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RESEARCH ARTICLE

Surface-enhanced Raman scattering of sulfate ion based on Ag/Si nanostructure

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Abstract Silicon nanowires (SiNWs) with tens of micrometer in length have been synthesized and modified with Ag nanoparticles, which were confirmed by X-ray diffractometer (XRD), scanning electron microscopy and transmission electron microscopy. The Ag/Si nanostructure was employed to detect inorganic ions SO_4^{2-} via surface-enhanced Raman scattering (SERS) with strong signals at low concentrations of 1×10^{-9} mol/L. This ultrasensitive method might be applied in other fields.

Keywords surface-enhanced Raman scattering (SERS), silicon nanowires (SiNWs), Ag nanoparticles, sulfate ions

1 Introduction

One-dimensional (1D) materials have drawn considerable attention due to their potential applications in various fields [1,2]. Nanowires are a bright member in the various nanostructures for their excellent properties such as high aspect ratios, fine flexibility, ease of combination [3,4], which are perfect for nano-devices and nanosensors. They can also be employed as substrate to create complex objects [4,5] and nanowire-based structures that also offer novel approaches and applications for detection of biomaterials and chemicals [6,7].

Silicon nanowires (SiNWs) are important materials [8,9], which are especially expected to exhibit potential useful electrical, optical, mechanical, and chemical properties, and have been used to fabricate field-effect transistors [10,11], *p*-*n* junctions, bipolar transistors, and complementary inverters [2], chemical and biomaterial sensors [10,12–15].

Raman spectroscopy is one of the most powerful methods in analysis because it can provide rich structural information as well as quantitative and qualitative information from sharp Raman bands in a nondestructive manner. However, conventional Raman signals are too weak for highly sensitive analysis. Surface-enhanced Raman scattering (SERS) can readily increase Raman signals [16–24], which pushes molecule detection up to an ultrahigh sensitive level. However, as inorganic ions have small Raman scattering cross sections, it is difficult to get enough strong signals at low concentrations.

Here, inorganic ion sensor based on SiNWs has been demonstrated, which enabled a low detecting limit of 1×10^{-9} mol/L for SO_4^{2-} using a Raman microspectrometer. To our knowledge, these are the lowest detecting limits for these inorganic ions.

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2 Experiments

2.1 Materials

All the chemical regents were analytical grade and used without further purification.

2.2 Preparation

In the preparation of SiNWs, 10 g SiO powder (Aldrich, 325mesh, 99.9%), 0.05 g Sn powder (Fluka, powder, 99%) were mixed in an alumina boat, which was then placed at the center of a horizontal alumina tube mounted inside a high-temperature tube furnace. The system was evacuated to a pressure of 1×10^{-2} Torr. A carrier gas of Ar was introduced and maintained at a pressure of 10 Torr with a constant flow rate of 150 sccm. The furnace was heated to 1350°C at 40°C·min^{-1} and was kept at this temperature for 1 h. Then temperature was decreased to 1250°C at 1°C·min^{-1} and kept for 10 h. The products grown on the

inside surface of alumina tube were collected.

SiNWs (0.05 g) were immersed into 5% hydrofluoric acid (HF) aqueous solution for 5 min to remove outer oxide layer and obtained hydrogen-terminated ones, then rinsed with deionized water and immersed in a 1×10^{-3} mol/L $AgNO_3$ aqueous solution, which was reduced with the hydrogen-terminated SiNWs and gained Ag/Si nanostructure.

Aqueous solutions of sodium sulfate were prepared with deionized water for Raman measurement.

2.3 Characterization

Shimadzu 6000 X-ray diffractometer (XRD) was equipped with Cu $K\alpha$ radiation ($\lambda = 0.15406$ nm), and a scanning rate of $0.02° \cdot s^{-1}$ was applied to record the patterns in the 2θ range of $10° - 80°$. The morphology of as-prepared products was analyzed with field emitting scanning electron microscope (FESEM) (Hitachi S-4800). The transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM, JEOL-2010) images were performed with an accelerating voltage of 200 kV.

SERS spectra were recorded with a Labram-HR confocal laser micro-Raman spectrometer equipped with an argon ion laser with excitation of 514.5 nm. An air-cooled charge-coupled device (CCD) was used as a detector, the accumulation time was 1 s and the incident power was 3 mW. Solid surface reflectance spectra were recorded by a Perkin Elmer Lambda 750 UV-vis spectrophotometer.

3 Results and discussion

Figure 1(a) is the XRD pattern of the as-prepared SiNWs. All the intense peaks may be indexed to cubic lattices with a cell constant of $a = 0.5427 \pm 0.0006$ nm, which is in agreement with the reported value, $a = 0.5430$ nm, of diamond-cubic silicon (JCPDS No. 27-1402). There is also a small and wide peak around $2\theta = 22°$ due to amorphous silicon oxide on the surface of SiNWs.

Figure 1(b) shows the XRD pattern of SiNWs treated with HF and $AgNO_3$ aqueous solutions successively. The amorphous peak disappears which means that the outer oxide layer was removed. Besides the silicon peaks, others can be indexed as cubic lattices with a cell constant of $a = 0.4074 \pm 0.0005$ nm, which is in agreement with the reported value, $a = 0.4086$ nm, of cubic Ag (JCPDS No. 04-0783).

Scanning electron microscope (SEM) image (Fig.2(a)) reveals that the sample is a wire shape with tens of micrometer in length. These wires are smooth and uniform with the average diameter of 30 nm.

Figure 2(b) presents a TEM image of one single wire with the average diameter of 30 nm modified with Ag

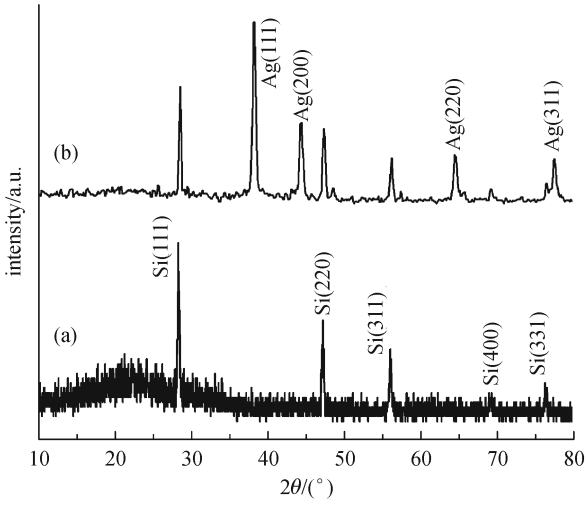

Fig. 1 XRD patterns of as-prepared products (a) and (b) products treated with HF and $AgNO_3$ solutions successively

nanoparticles, which are densely grown on the surface of SiNW, taking an average diameter of 9 nm. Result of HRTEM (Fig. 2(c)) reveals the lattice fringe of Si and Ag nanoparticles, both showing (111) crystal planes.

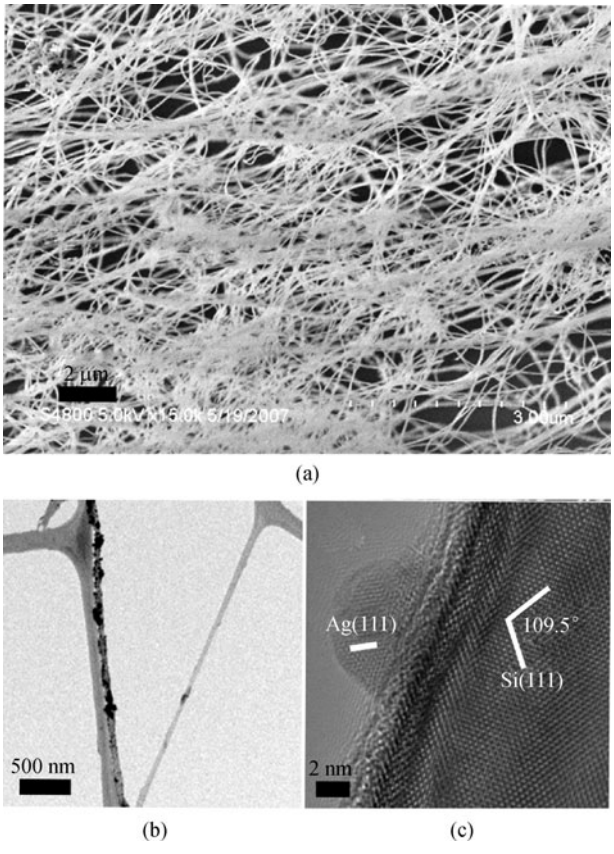

Fig. 2 (a) SEM image shows as-prepared SiNWs in larger scale; (b) TEM image of a single Ag-modified SiNW with the average diameter of 30 nm; (c) HRTEM image showing Si(111) and Ag(111) crystal planes

All of the above characterization are consistent with each other and adequately prove that the SiNWs have been modified with Ag nanoparticales.

Inorganic ion SO_4^{2-} was selected as a model to demonstrate the performance of this Ag/Si heterostructure for SERS, because it is commonly used in various fields.

When sodium sulfate solution (25 μL) was added onto the Ag/Si heterostructure, the SERS was collected as shown in Fig. 3. When the concentration of sodium sulfate solution is 1×10^{-9} mol/L, there are three groups of Raman peaks, sited in 620–650, 996 and 1100–1170 cm^{-1}, which are related to S–O asymmetric stretching vibration, S–O symmetric vibration and O–S–O asymmetric stretching vibration, respectively. When the sodium sulfate solution was diluted to 1×10^{-10} mol/L, there is only one Raman peak at 996 cm^{-1}. Therefore, the detecting limit of sulfate is determined as 1×10^{-9} mol/L, which is much lower than the reported value of 4.6×10^{-3} mol/L [25].

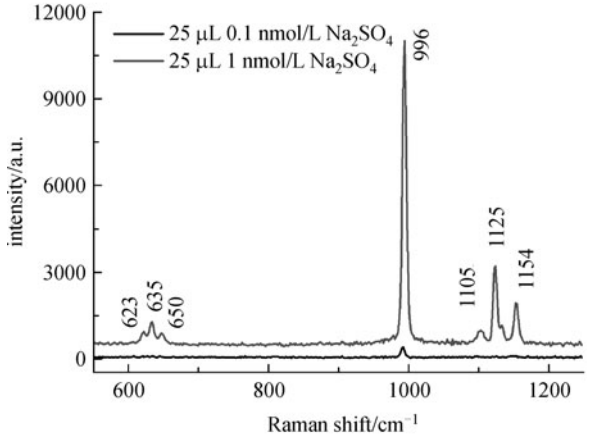

Fig. 3 SERS spectra of sodium sulfate solution (25 μL) using Ag-modified SiNWs as substrate at concentration of 1.0×10^{-9} and 1.0×10^{-10} mol/L, respectively

SERS is a powerful technique for the detection of molecule attached to nanometer sized metallic structures. It is generally believed that more than one factor contribute to the observed large effective SERS cross section, such as electromagnetic effect and chemical effect. The electromagnetic effect is usually a few orders of magnitude more than that of the chemical effect. In our study, Ag nanoparticles have narrow distribution in size and uniformly locate on the surface of SiNWs. All these might have contributions to the enhanced Raman signals.

Further the Raman enhancement mechanisms of the present SERS substrate were investigated using extinction spectrum. Solid surface extinction spectra of different substrates are shown in Fig. 4. It shows that the absorption of SiNWs gradually decreases toward the long wavelength from 240 to 850 nm (Fig. 4(a)), because SiNWs have a large surface area and a huge amount of surface electrons. The extinction spectrum of Ag modified SiNWs (Fig. 4(b)) shows a broad peak centered at 400 nm associated with Ag nanoparticles. In our substrate, the Ag nanoparticles are distributed on SiNWs, and the dipoles induced by plasmon resonance would couple and transmit on the whole surface. Consequently, the plasmon resonance absorption of our substrate is broad and strong.

Other reason for the excellent SERS on Ag-modified SiNWs is that the Ag nanoparticles were grown epitaxially on the SiNW. Both Si and Ag are face-centered cubic in structure, and their cell parameters are 0.5430 and 0.4086 nm with the approximate ratio of 4∶3. Figure 5 is a clear HRTEM image of Ag nanoparticle on a SiNW, it can be

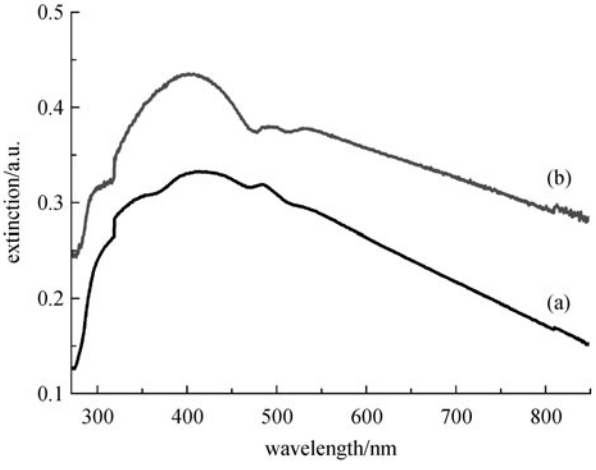

Fig. 4 Solid surface reflectance spectra of (a) SiNWs and (b) Ag-modified SiNWs

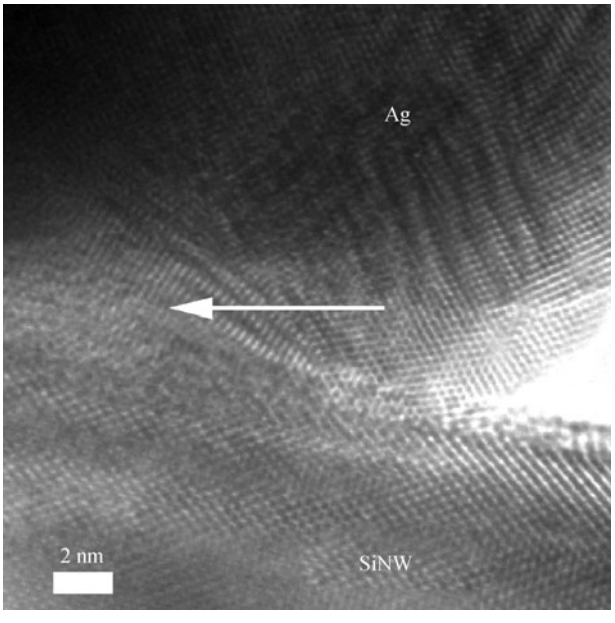

Fig. 5 HRTEM reveals Ag nanoparticle epitaxially grown on SiNW (marked with an arrow)

observed that Ag nanoparticle was epitaxially grown on the SiNW (marked with an arrow). The structure may prevent the Ag nanoparticles from coalescence under the laser irradiation in Raman detection and resulted in the high SERS effect.

4 Conclusions

In summary, this study presents an initial fabrication step of Ag-modified SiNW sensor with the capability of detecting inorganic ions with low detecting limit using SERS technology, which exhibited intense Raman signals with detecting limits down to 1×10^{-9} mol/L for SO_4^{2-} ions. Our findings might offer a unique experimental technique to develop a sensor capable of monitoring ionic pollutants continuously, in real-time, and *in situ*.

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