Gold-silver bimetallic porous nanowires for surface-enhanced Raman scattering

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Electronic Supplementary Information

Experimental Section

Silver nitrate (AgNO₃), ethylene glycol (EG), sodium chloride (NaCl), and gold chloroauric acid (HAuCl₄) were purchased from Fisher Scientific. Poly(vinyl pyrrolidone) (PVP, Mw = 1,300,000) was purchased from Alfa Aesar, and the water (18.0 MΩ⋅cm) was supplied by Nanopure System. All of the chemicals were used without further purification.

A polyol process was adopted to synthesize silver nanowires, and the experimental procedures and/or conditions were similar to those reported by Xia and coworkers. Prior to the synthesis, 0.60 g of PVP was dissolved in 30 mL of EG and then heated to 160 °C for 1 h. A AgNO₃ solution was prepared by dissolving 0.31 g of AgNO₃ into 15 mL of EG through general stirring without sonication. The AgNO₃ solution was subsequently added to the PVP solution using a titration method. The reaction was allowed to proceed for 1 h until a gray-silhouette mixture was formed. The resulting Ag NWs were then washed for several times using a repeating centrifugation and re-dissolution method to remove PVP. Thereafter, the silver nanowires were kept in methanol for further use.

Bimetallic gold/silver porous nanowires were synthesized through galvanic replacement reactions on silver nanowires at room temperature, as illustrated in Figure 1. To facilitate the characterization of individual nanowires, appropriate amounts of Ag NWs were spin-casted onto clean glass/silicon substrates and then galvanic replacement reactions were conducted. For a typical galvanic reaction, a HAuCl₄ solution (typically 4.8 mM) was dropped onto the substrate; and the reaction occurred at room temperature. After 20 s, the substrates were washed thoroughly with Nanopure water to terminate the reaction. The resulting bimetallic Au/Ag nanowires were further characterized to confirm their structure, composition, and properties.

Transmission electron microscopy (TEM) was conducted on a FEI Tecnai electron microscope with an acceleration voltage of 120 kV. To prepare the samples for TEM examination, bimetallic nanowires on glass substrates were transferred onto lacey-carbon coated copper girds by using a thin film of poly(methyl methacrylate) (PMMA) as a transfer media. Atomic force microscopy (AFM) was employed to observe the morphologies and sizes of the silver nanowires and bimetallic porous nanowires. AFM images were acquired in close-contact mode using a Nano-R² from Pacific Nanotechnology. Scanning electron microscopy (SEM) was used for the morphologies and compositions of the porous nanowires. SEM micrographs were obtained on a Zeiss Supra40VP variable-pressure field-emission SEM. During the SEM investigation, energy-dispersive X-ray spectroscopy (EDS) was utilized in the sample characterization and the EDS elemental maps were obtained for the composition analysis.
Rhodamine 6G (R6G) was selected as a molecular probe to study the localized SERS of bimetallic nanowires. Prior to the Raman testing, the glass substrates with gold/silver bimetallic nanowires were immersed in a R6G solution for 2 h followed by rinsing with Nanopure water and dried with nitrogen gas. In the experiment to compare the bimetallic nanowires with pristine silver nanowires, we made an additional deposition of silver nanowires onto the substrate before the R6G immersion process. All SERS spectra and confocal Raman images were collected on an Aramis confocal microscope (Horiba Jobin Yvon, Edison, NJ) equipped with a diode-pump solid state (DSPP) laser (532 nm). The laser, with an intensity of 0.15 mW, was focused using a 50× objective (NA 0.75) onto the samples on the glass slides, which were mounted onto a 200×200×200 μm piezo scanner. The SERS signals were collected with the same objective under a 180° back-scattering configuration and passed through an edge filter into a monochromator and electric-cooled charge-coupled devices (CCD) camera. To obtain a Raman map, an array of Raman spectra was collected when the laser was raster scanned across a selected area of the sample. The Raman spectra were acquired for 1 s at each pixel. The spectra were then mathematically processed, and the intensity distribution of the Raman peaks of interest can be revealed.

**EDS Analysis**

The SEM-EDS result of the nanowire at the red-circle location indicated the existence of silver, gold, chlorine, as well as the silicon and oxygen elements. The silicon and oxygen signals are attributed to the silicon substrate with a thin layer of silicon dioxide.

![EDS spectrum and mapping results](image)

**Fig. S1** – (a) EDS spectrum of typical bimetallic porous nanowire (b-d) EDS mapping results for gold, silver, and chlorine, respectively.
In the range of 2 to 4 keV, there are several peaks which are attributed to the characteristic M and L lines of gold and silver. The peak at 2.1 keV corresponds to the M$\alpha$ peak of gold; while the peaks at 2.9 and 3.1 keV correspond to the L$\alpha$ and L$\beta$ peaks of silver, respectively.$^2$ The intensities of the silver peaks are stronger than those of gold, indicating that the nanostructures are composed of more silver than gold. The observed ratio of Au/Ag was approximately 1/4 for that particular bimetallic nanowire. This ratio could be tailored by controlling the conditions of the galvanic reactions.

The small amount of chlorine could be in the form of silver chloride, which might be deposited on the porous nanowire due to its low solubility when the galvanic replacement reactions were conducted at room temperature. There have been several reports on the precipitation of silver chloride in the galvanic replacement reaction at room temperature and the formation of core-shell nanostructures.$^{3, 4}$ When the reaction temperature is increased, the solubility of silver chloride will increase and there will be no precipitation on the nano-templates.$^5$ Elemental mapping results in Figures S1b-d depict the distribution of gold, silver and chlorine elements in these nanostructures. From the maps, it was evident that all of those elements were distributed uniformly throughout the nanowire. Together with the electron microscopic results discussed below, it is believed that the porous bimetallic nanowires were fabricated through a simple galvanic replacement reaction.

**TEM Characterization**

Structures and morphologies of the bimetallic porous nanowires were then studied with transmission electron microscopy (TEM). The TEM micrographs in Figure S2 show the morphologies of silver nanowires and their products after the galvanic replacement reactions for 10 s and 20 s, respectively.

![Fig. S2](image)

The pristine Ag NWs (shown in Figure S2a) were straight and solid with an average diameter of ~120 nm, as obtained by a Gaussian fit of the TEM data. These Ag NWs were thoroughly washed to remove the capping polymer of PVP; therefore, we did not observe any amorphous polymer on the surface of Ag NWs. We believe that the cleaning procedure can facilitate the galvanic relation on the silver nanowires. Another important parameter for the galvanic replacement reaction is the reaction time, which can significantly affect the morphology and structure of the final products. Figure S2b and S2c show the TEM micrographs of typical porous nanowires prepared from the galvanic reaction for 10 s and 20 s, respectively. Gold nanoparticles with diameters of tens of nanometers can be observed on the surface of the nanowires (Figure S2b). The modified Ag NWs exhibited a certain degree of hollow structure, which was due to the dissolution of silver metals from the inside of the nanowires. The appearance of tubular structures is consistent with the characteristic of the galvanic replacement reactions as reported before.$^5$
In addition to the change of morphology, the size of the nanowires can also vary during the galvanic replacement reaction. With increasing reaction time, the bimetallic nanowires became more porous, and more protrusions could be observed in the TEM micrograph, as shown in Figure S2c. We found that the diameters of the nanowires also increased with increase of reaction time. The average diameter of the porous nanowires after reaction for 10 s and 20 s was 230 nm and 350 nm, respectively. The increase of nanowire diameter is due to the additional formation of nanometer-sized gold particles on the surface of the bimetallic nanowires. It is noteworthy that many porous nanowires showed the deposition of gold nanoparticles only on one-side of the wire. The formation of such structures was presumably because of our experimental procedures; i.e., the silver nanowires were first deposited (immobilized) onto glass substrates and then immersed in the HAuCl₄ solution. The side (of nanowires) that attached to the glass substrate could be spatially difficult to access, resulting in less deposition of the gold nanoparticles.

References