

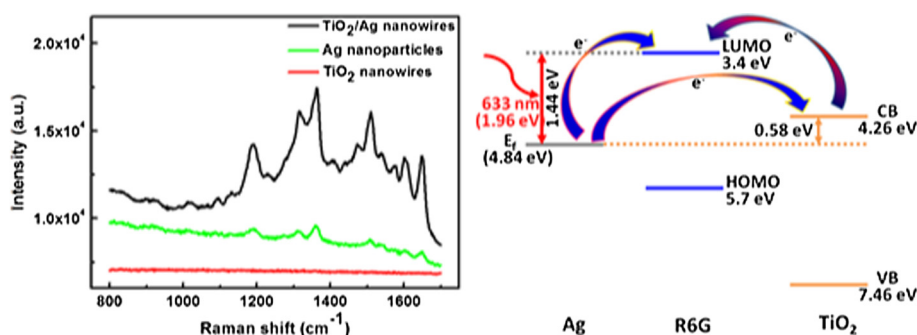
Regular Article

Sensitive surface-enhanced Raman scattering of TiO₂/Ag nanowires induced by photogenerated charge transfer

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GRAPHICAL ABSTRACT



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ABSTRACT

In this work, the semiconductor TiO₂ nanowires were successfully coupled with plasmonic metal Ag nanoparticles to fabricate hybrid nanostructures with enhanced sensitive Raman substrate. The SERS activities of fabricated hybrid nanostructures were evaluated by detecting the Raman signals of R6G molecules. The fabricated TiO₂/Ag nanowire/nanoparticle hybrid nanostructures show sensitive detection ability for R6G molecules. Based on the band structures of Ag nanoparticle, TiO₂ nanowire and R6G molecule, the enhanced sensitive SERS activities of hybrid nanostructures is ascribed to an efficient charge transfer process, in which the photogenerated electrons transfer to the conduction band of TiO₂ nanowires from metal Ag nanoparticles, and then to LUMO level of R6G molecules, leading to enhanced SERS activities. This efficient charge transfer process is achieved by the synergistic effects of plasmonic metal Ag nanoparticle, semiconductor TiO₂ nanowire and R6G molecule. Furthermore, the transfer process of photoexcited electrons from metal Ag nanoparticle to conduction band of TiO₂ nanowire is evidently confirmed by the photoresponse properties of hybrid nanostructures under illumination only with visible light ($\lambda > 420$ nm). The findings achieved in this work demonstrate that efficient turning the charge transfer in plasmonic metal nanoparticle/semiconductor/molecule hybrid nanostructure can significantly enhance its SERS activity.

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1. Introduction

As an efficient and powerful analytical technology for ultrasensitive analysis of surface and interfacial chemical property [1–3],

surface-enhanced Raman scattering (SERS) has currently been applied to detect vibrational spectroscopic information of single molecules [4,5]. Conventionally, SERS is achieved by the interaction of laser source, metal nanostructure and the absorbed molecule [6–13]. Thus the metal nanostructures, especially plasmonic Au and Ag nanostructures with various morphologies, have been widely employed as testing substrates for SERS analysis of surface

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and interfacial chemical properties due to their unique surface plasmon resonance (SPR) property [6–13]. For example, chemical imaging of single meso-tetrakis (3,5-di-tertiarybutylphenyl)-porphyrin (H_2TBPP) molecules was achieved by absorbing this molecule on (1 1 1) surface of plasmonic Ag [4].

In general, ultrasensitive detection ability to the single molecule level in surface and interface by exploiting metal-based SERS is ascribed to the significantly local electromagnetic field enhancement of the plasmonic metal nanostructures [7,14,15]. However, a strong local electromagnetic field enhancement induces energy dissipation through radiative and nonradiative transfer process, which usually causes local thermal (heating), photothermal, and/or photochemical reactions, possibly leading to low reproducibility of the detective data [16–20], and to the change of the composition and native folding of biomolecules as well as properties of other proteins [21,22]. For instance, the plasmonic heating generated by Au nanoparticles can alter the protein corona composition in SERS detective process [21]. Although the plasmonic metal nanostructures are commonly employed for the ultrasensitive analysis of surface and interfacial chemical property down to single molecule level, these plasmonic nanostructures possibly suffer from some disadvantages as mentioned above. Therefore, it is essential to develop other nanostructures to exploit as substrates for SERS testing such as hybrid nanostructures of plasmonic metal nanoparticles/semiconductor nanostructures and/or inorganic nanostructures with controlled morphologies.

It has been demonstrated that the hybrid nanostructures fabricated by coupling plasmonic metal nanoparticles with semiconductors exhibit high SERS sensitivity [23,24]. Compared to plasmonic metal nanostructures, these hybrid nanostructures can offer some advantages achieved by synergistic effects of plasmonic metal nanoparticles and semiconductor nanostructures. First, plasmonic metal nanoparticles are expected to make a contribution to SERS due to their capability of inducing the local electromagnetic field intensification. Second, semiconductor nanostructures can enhance and extend the functionalities and applications of the SERS-active substrate because of their unique physical, optical and chemical properties. Third, semiconductor nanostructures can facilitate preconcentration and absorption of the testing molecules on SERS-active sites because they are capable of controlling their surface wettability. Final, semiconductor nanostructures can enhance Raman sensitivity by evanescent fields, which have a minimal and insignificant perturbation for analytical molecules under testing process [3]. Benefiting from the advantages of hybrid nanostructures fabricated by plasmonic metal nanoparticles and semiconductor nanostructures, several hybrid nanostructures have been designed and prepared, and have been used for ultrasensitive SERS analysis, such as Si/Ag nanowire arrays [24–26], Fe_3O_4/Au core/shell spheres [27], Ag/ TiO_2 nanocomposites [28], TiO_2/Ag nanofibers [29], three-dimensional (3D) TiO_2/Ag nanostructures [30], TiO_2/Au nanotube arrays [31], porous TiO_2/Ag core/shell nanostructures [32], TiO_2/Au sphere/semishell ordered arrays [33], and TiO_2/Ag nanobelt structures [34]. However, compared to plasmonic metal nanostructures, the researches and applications of hybrid nanostructures fabricated with plasmonic metal nanoparticles and semiconductors for SERS are very limited.

In this paper, we demonstrate that the hybrid nanostructures of TiO_2 nanowires decorated with Ag nanoparticles exhibit sensitive SERS detection for rhodamine-6G (R6G) molecules. The superior SERS activity achieved in this hybrid nanostructure is attributed to photoexcited charge transfer from plasmonic metal Ag nanoparticles to semiconductor TiO_2 , which is evidently confirmed by photoresponse properties of the nanostructures under illumination only with visible light ($\lambda > 420$ nm).

2. Materials and methods

2.1. Materials

Titanium (Ti) foil, 2-propanol, acetone, sodium hydroxide (NaOH), silver nitrate ($AgNO_3$), hydrochloric acid (HCl), absolute ethanol (EtOH) and rhodamine-6G (R6G) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). No further purification was conducted for the as purchased materials. A mini-Qx-3000 (Quanxian, China) water purification system was applied to produce deionized water.

2.2. Synthesis of TiO_2 nanowires

TiO_2 nanowires were synthesized by a facile hydrothermal method described as following. The Ti foil, which was washed by a mixed solution of deionized water, acetone and 2-propanol with 1:1:1 vol ratio, was put into a 50 mL Teflon-sealed autoclave with 40 mL 1 M NaOH solution, heated at 220 °C for 48 h, and cooled to room temperature. The Ti foil treated with hydrothermal process was kept for 1 h in dilute HCl solution, followed by annealing at 650 °C for 2 h to form TiO_2 nanowires.

2.3. Decoration of Ag nanoparticles on TiO_2 nanowires

The Ag nanoparticles were decorated on surface of TiO_2 nanowires by an easy solution method. Briefly, 20 mg of prepared TiO_2 nanowires was suspended into 10 mL water under ultrasonic condition, thereafter, 5 mL EtOH, 2 mL 1 M NaOH solution and 2 mL 0.014 M $AgNO_3$ solution were added successively, followed by heating mixed solution at 50–60 °C for 8 h to grow Ag nanoparticles on the surface of TiO_2 nanowires. The synthesized sample is denoted as TiO_2/Ag nanowires.

2.4. Characterizations

A D-D1 X-ray diffractometer (XRD) (Schimadzu, Japan) was employed to record XRD patterns of the prepared samples. The morphological feature of obtained samples was evaluated by a field-emission scanning electron microscope (SEM). The microstructure feature and size of the synthesized nanostructures were studied by a transmission electron microscope (TEM) (JEOL-2100). UV–vis absorption properties of obtained nanostructures were investigated by a lambda 950 spectrometer. An ESCSLAB 250Xi X-ray photoelectron spectroscopy (XPS) was applied to investigate the elemental composition and surface electronic valence state.

2.5. Photoresponse property

Photoresponse properties of prepared nanostructures were evaluated by a three-electrode testing system. Before testing, the photoanode was fabricated by dropping 0.5 mL dispersion solution of TiO_2/Ag nanowires with 1.0 mg mL⁻¹ sample concentration on a FTO glass (2.0 × 2.0 cm²). The fabricated photoanode was used as working electrode; a Pt wire and Ag/AgCl electrode were used as counter and reference electrode, respectively. The photoresponse properties of photoanode were investigated by recording the chronoamperometric J–t curves, which were obtained in 0.1 M Na_2SO_4 solution under visible light irradiation with $\lambda > 420$ nm (AM 1.5 G, 100 mW/cm²).

2.6. SERS measurements

R6G was applied as probe molecule for evaluating SERS activities of TiO_2/Ag nanowires. R6G solutions with various

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