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Visible-light-driven charge transfer to significantly improve surface-enhanced Raman scattering (SERS) activity of self-cleaning TiO_2/Au nanowire arrays as highly sensitive and recyclable SERS sensor

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ABSTRACT

We apply a facile photoreduction deposition strategy to grow Au nanoparticles (NPs) on the surfaces of TiO_2 nanowire arrays (TiO_2/Au NWAs) as a Raman sensitive substrate. The fabricated TiO_2/Au NWAs can be used as a highly sensitive and recyclable SERS sensor for detecting the rhodamine 6 G (R6 G) molecules with a concentration as low as 10^{-9} M. Moreover, when irradiated with UV light, the SERS sensor with high sensitivity can be fully reproduced due to the superior self-cleaning capability of the substrate. By a comparative study on the SERS activities of R6 G molecules over the substrates of pure TiO_2 NWAs, pure Au NPs and TiO_2/Au NWAs, as well as the photoresponse performance of pure TiO_2 and TiO_2/Au NWAs under visible light illumination, we provide an illuminating insight into enhanced mechanism of SERS activity for TiO_2/Au NWAs. The photoresponse performances and SERS activities provide experimental evidence that enhanced SERS activity of TiO_2/Au NWAs is ascribed to the efficient charge transfer among Au, TiO_2 and R6 G. This work throws a new light on enhanced mechanism for SERS activity of semiconductor/noble-metal substrates, which are expected to find potential applications to fabricate highly sensitive SERS sensors for the detection of analytes.

1. Introduction

As a powerful technique to detect spectroscopic signals of molecules in the single molecule level [1] surface-enhanced Raman scattering (SRES) has attracted extensive attention and has found increasingly wide applications in many fields [2,3]. Thus various Raman substrates have been developed recently for detecting the SERS signals of analytes. However, the choice of an appropriate substrate is a key to achieve highly sensitive, recyclable and stable SERS signals [4]. Although noble-metal micro/nanostructures are still considered as the optimal SRES substrates due to their capability to present satisfactory SERS activity [4,5], photothermal and local heating of the noble-metal micro/nanostructures possibly result in low reproducibility for SERS data [6–9]. Therefore, it is highly desirable to design and fabricate other substrates to achieve highly sensitive, reproducible and stable SERS signals.

Recently, it has demonstrated that the semiconductor/noble-metal heterostructure substrates fabricated by combining suitable semiconductor nanostructures with noble-metal nanoparticles (NPs) show highly sensitive, reproducible, and stable SERS activity [10–12]. In contrast with noble-metal substrates, the superior SERS activity of these substrates is attributed to their following unique properties. (1) The capability to preconcentrate and absorb the probe molecules on the active sites of the substrate due to the unique surface wettability of semiconductor nanostructure. (2) The capability to produce an evanescent field by semiconductor nanostructures to enhance the SERS sensitivity and reproducibility with the negligible perturbation for probe molecules. (3) The capability to provide highly sensitive, reproducible and stable SERS activity due to its superior self-cleaning ability under UV or visible light irradiation. These multiple functionalities make semiconductor/noble-metal nanostructures to be as suitable substrates for fabricating SERS sensors, which have been widely applied in detecting and analyzing structural information of chemical and/or biological analytes [13–17]. However, for the practical applications, the SERS sensor needs to have good sensitivity, recyclability and stability, thus a key issue to achieve the semiconductor/noble-metal substrate-based SERS sensor with high sensitivity, recyclability and stability is to understand the enhanced mechanism of SERS activity.

In few published works, a charge transfer mechanism has been applied to interpret the SERS enhancement of semiconductor/noble-metal

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nanostructure substrates [18–20]. For instance, the enhanced SERS activity of Ag/TiO_2 nanoparticle substrate was attributed to the charge transfer from TiO_2 to the probe molecule of 4-Mercaptobenzoic acid (4-MBA) and from Ag to 4-MBA molecule through TiO_2 conduction band (CB) [21]. Another important example is the Ag/N719/TiO_2 nanocomposite substrate (where N719 is dye $(Bu_4N)_2[Ru(dcbpyH)_2(NCS)_2]$). In this substrate, the enhanced SERS activity was ascribed to the charge transfer from Ag to N719 molecule and from N719 molecule to TiO_2, besides the contributions from the electromagnetic enhancement of Ag NPs and resonance effect of N719 molecule [20]. These studies have demonstrated that the selective SERS enhancement for specific Raman signals of molecules is usually considered as the evidence that enhanced SERS activity is attributed to the charge transfer between constituents of the substrate. However, it has been proven that the selective SERS enhancement for specific Raman signals of molecules is greatly depended on the light wavelength and the testing molecules [19,20].

In the present study, we apply a facile photoreduction deposition strategy to grow Au NPs on the surfaces of TiO_2 nanowire arrays (TiO_2/Au NWAs) as a Raman sensitive substrate. The fabricated TiO_2/Au NWAs can be used as a highly sensitive and recyclable SERS sensor for detecting the rhodamine 6 G (R6 G) molecules with a concentration as low as 10^{-9} M. Moreover, when irradiated with UV light, the SERS sensor with high sensitivity can be fully reproduced due to the superior self-cleaning capability of the substrate. By a comparative study on the SERS activities of R6 G molecules over the substrates of pure TiO_2 NWAs, pure Au NPs and TiO_2/Au NWAs, as well as the photoresponse performance of pure TiO_2 and TiO_2/Au NWAs under visible light illumination, we provide an illuminating insight into the enhanced mechanism of SERS activity for TiO_2/Au NWAs. This work throws a new light on enhanced mechanism for SERS activity of semiconductor/noble-metal substrates, which is expected to find potential applications to fabricate other semiconductor/noble-metal SERS sensors with high sensitivity for the detection of analytes.

2. Experimental section

2.1. Preparation of TiO_2 NWAs

The TiO_2 NWAs were grown on glass (fluorine-doped tin oxide, FTO) substrate via an easy hydrothermal process described as the following. 15 mL HCl (38%) was firstly added into 15 mL ultrapure water, and then 0.5 mL titanium butoxide was added drop by drop under stirring. Finally, the solution was put into an autoclave, followed by placing a cleaned FTO piece against the autoclave wall. Afterwards, the autoclave was sealed and heated for 3.5 h at 150 °C. Then, the sample was washed with ultrapure water and ethanol, dried and annealed for 30 min at 450 °C.

2.2. Fabrication of TiO_2/Au NWAs

The TiO_2/Au NWAs were fabricated by using a facile photoreduction deposition method to grow Au NPs on the nanowire surface of TiO_2 NWAs. Briefly, the FTO covered with TiO_2 NWAs was placed into 60 mL aqueous solution containing 10 mL of 1.5 mg mL^{-1} gold chloride ($HAuCl_4 \cdot 3H_2O$), and then irradiated for 3 min by a Xe lamp (300 W) with $\lambda < 420$ nm light. After that, the FTO sample was thoroughly washed with ultrapure water, dried and heated for 1 h at 450 °C.

2.3. Characterization

X-ray powder diffraction (XRD) was applied to study the composition and crystalline phase of the samples. The experiments were carried out on a XD-D1 diffractometer employing Cu Kα ($\lambda = 1.5406$ Å) irradiation. Shape and size of the samples were observed by a scanning electron microscope (SEM). Optical absorption properties of the samples were studied by a Lambda 950 spectrometer.

2.4. Photoresponse evaluation

The photoresponse activities of the pure TiO_2 and TiO_2/Au NWAs were studied by a photoelectrochemical (PEC) cell containing working electrode (TiO_2 or TiO_2/Au NWAs), reference electrode (Ag/AgCl) and counter electrode (a Pt wire). All experiments were conducted in Na_2SO_4 electrolyte solution (0.1 M) under illumination with $\lambda > 420$ nm visible light (AM 1.5 G, 100 mW/cm^2).

2.5. SERS measurements

The SERS properties of achieved TiO_2/Au NWAs were investigated through detecting the Raman spectra of R6 G molecules at different concentrations (10^{-4} to 10^{-9} M). For SERS testing, the R6 G solution with concentrations of 10^{-4} to 10^{-9} M was dropped on the TiO_2/Au NWAs. A confocal microprobe Raman spectrometer (Horiba LABRAM-HR-800) was applied to collect Raman spectra of samples excited with 633 nm light at room temperature. To study enhanced mechanism for SERS performance of TiO_2/Au NWAs, the SERS activities of pure Au NPs and bare TiO_2 NWAs were also investigated by testing the Raman spectra of R6 G molecules at the same conditions.

2.6. Reproducible characterization

For reproducible SERS activity characterization, after the SERS performance was measured, the used TiO_2/Au NWAs were placed into ultrapure water and then irradiated for 2 h by a Xe lamp. The irradiated TiO_2/Au NWAs were rinsed with ultrapure water to remove residues such as ions and molecules, followed by drying under room temperature. Then, the substrate of the cleaned TiO_2/Au NWAs was applied again to detect the Raman signals of R6 G molecules. The reproducible tests were repeated five times to evaluate the reproducibility and stability of the fabricated TiO_2/Au NWAs.

3. Results and discussion

3.1. XRD and SEM characterizations

Fig. 1a shows the XRD patterns of the samples. Before growing Au NPs, the diffraction peaks of the sample can be assigned to those of rutile phase TiO_2 (JCPDS No. 78-2485), besides the diffraction peaks from FTO substrate. After growing Au NPs, the sample also shows the dominate diffraction peaks of rutile phase TiO_2. However, a weak shoulder peak of one diffraction peak of FTO at around 38.0° and an obvious diffraction peak at around 44.6° are observed. The enlarged patterns (insets of Fig. 1a) show that these two peaks can be easily assigned to (111) and (200) planes of Au (JCPDS No. 4-784), demonstrating the formation of Au NPs in sample.

Fig. 1b shows the SEM images of the sample before growing the Au NPs. It can be found that the sample is composed of aligned nanowires (NWs) with end diameter of about 150 nm. Thus the rutile phase TiO_2 NWAs were prepared on the FTO substrate. Another feature is that the surface of the NWs is smooth. After growing the Au NPs, the SEM images evidently show that a lot of Au NPs are grown on the surfaces of NWs as shown in Fig. 1 c,d. The nominal particle size determined by SEM images is about 3–63 nm. The particle sizes were obtained by statistically analyzing over 300 particles through an image processing software of ImageJ, in which the particle sizes were determined by measuring the greatest pixel length between the boundaries of the particles and converting to nm as used in previously published article [22]. SEM studies demonstrate that TiO_2/Au NWAs have been prepared by using a facile photoreduction deposition method to grow Au NPs on the surface of TiO_2 NWAs.