respectively.



(a) Top view



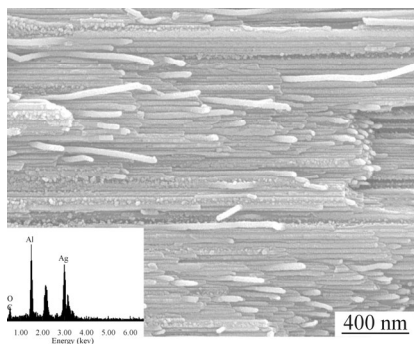
(b) Cross-section view

Fig.2 SEM images of the AAO template

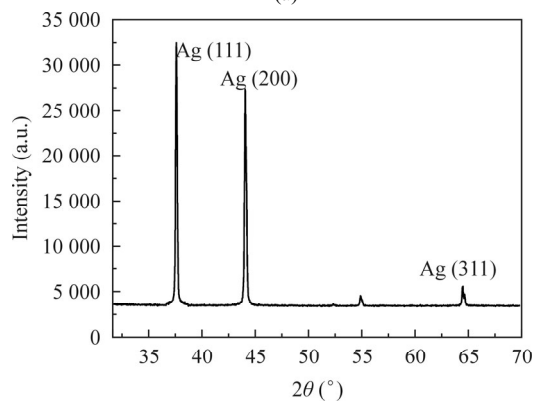
Fig.4(a) indicates that the Ag nanowire has a uniform diameter of 70 nm, which corresponds to the average diameter of the AAO template channels. The high resolution transmission electron microscopy (HRTEM) image of Ag nanowire and the corresponding fast Fourier transformation (FFT) patterns in Fig.4(b) indicate the single crystalline feature of Ag nanowire. Twin boundaries across the wire are seen clearly in Fig.4(b), which is the primary twinning system in fcc noble metals^[20].

Directly reducing metal ion with sodium borohydride for the growth of metal nanowire inside the nanochannel of the AAO template seems to be similar to a so-called three dimensional (3D) self-seeding nucleation-coalescence process^[21] with schematic representation shown in Fig.5. The confinement of the nanopore structure in the AAO template facilitates the formation of columnar nanowires in the nanopores. The metal ion and reductants are conversely transported into the nanochannels of AAO templates where they encounter and react with each other. In the initial stage of growth, the orientation of metal nuclei is random, and a newly coalesced compact deposit has perfectly random orientation. The texture of thicker metal deposits is a result of competitive growth between adjacent grains occurring in a stage of growth after the coalescence stage. Low-surface-energy grains grow faster than high-energy grains^[22]. The rapid growth of low-surface-energy at the expense of the high-energy grains results in an increase

in grain size. The distribution of grains in the nanochannel controls the morphological evolution of silver or nickel nanostructures. In region 1, the concentration of grains is high, and the nanowires are formed. In region 3, the concentration of grains is less than that in region 1, so the nanoparticles are formed. In region 2, only the nanotubes are formed for the lack of grains.



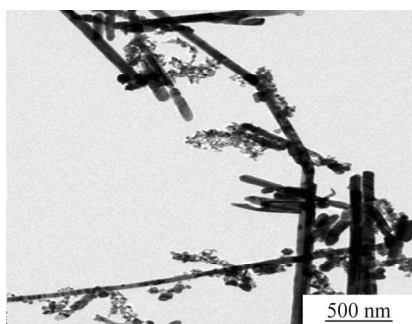
(a)



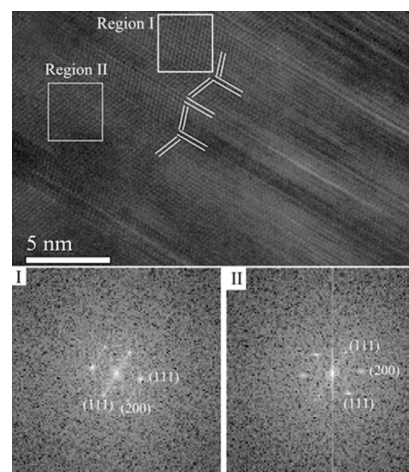
(b)

Fig.3 (a) SEM image (inset: EDS spectrum) and (b) XRD pattern of the Ag/AAO sample

Fig.6 shows that the AAO template has a very weak absorption at the wavelength longer than 350 nm, indicating that it is an excellent matrix for the fabrication of optical devices. The absorption spectrum of Ag/AAO sample displays a main peak at 414 nm with a shoulder at 383 nm, which can be assigned to the transverse dipole resonance and transverse quadrupole resonance, respectively, when unpolarized light beam is parallel to the major axis of Ag nanowire^[23].



(a)



(b)

Fig.4 (a) TEM image of an individual Ag nanowire; (b) HRTEM image of the Ag nanowire and the corresponding FFT patterns of regions I and II

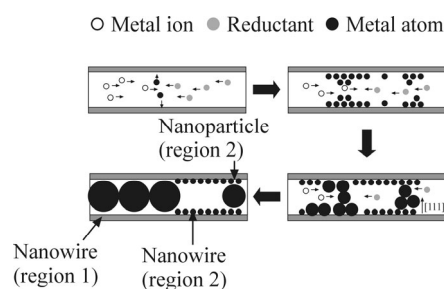


Fig.5 Schematic representation of the 3D self-seeding nucleation-coalescence process

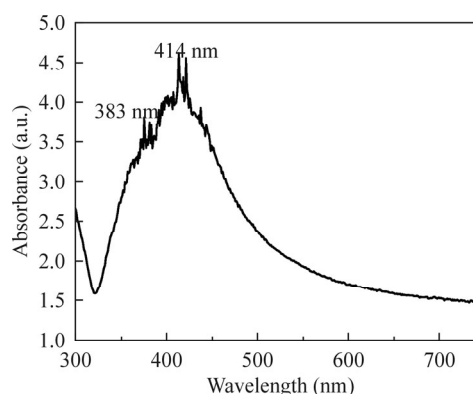


Fig.6 Optical absorption spectrum of Ag/AAO sample

The normal Raman and SERS spectra of pyridine adsorbed on the silver nanoparticles fabricated on the AAO template are shown in Fig.7. They were measured by the excitation with a 514.5 nm laser. The characteristic peaks at 1 192 cm^{-1} , 1 359 cm^{-1} , 1 505 cm^{-1} and 1 598 cm^{-1} are associated with C-C stretching vibrations, C-H in-plane bend, C-C-C ring in-plane bend and C-N stretching vibrations, respectively^[24]. The intensity of the SERS peak is 23 times larger than that of the normal Raman peak of empty AAO template.

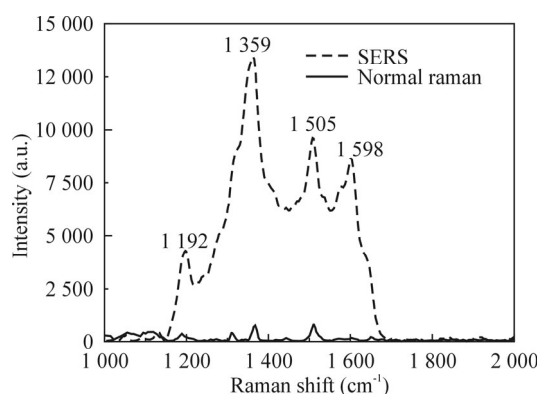


Fig.7 SERS and normal Raman spectra of pyridine adsorbed on the silver nanowires fabricated on the aluminum template

In summary, we fabricate high-density silver nanowire arrays by a simple paired cell method. The resulted silver nanowires are very homogeneous with regard to their diameter and are well ordered and almost perfectly aligned vertically with respect to the template. A good SERS spectrum is observed for the molecules adsorbed at the tip of the isolated silver nanowires. This technique will be very useful to fabricate the high efficiency SERS substrates.

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