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Fabrication and SERS properties of Ag/Cu₂S composite micro–nanostructures over Cu foil

Wei Song, Jinjie Wang, Zhu Mao, Weiqing Xu, Bing Zhao*

State Key Laboratory of Supramolecular Structure and Materials, Jilin University, Qianjin Street 2699, Changchun 130012, PR China

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1. Introduction

In the past few years, various metallic or semiconductorial nanoparticles with controllable size, shape and composition have been widely developed and applicable in many kinds of fields such as catalysis, size quantum effects, luminescence, third-order nonlinearity, surface enhanced Raman scattering (SERS), biomedical engineering, and so on [1-8]. Among these, SERS have attracted more and more attention to surface scientists for its simple and super-sensitive detection of adsorbed molecules on the chemical, physical, and biological surface and interfaces. Formerly, the SERS substrates were mainly based on various kinds of rough solid metal support or metallic colloids. Recently, semiconductors, such as ZnS, CdS, CuO, CdTe, ZnO, TiO₂, etc., have also been used as the SERS substrates [7,9-13], which could directly produce weak SERS signals with typical enhancement factor (EF) up to 10⁴. However, the SERS activities based on such semiconductors were much lower than that of metal nanoparticles, hampering their practical applications. Previous reports have announced that combination of metal nanoparticles with semiconductors is a meaningful approach to enhance the SERS activity of semiconductors. For example, Wang et al. fabricated Ag/TiO₂ composite particles with nanometer size by irradiation of an AgNO₃ solution with light of wavelength >330 nm in the presence of TiO₂ nanoparticles and observed the SERS effects [14]. We have fabricated a SERS active Ag/TiO₂ composite nanofibers, exhibiting a high EF of 4-mercaptopyridine (4-Mpy) adsorbed on their surface [15]. The improvement of SERS activ-

E-mail addresses: zhaob@mail.jlu.edu.cn, zhaobing@jlu.edu.cn (B. Zhao).

ABSTRACT

A new kind of Ag/Cu_2S composite micro/nanostructures has been prepared via a convenient galvanic reduction method. SEM images of these micro/nanostructures showed that Ag nanoparticles with the size of around 50–100 nm were well deposited on the surface of Cu_2S micro/nanostructures. The SEM images also indicated that the Ag nanoparticles were preferentially grown on the big polygonal Cu_2S microstructures, which could be explained by a localization of the electrons on the surface of the polygonal Cu_2S microstructures after the electron transfer step. Owing to the introduction of Ag nanoparticles on the surface of Cu_2S micro/nanostructures, the resulting Ag/Cu_2S composite micro-nanostructures could be used as a versatile substrate for surface enhanced Raman scattering.

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ity might be due to the long-range electromagnetic enhancement for the localized surface plasmonic resonance (LSPR) excited by Ag nanoparticles under the irradiation of a suitable laser. The similar phenomenon was also observed in the system of Ag/ZnO composite microspheres [16].

For the preparation of metal/semiconductor composite nanostructures, a simple and common method is in situ reduction of metallic salt on the surface of semiconductor nanostructures [15,16]. As the reaction is fast, the shape and size of the metal nanostructures are not well controlled. Recently, we have proposed that metal nanoparticles could be site-specific deposit on the tip of ZnO nanorod arrays through a simple galvanic reduction method [17]. By tuning the reaction time and the concentration of silver nitrate, the density of Ag nanoparticles on the tip of ZnO nanorods could be controlled. In this paper, we demonstrate that such method could also be applicable in the fabrication of metal/sulfide composite micro-nanostructures. Moreover, the resulted preferential deposition of silver nanoparticles on the big polygonal Cu₂S microstructures further proved the rich localization of the electrons on the top surface of semiconductors which generated by the galvanic reaction. The results also indicated that the Ag/Cu₂S composite micro-nanostructures could be used as a versatile substrate for SERS.

2. Experimental

2.1. Materials

Cu foil was obtained from Sinopharm Chemical Regent Co., Ltd. Ethylenediamine was obtained Tianjin Bodi Chemical Holding Co., Ltd. Sulphur powder was purchased from Shenyang No.

^{*} Corresponding author. Tel.: +86 431 85168473.

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Fig. 1. (a) SEM images of Cu₂S micro–nanostructures over copper foil. (b) SEM images of Ag/Cu₂S composite micro–nanostructures over copper foil. (c) Proposed deposition of Ag nanoparticles on the Cu₂S micro–nanostructures via a galvanic reduction.

5 Chemical Regent Factory. 4-mercaptopyridine (4-Mpy) and *p*aminothiophenol (PATP) were obtained from Sigma Chemical Company. AgNO₃ and ethanol were obtained from Shanghai Kefeng Chemical Regent Co., Ltd. and Beijing Chemical works, respectively.

2.2. Synthesis of Cu_2S micro-nanostructures over copper foil

The fabrication of Cu₂S micro–nanostructures was similar with the previous report [18]. A piece of Cu foil was washed with water and ethanol for several times and blew with N₂. After drying, it was put into a 40 mL Teflon-lined stainless steel autoclave. Followed, a 30 mL sulphur solution in ethylenediamine with a concentration of 10^{-3} M was introduced into the above Teflon-lined stainless steel autoclave. The autoclave was maintained at 130 °C for 12 h and subsequently cooled to room temperature. The resulted product was washed with water and ethanol carefully.

2.3. Deposition of Ag nanoparticles on Cu₂S micro–nanostructures via galvanic reduction route

The prepared Cu₂S micro–nanostructures over copper foil were carefully immersed into an AgNO₃ solution with certain concentration and reaction time. After that, the obtained Ag/Cu₂S composite micro–nanostructures were taken out from the AgNO₃ solution, and washed with deionized water for several times. Finally, the product was dried under nitrogen atmosphere at room temperature.

2.4. Materials characterizations

The shape and size of Ag nanoparticles on the Cu₂S micro-nanostructures over copper foil were characterized by

SEM measurements, which were performed on a JEOL JSM-6700F field emission scanning electron microscope (FE-SEM) operated at 3.0 kV. The X-ray diffraction (XRD) patterns of Ag nanoparticles on the Cu₂S micro-nanostructures over copper foil were recorded in a Seiemens D5005 diffractometer using Cu Ka radiation. Raman spectra of Ag nanoparticles on the Cu₂S micro-nanostructures over copper foil were obtained with a Renishaw Raman system model 1000 spectrometer. The 514.5 nm radiation from a 20 mW aircooled argon ion laser was used as an exciting source. The laser power at the sample position was typically 40 µW with an average spot size of $1 \,\mu m$ in diameter. Data acquisition involved the 30-s accumulations for 4-Mpy and PATP adsorbed on Ag nanoparticles on the Cu₂S micro-nanostructures over copper foil. To record the Raman spectrum of 4-Mpy and PATP adsorbed on Ag nanoparticles on the Cu₂S micro-nanostructures over copper foil, the substrate was immersed in 1 ml of a 4-Mpy and PATP ethanol solution for 20 min and rinsed with an ethanol solution three times.

3. Results and discussion

3.1. Morphologies and structure characterization of the obtained Ag/Cu₂S composite micro–nanostructures

Cu₂S is widely used as an excellent p-type semiconductor material applicable in solar cells, super ionic materials and optical filters [19,20]. In the present work, Cu₂S micro–nanostructures were prepared over copper foil through a solvothermal reaction using Cu foil and sulphur as sources. Fig. 1a showed representative SEM images of starting Cu₂S micro–nanostructures over copper foil. It was found that two main structures including big polygonal Cu₂S microstructures and small Cu₂S nanoparticles were observed. The



Fig. 2. XRD patterns of Cu_2S micro–nanostructures over Cu foil and Ag/Cu_2S micro–nanostructures.

size of the big polygonal Cu₂S microstructures is about several micrometers, while that of the small Cu₂S nanoparticles is in the range of 100-800 nm. Fig. 1b showed the deposition of Ag nanoparticles on the surface of Cu₂S micro-nanostructures. The deposition was conducted under a concentration of the silver salt of 10 mM and the reaction time was 30 s. As can be seen, Ag nanoparticles with the size of around 50-100 nm were well deposited on the surface of Cu₂S micro/nanostructures. Moreover, the SEM images indicated that the Ag nanoparticles were preferentially grown on the top surface of big polygonal Cu₂S microstructures, which could be explained by a localization of the electrons on the top surface of the polyhedral Cu₂S microstructures after the electron transfer step. The SEM images also showed that the density of Ag nanoparticles on the edge of the polyhedral Cu₂S microstructures is much higher than that of the facet of polyhedral Cu₂S microstructures, indicating that the electrons are apt to localize on the edge of the polyhedral Cu₂S microstructures. Fig. 1c illustrates a generalized process of the deposition of Ag nanoparticles on the surface of Cu₂S micro-nanostructures. In fact, this reaction is a similar galvanic reduction of Ag⁺ by more active copper foil into Ag nanoparticles. Electrons will be generated when copper was oxidized, then it will transfer into the surface of Cu₂S micro-nanostructures, where the silver ions are reduced by the electrons. Because the big polyhedral Cu₂S microstructures lie on the top of the Cu₂S nanoparticles, electrons tend to localize on that region, resulting in more Ag nanoparticles are grown on the top surface of Cu₂S microstructures.

The structure of the as-synthesized Ag/Cu₂S composite micro-nanostructures was supported by powder XRD measurement. Fig. 2 shows typical XRD patterns of the as-prepared Cu₂S micro-nanostructures and Ag/Cu₂S composite micro-nanostructures. In the XRD pattern of Cu₂S micro-nanostructures, all of the main peaks were similar with the previous reports, which could be indexed to the structures of Cu₂S and β -Cu₂S except the peaks of copper foil [18]. Even though the peak intensity of Ag nanoparticles are lower than the Cu₂S micro-nanostructures, this does not contradict the appearance of the peak of Ag (111), indicating that Ag nanoparticles were deposited on the surface of Ag/Cu₂S composite micro-nanostructures.



Fig. 3. SERS spectra of PATP with different concentrations adsorbed on ${\rm Ag}/{\rm Cu}_2{\rm S}$ composite micro-nanostructures.

3.2. SERS spectra of PATP and 4-Mpy on Ag/Cu₂S composite micro–nanostructures

In this article, we firstly choose PATP as probe molecules because it could be well adsorb on the surface of metal and sulfide nanostructures [21,22]. Fig. 3 (top line) shows the SERS spectrum of PATP (10^{-3} M) adsorbed on Ag/Cu₂S composite micro-nanostructures over copper foil. From it, two main peaks at 1576 and 1077 cm⁻¹ were observed. The 1576 cm^{-1} line is the C=C stretch, and the 1077 cm⁻¹ line is the C-S stretch for PATP molecules, respectively [23]. These two signals are attributed to the a_1 modes of the PATP molecules. Furthermore, the peaks at 1142, 1188, 1389, and 1436 cm⁻¹ are also observed. These lines are all ascribed to the b₂ symmetry of PATP molecules. The SERS enhancement of b₂ symmetry on Ag/Cu₂S composite micro-nanostructures is owing to the charge-transfer mechanism, which is in accordance with the Herzberg-Teller selection rule [24]. The SERS properties of PATP molecules with different concentrations on the surface of Ag/Cu₂S composite micro-nanostructures have also been studied (Fig. 3). As the concentration of PATP decreases, the SERS intensities of PATP decrease accordingly. However, the SERS signals could be still detected even the concentration of PATP molecules was decreased to 10⁻⁶ M.

Besides the PATP, 4-Mpy molecules are also used as probe to evaluate the SERS enhancement mechanism on the surface of Ag/Cu₂S composite micro-nanostructures. From Fig. 4, it is found that a strong peak at $1585\,\mathrm{cm}^{-1}$ and a weak shoulder peak at around 1609 cm⁻¹ are observed. These two peaks could be ascribed to the ring mode of 4-Mpy molecule with deprotonated and protonated nitrogen, respectively [25]. In order to investigate the SERS effect of 4-Mpy molecules on the surface of Cu₂S micro-nanostructures, the difference spectrum between the Raman spectra of 4-Mpy adsorbed on Ag/Cu₂S composite micro-nanostructures and Ag mirror is also shown in Fig. 4c. It is found that three additional obvious peaks at 1034, 1212 and $1589 \,\mathrm{cm}^{-1}$ appeared. The peak at $1034 \,\mathrm{cm}^{-1}$ is related to the pyridine ring C-H in-plane bending mode, while the band at 1212 cm⁻¹ is ascribed to CH/NH deformation mode of 4-Mpy. Obviously, these three peaks could be attributed to the SERS of 4-MPy molecules adsorbed on bare Cu₂S micro-nanostructures. Generally, most of the SERS peaks on Ag/Cu_2S composite micro-nanostructures should be attributed to the Ag nanoparticles with size between 50 and 100 nm. And the enhancement of the SERS signals of 4-Mpy at 1034, 1212 and 1589 cm^{-1} adsorbed on bare Cu₂S



Fig. 4. Raman spectra of 4-Mpy adsorbed on (a) Ag/Cu₂S composite micro-nanostructures, [4-Mpy]= 10^{-3} M and (b) Ag mirror. (c) The difference spectrum of (a) and (b).

micro-nanostructures should be come from the long-range electromagnetic enhancement because Ag nanoparticles formed on the surface of Cu_2S micro-nanostructures would excite Localized Surface Plasmon Resaonace (LSPR) under the irradiation of suitable laser.

4. Conclusions

In summary, we have developed a facile galvanic reduction route for producing Ag/Cu_2S composite micro–nanostructures over copper foil. The SEM images indicated that Ag nanoparticles are preferential deposited on the edge of the surface of big polygonal Cu_2S microstructures due to a localization of the electrons at the edge of Cu_2S microstructures as the reducing agent. The Raman spectra confirm that the SERS effect was attributing to the interaction between the Ag nanoparticles and Cu_2S micro–nanostructures. Meanwhile, a stronger enhanced electromagnetic field was produced between Ag nanoparticles and Cu_2S micro–nanostructures owing to the long-range electromagnetic enhancement.

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