Materials Letters 216 (2018) 287–290

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/mlblue

A solar cell endows the Surface-enhanced Raman scattering substrate with extra enhancement

Xiao-yu Liu *, Dong-yue Liu, Hui-juan Zhang

Shanxi Province Key Laboratory of Functional Nanocomposites, School of Materials Science and Engineering, North University of China, Taiyuan 030051, China

ARTICLE INFO

Article history:
Received 18 December 2017
Received in revised form 17 January 2018
Accepted 22 January 2018

Keywords:
E-SERS
Solar cell
Au nanoparticles

ABSTRACT

Electrochemical Surface-enhanced Raman spectroscopy (E-SERS) can effectively enhance the Raman signal intensities. However, the complex appliance and operation conditions hampered its application in quick and on-site detection. To solve this problem, a SERS substrate consisting of solar cell film and Au nanoparticles was prepared. The solar cell provides electrical potential by the laser irradiation to take place of electrochemical workstation which is essential in conventional E-SERS. The Au nanoparticles were loaded on the surface of solar cell film to provide electromagnetic enhancement. The sensitivity of the Raman signals on solar cell film-Au (SCAu) SERS substrate has been demonstrated to increase up to 6.7 times compared with that on the bare Au nanoparticles. Various molecules tests demonstrated the widespread prospect of the SCAu substrate in micro chemical detection.

1. Introduction

Surface-enhanced Raman scattering (SERS) has attracted considerable attention in chemical and biochemical analysis [1,2] because it reveals unique vibrational fingerprint of analytes, high sensitivity, and has a very low detection limits even down to single molecule level [3–5]. The generally accepted mechanism for SERS is electromagnetic enhancement (EM) and chemical enhancement (CE) [6,7]. EM, the dominated contribution to SERS, has been vastly studied due to the localized surface plasmon resonance (LSPR) inspired by the noble metal nanoparticles under light radiation [8,9]. CE, another significant contribution to SERS, has not been taken general attention due to its relatively weak enhancement and complex research methods. The primary methods to study chemical enhancement including simulation [10,11], adopting nonmetal substrate [12] and E-SERS [13,14].

Additionally, E-SERS has been widely used for spectroelectrochemical analysis [15]. Actually, the E-SERS can effectively increase the Raman signal intensities [13,16–18]. If the energy difference between Fermi level of the metal substrate and the molecular energy level equal to laser energy (photon energy), the charge transfer between metal substrate and molecular will occur giving rise to CE and increasing Raman signals [19]. The Fermi level of metal substrate can be adjusted by the electrode potential in E-SERS Moreover, the external electrostatic field can modulate the plasmon resonance of metal substrate [20,21]. For instance, the increasing density of free electrons in metal substrate leads to stronger electron oscillation which further increase the Raman signals [22,23]. Despite the enhancement ability in E-SERS, the complexity instrumental setup of E-SERS hampered its applications in fast and on-site detection.

To solve this problem, a solar cell film consisting of CdTe/CdS p-n junction and Au nanoparticles were combined to construct SERS-active substrate. Fig. 1 schematically illustrates the SCAu composite structures, wherein the top layer is Au nanoparticles and CdTe/CdS p-n junction and a Ni foil act as interlayer and bottom layer, respectively. The CdTe/CdS solar cell was selected because of its absorbance wavelength is 400-–800 nm which including the general Raman laser wavelength (532, 633, 785 nm). When the laser irradiating the SERS substrate, tremendous electron-hole pairs generated, the electrons move to the n-type region and holes move to the p-type region in the effect of built-in electric field formed by p-n junction. The Au nanoparticles were deposited on the surface of n-type semiconductor. The surface potential of CdS further injects the free electrons into Au nanoparticles. The potential of Au nanoparticles will be decreased and the density of free electrons in Au nanoparticles will be increased and promotes the SERS intensity under the laser irradiation. In addition, the potential of the Au nanoparticles can be adjusted by the intensity of the laser. In this work, different intensity of laser will be adopted to compare the SERS performance of the SCAu. The SERS performance of the SCAu substrate was tested by detecting various molecules including 4-Aminothiophenol (4-ATP), Fluoranthene and 3,3′,4,4′-Tetra

* Corresponding author.
E-mail address: s1508109@st.nuc.edu.cn (X.-y. Liu).

https://doi.org/10.1016/j.matlet.2018.01.129
0167-577X/

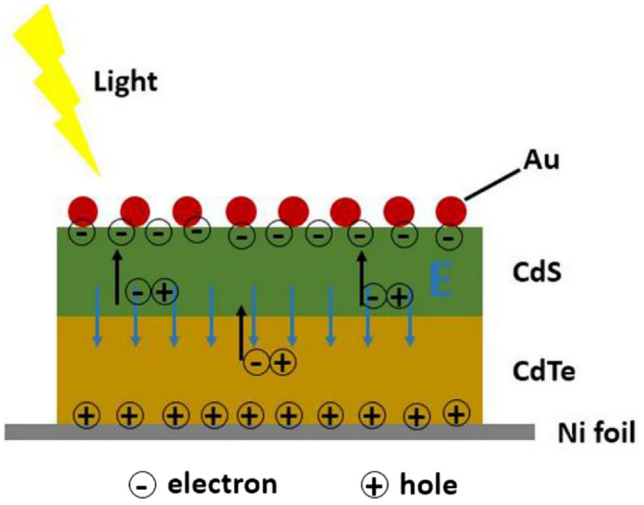

Fig. 1. Schematic illustration of the SCAu device, which is composed of three parts: A layer of Au nanoparticles, a piece of solar cell film composed of CdTe and CdS and a piece of Ni foil. The blue arrows is the direction of the built-in electric field, and the black arrows is the motion direction of the electrons. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

chlorobiphenyl (PCB-77). Compared with the bare Au nanoparticles, the SCAu substrate exhibits a remarkable enhancement ratio of 6.7, which demonstrates the wide application foreground of the substrate in fast and on-site detection.

2. Materials and methods

2.1. Materials

Cadmium sulfate octahydrate ($CdSO_4{\cdot}8/3H_2O$, 99%), Sodium tellurite (Na_2TeO_3, 98%), L(+)-Ascorbic acid (AA) and Nickel slice were purchased from Aladdin. Sodium thiosulfate ($Na_2O_3S_2$, 99%), Hexadecyl trimethyl ammonium bromide (CTAB), Sodium borohydride ($NaBH_4$) and Citric acid were obtained from Tianjin Mao Tai Chemical Reagent. Hydrogen tetrachloroaurate(III) ($HAuCl_4{\cdot}3H_2O$, 99.9%) was purchased from Macklin. Ultrapure water (resistivity of 18.2 MΩ·cm) was used through all of the experiments.

2.2. Preparation of SCAu SERS substrate

The CdTe/CdS solar cell film was prepared by means of electrochemistry method. A piece of Ni slice (2 × 2 cm) was cleaned by ultrasonication for 10 min in isopropanol, etanol, acetone and ultra pure water sonication bath, sequencially. Then the Ni slice served as working electrode to synthesize CdTe film in electrolyte containing $CdSO_4{\cdot}8/3H_2O$ (0.1 M), Na_2TeO_3 (0.005 M), CTAB (0.002 g/mL) and H_2SO_4 (0.12 M). The graphite and Ag/AgCl served as counter electrode and reference electrode, respectively. After electrolysis time of 1 h at a potential of −0.5 V, the CdTe film was prepared. For CdS film synthesis, the deposition potential and time were 0.92 V and 30 min. The electrolyte was consisted of $CdSO_4{\cdot}8/3H_2O$ (0.1 M), $Na_2O_3S_2$ (0.01 M) and Citric acid (0.04 M).

The Au nanoparticles were synthesized using a seed-growth method. Briefly, the Au seeds were prepared by the addition of ice-cold $NaBH_4$ solution (0.01 M, 0.3 mL) into an aqueous solution containing $HAuCl_4$ (0.01 M, 0.125 mL) and CTAB (0.1 M, 3.75 mL), followed by rapid stirring for 2 min. The seed solution was kept undisturbed for about 1 h at room temperature. Next, 20 μL Au seeds diluted 10 times with water was added into the growth solution containing $HAuCl_4$ (10 mM, 0.8 mL), CTAB (100 mM, 6.4 mL) and 32 mL H_2O, then AA solution (100 mM, 3.8 mL). The resulting solution was mixed by gentle stirring for 10 s and then left undisturbed overnight. After centrifugation and washed with water two times, the Au nanoparticles were redispersed in 8 mL water. Then, the prepared Au nanoparticles were spin-coated on the surface of CdTe/CdS films.

2.3. Characterization and measurement

Optical characterization of samples was performed on X-ray diffraction (XRD, HaoYuan, DX-2700B). The open-circuit voltage and closed-circuit current of the SCAu were tested by electrochemical workstation (CH Instruments Ins, CHI660E) and a xenon lamp with 500 W. The morphology samples were characterized by scanning electron microscope (SEM, JEOL 2100F).

The SERS performance of the SCAu was tested by Renishaw Invia Raman spectrometer. Different concentrations of 4-ATP were dropped on the surface of SCAu and dried in the air for SRES measurement. The acquisition time was 10 s, and 532 nm laser with different power was used as excitation source.

3. Results and discussion

Fig. 2A-–C show the micro morphologies of the SCAu substrate. In the presence of CTAB, a flat film of CdTe was obtained (Fig. 2A). Fig. 2B shows the SEM image of CdS flat film, obtained in acidic condition. Fig. 2C indicates that the Au nanoparticles were successfully and uniformly spin-coated on the surface of CdS which could act as conventional SERS materials. The insert picture in Fig. 2C is the SEM image of Au nanoparticles deposited on the surface of CdS. Fig. 2D is the practicality picture of SCAu substrate. Fig. 2E shows the typical XRD patterns of CdTe, CdTe/CdS and the SCAu. Compared with the XRD curves of CdTe and CdTe/CdS, the SCAu XRD pattern shows a new diffraction peak at 64.5° and 77.5° which belong to Au (220) and Au (311) lattice planes, respectively. Compared to t the typical Au XRD pattern, a diffraction peak at 44.4° disappeared, which may be due to the strong intensity of diffraction peaks of the Ni at 45°. Other diffraction peaks presenting at 23.8°, 39.4°, 46.6°, 26.8° and 28.4° in the XRD pattern of SCAu, could be corresponded to the lattice planes of CdTe (111), CdTe (220), CdS (100) and CdS (002), respectively, indicating the preparation of SCAu substrate. Fig. 2F shows the J-V curves of the SCAu at different intensity of light, representing the photoelectricity property of the SCAu including open-circuit voltage and closed-circuit current. It is obvious that the potential of the SCAu produced is highly associated with the intensity of light. When the intensity of light changed from 100 to 80 mW/cm^2, the open-circuit voltage changed from 0.76 to 0.49 V, indicating that the potential can be easily adjusted by the intensity of light.

4-ATP, PCB-77 and Fluoranthene molecules were used as probing molecules to demonstrate the capability of signal enhancement of the SCAu substrate to promote SERS signals. As shown in Fig. 3A, the SERS signal of 4-ATP on SCAu substrate was increased 2.3 times compared to that on the bare Au nanoparticles. In addition, the absorption peaks at 1076, 1141 and 1583 cm^{-1} obviously shifted to 1083, 1126 and 1592 cm^{-1}, respectively, which were different from the regular SERS spectra on Au nanoparticles. It implies that the new vibration mode of the detected molecules was generated due to the chemical enhancement. The potential or the electron density of the SCAu surface can be adjusted by the intensity of laser. Fig. 3B shows the Raman spectra of 4-ATP detected on bare Au nanoparticles and SCAu substrate under different intensities of laser. With the increase of laser intensity, the signals of 4-ATP on Au and SCAu both increased. The enhancement for the 4-ATP signal acquiring from SCAu substrate is higher than that of bare