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Full Length Article

Ordered CdSe-sensitized TiO_2 inverse opal film as multifunctional surface-enhanced Raman scattering substrate

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ABSTRACT

The surface-enhanced Raman scattering (SERS) study on semiconductor material has attracted much attention, but the traditional semiconductor materials possess low SERS sensitivity and single function, which cannot meet the need of people very well. Here, the ordered three-dimensional CdSe-sensitized TiO_2 (CdSe-TiO_2) composite film with inverse opal structure (IOS) and multifunction was synthesized successfully. The as-prepared CdSe-TiO_2 IOS film was first used as the excellent SERS substrate and photoelectrochemical material. The synergistic effect of slow photons, multiple scattering and CdSe sensitization make the SERS substrate more sensitive. The detection limit of the methylene blue (MB) on CdSe-TiO_2 IOS film can be as low as 7×10^{-9} M. In addition, CdSe-TiO_2 IOS exhibits excellent photoelectric converting performance, the photocurrent density of CdSe-TiO_2 IOS can achieve 0.924 mA/cm^2 under chopped light illumination at a fixed bias of 0 V versus Ag/AgCl. The above performance enhancement of CdSe-TiO_2 IOS film makes it becoming a promising multifunctional material to be used in SERS detection and photoelectrochemical field.

1. Introduction

Surface-enhanced Raman scattering (SERS) has been widely utilized as a powerful tool for molecular analysis for its high sensitivity and molecular specificity [1–5]. The noble metal materials as SERS substrates have been widely reported, such as Au [6], Ag [7], but due to the high cost, their application in SERS field was gradually limited. In recent years, the researchers found that some semiconductor materials as SERS substrates can effectively enhance the Raman signals [5,8]. The Lombardi's group have been working most intensively and systematically on this topic over about two decades, on both bulk and nano-semiconductors, such as ZnO [9], MoS_2 [10], CdSe [11], CdTe [12] and TiO_2 [13]. As a typical semiconductor material, TiO_2 nanoparticles (TiO_2 NPs) have received a lot of research interest for their good biocompatibility, chemical stability, excellent photoactivity [14]. Recently the SERS performance of TiO_2 NPs as noble metal-free SERS substrate also attracted people's attention. For instance, Yang et al. [15] prepared the highly-dispersed TiO_2 NPs with plentiful active sites as a SERS substrate, the detection limit of 4-aminobenzoic acid is 1×10^{-8} M. In fact, the TiO_2 NPs possess large band gap, which result in the limited light harvesting and the lower SERS sensitivity, further limit the application of TiO_2 NPs as SERS substrate. Therefore, tremendous works have been done to narrow the band gap of TiO_2 NPs. In general, the band gap can be narrowed by doping with nonmetal elements [16], sensitizing by narrow-band gap semiconductor quantum dots [17] or the inverse opals structure (IOS) [18].

As far as we know, the IOS can narrow the band gap of semiconductor material, which resulted from the multiple scattering effect and slow photon effect [18]. Besides, due to the enhanced light absorption and the interaction between the light and mater, the semiconductor material with IOS can also improve the SERS sensitivity and photoelectric converting performance. Our group [19] prepared the N-CDs/Bi_2O_3 IOS with enhanced photoelectrochemical performance and photocatalytic activity via sol-gel method, which demonstrated that the IOS can narrow the band gap of Bi_2O_3 from 2.7 eV to 2.4 eV. Ankudze et al. [20] prepared the Au-loaded SiO_2 IOS by infiltrating as high active SERS substrate, the detection limit of 4-aminothiophenol is 1×10^{-10} M. So the nanomaterials with IOS can be expected to apply in SERS detection and photoelectrochemical field as bifunctional materials.

Furthermore, some narrow-band gap semiconductor quantum dots can also narrowed the band gap by sensitizing, such as CdSe [21], CdS [22] and so on. Among them, as the most attractive narrow-band gap sensitizer, the CdSe possesses excellent optical property. The CdSe sensitization can extend the absorption band of semiconductor materials to the visible light-near infrared region and effectively enhance the

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light absorption [23]. Qin et al. [24] prepared CdSe/TiO_2 nanotube array by electrochemical electrodeposition, the photocurrent density is 138 μA/cm^2. As we know, the plasma resonance bands of the semiconductor material locate in the near infrared region, so when the light absorption is occurred in the near infrared region, the SERS signal intensity will become strong [25]. Therefore, the sensitization by CdSe can effectively enhance the sensitivity of TiO_2 with IOS as SERS substrate. However there is still no report about the combination of CdSe sensitization and IOS on TiO_2 as SERS substrate applying in contaminants detecting field.

Considering the above-mentioned advantages of the IOS and CdSe sensitization, here, we synthesized the ordered three-dimensional CdSe-TiO_2 IOS film. We found that the unique inverse opal structure benefits the electron transportation and light absorption, which further enhanced the sensitivity and photoelectrochemical property of the SERS substrate. Moreover, the CdSe sensitization can effectively extend the absorption band to the visible light-near infrared region, which enhanced the sensitivity of the CdSe-TiO_2 IOS SERS substrate for MB detection and improved photoelectric converting performance as well as photocurrent density. The prepared CdSe-TiO_2 IOS as multifunctional SERS substrate exhibits the potential application in environmental detection and solar cells, etc.

2. Experimental

2.1. Chemicals

Styrene (St), polyvinyl pyrrolidone (PVP, K-30), diethanolamine ($C_4H_{11}NO_2$), potassium persulfate (KPS), ethanol (C_2H_6O), cadmium chloride ($CdCl_2{\cdot}2H_2O$), sodium sulfide ($Na_2S{\cdot}9H_2O$), selenium powders (Se), sodium sulfite (Na_2SO_3), sodium borohydride ($NaBH_4$) and methylene blue(MB) were purchased from Sinopharm Chemical Reagent Co., Ltd (P. R. China). Titanium isopropoxide (TIPT) was purchased from Aladdin Reagent Company (P. R. China). Concentrated sulfuric acid (H_2SO_4) and hydrogen peroxide (H_2O_2) were obtained from Shanghai Chemical Reagent Co., Ltd (P. R. China). Deionized water is obtained from Millipore Milli-Q system (resistivity: 18.2 MΩ·cm).

2.2. Preparation of the PS opal template

Firstly, we prepared PS spheres by a adapted surfactant-free emulsion polymerization reaction according to our previous work [19]. 12.1 g of St and 0.6 g of PVP were mixed with 100 mL of deionized water in round-bottomed flask in a water bath, the mixture was stirred for 15 min at room temperature. Then 20 mL of KPS solution (The solvent is ethanol) was added to the above mixture dropwise, and the flask was replenished with N_2 for 20 min to remove O_2. The temperature of mixture was increased to 70 °C and kept for 24 h with stirring. After natural cooling down to room temperature, the precipitate was separated and then washed by ethanol and deionized water for three times. Thus, PS spheres were obtained.

PS opal was fabricated by the vertical deposition method, using an aqueous monodispersed PS sphere colloidal suspension at 0.1 vol% and fluorine-doped SnO_2 (FTO) coated glass substrates. FTO conductive glass was cleaned by immersing in acetone, ethanol, and deionized water for 10 min with sonication, and dried under a N_2 stream. Then the prepared monodispersed PS spheres were assembled onto the FTO-coated glass substrates via a vertical deposition process at 45 °C. After the thin films were developed, they were heated to 70 °C for 3 h to enhance the connection between these neighboring PS spheres, which improves the structural stability of the film [26].

2.3. Preparation of CdSe-TiO_2 IOS

5.2 mL of TIPT was added to a solution containing 35 mL of ethanol and 1.1 mL of diethanolamine under vigorous stirring and kept stirring at room temperature for 24 h. Then the TiO_2 collosol was obtained by ageing of the mixture for 1–2 days. The PS opal film was dipped in the TiO_2 collosol for 30 min, then dried for 1 h in air. Finally, the composite film was sintered in a muffle furnace at 500 °C (ramping rate of 1 °C/min) in air for 3 h to remove the polymer template for obtaining TiO_2 IOS film.

The prepared TiO_2 IOS film was immersed into a $CdCl_2$ solution (50 mM) for 5 min in order to the absorption of Cd^{2+} on the thin film. Then the film was immersed into a Se^{2-} solution (50 mM) for 5 min. Thus the CdSe particles were formed on the TiO_2 IOS framework. Finally the above films were washed by deionized water to remove the excess ions, and dried with N_2. Thus, CdSe-TiO_2 IOS was obtained.

The TiO_2 NPs were prepared by calcinations of the above obtained TiO_2 collosol.

2.4. Characterization

The X-ray diffraction (XRD) patterns were performed on a DX-2700 (Dandong Haoyuan instrument Co., Ltd.,) using Cu-Kα (λ = 1.5406 A°) radiation, the accelerating voltage was 35 kV and applied current was 25 mA. Field emission scanning electron microscopy (FESEM) images were taken with a Hitachi S4800 scanning electron microscope. Energy dispersive spectra (EDS) were measured on an INCA x-act energy dispersive spectrometer with a voltage of 15 kV (Oxford Instruments). Raman spectra were obtained on a focusing Raman spectrometer (Renishaw inVia) with a 532 nm laser excitation. UV–Vis spectra were measured using a UV-4100 model UV–Vis-NIR spectrophotometer (Shimadzu, Japan).

2.5. Photoelectrochemical measurements

The photoelectrochemical performance measurements were conducted in three electrode configuration, the as-prepared nanostructured photoanodes were deposited on the FTO as working electrodes [27], the Ag/AgCl in saturated KCl solution was used as a reference electrode, Pt foil was used as the counter electrode. The mixed solution of Na_2S (0.24 mol/L) and Na_2SO_3 (0.35 mol/L) was used as the electrolyte. The photocurrent versus time tests were carried out in electrochemical workstation at room temperature, and the photoresponse was measured under chopped light illumination (350 W Xe lamp equipped with a filter, light/dark cycles of 20 s) at a fixed bias of 0 V versus Ag/AgCl.

3. Results and discussion

The prepared opal template composed of the PS spheres with the diameter of 260 nm is presented in Fig. 1a and b. It is clearly seen that the PS opal template exhibits a dense face-centered cubic (fcc) arrangement of monodispersed spheres with the (1 1 1) plane oriented parallel to the underlying FTO substrate. SEM images of TiO_2 IOS are shown in Fig. 1c and d, we can see that the 3D macroporous ordered TiO_2 IOS has been successfully synthesized, its pore size is about 220 nm, less than the diameter of the PS spheres due to sol shrinkage and polymer collapse during calcination [28]. But the ordered three-dimensional macroporous structure is well maintained, speculating that the slow photon and multi-scattering effect of the unique structure can improve the SERS signal of substrate and photoelectric conversion performance. The CdSe-TiO_2 IOS composite films were obtained by the CdSe growth in situ resulted from the interaction of Cd^{2+} with Se^{2-} on TiO_2 IOS skeletons. Its morphology is shown in Fig. 1e and f, compared with pure TiO_2 IOS, the skeleton thickness of CdSe-TiO_2 IOS is obviously increased. And it can be seen that the surface of the skeleton is no longer smooth, suggesting that we have fabricated a three-dimensional macroporous CdSe-TiO_2 IOS composite film.

Fig. 2a presents the XRD patterns of TiO_2 IOS and CdSe-TiO_2 IOS. The peaks at 2θ of 25.3°, 38°, 47.7° and 54.8° could be indexed to the crystal planes of anatase phase (JCPDS card, No. 65–5714) after