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Micro-nano zinc oxide film fabricated by biomimetic mineralization: Designed architectures for SERS substrates

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ABSTRACT

In this study, we have investigated the effect of the surface morphologies of the zinc oxide (ZnO) substrates on surface enhanced Raman spectroscopy (SERS). During synthetic process, the self-assembly monolayers (SAMs) with different terminal groups are used as templates to induce the nucleation and growth of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ crystals, then different morphologies micro-nano ZnO powders are obtained by annealing $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ crystals at 450 °C. The products obtained at different conditions are characterized by means of X-ray diffraction (XRD) patterns, scanning electron microscopy (SEM) and Raman spectra. The as-prepared ZnO micro-sized particles have been used the efficient Surface enhanced Raman scattering (SERS) substrates, and the SERS signals of 4-mercaptopyridine (Mpy) probe molecules are much influenced by the morphologies of the ZnO structures. Results indicated that the more (0001) facets appear in the of ZnO morphology, the greater degree of charge-transfer (PCT) for the SERS enhancement on the surface of semiconductors is achieved. The chemical interaction between ZnO structures and Mpy molecules plays a very important role in the SERS enhancement.

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1. Introduction

Due to the unique sensitive detection, surface enhanced Raman scattering (SERS) has been widely used in the fields of single molecule detection, surface adsorption, catalytic reaction monitoring, chemical and biological sensors, biomedicine, and trace analysis of pollutants [1–6]. The most important issue for SERS analysis is the preparation of active substrate. In general, rough noble metals such as Au, Ag and Cu have been widely studied as efficient SERS substrates with a high enhancement factor (generally up to 10^6). Recently, semiconductor nanomaterials have also been used as SERS substrates and the charge-transfer (CT) between semiconductors and probe molecules contribute the SERS enhancement [7–11].

Among various types of semiconductors, ZnO nanoparticles has been widely studied as SERS substrates. ZnO micro-nano architectures with a wide direct band gap (3.37 eV) shows a large variety of potential opportunities for high technological applications in photonics, electronics, advanced catalysis, photodetectors, shortwave laser, solar cell electrodes, and SERS [12–15]. In the previous studies, the influence of the factors such as the size of nanoparticles, doping with metal ions, and excitation energy on the adsorption of organic molecules on the SERS activities of ZnO have been investigated in detail. Furthermore, it is

well-known that different crystal facets of a semiconductor have different atomic arrangements and electronic structures, endowing them with distinctive activities [16,17]. Recently, numerous researchers have been focusing on preparing different morphologies of ZnO, which are important in analyzing their facet-dependent physical and chemical properties. According to previous studies, ZnO nanostructures tend to grow along the c-axis with predominantly low energy {1010} nonpolar facets [18–20]. Compared with the nonpolar facets, the ZnO semipolar {1011} or polar {0001} facets usually grow too fast to be observed in the final shape due to the higher surface energy. However, the high energy facets with unique surface structures are usually more active than the low energy facets. It has been demonstrated that high energy polar and semipolar surfaces may have excellent performance in photocatalysis [21], gas sensors [22] or dye sensitized solar cells [23]. Thus, the crystal facet engineering may be an exciting direction to affect the SERS activities of ZnO. It has been pointed out that the size of the semiconductor nanoparticles is usually below 100 nm as SERS substrate in the previous reports, and there are few studies on the micro-nano structures of semiconductors based SERS substrates.

Herein, we present a simple biomimetic mineralization and annealing treatment approach for the fabrication of different ZnO micro-nano structures as SERS substrate. Different group-terminated self-assembly monolayers (SAMs) are employed to control the deposition and crystallization of ZnO on their surfaces. Due to template effect, four kinds of ZnO micro-nano structures exposing various kinds of facets, including

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{0001}, {1011}, and {1010}, were successfully synthesized. The prepared ZnO micro-nano structures have been proved to be efficient SERS substrate by using 4-mercaptopyridine (4-Mpy) as probing molecules. The facet-dependent SERS performance of ZnO has been investigated in detail. From the crystal face of ZnO micro-nano structures, the work provides an evidence of the contribution of CT between semiconductors and probe molecules on the SERS enhancement.

2. Experimental Section

2.1. Chemicals

(3-Mercaptopropyl)trimethoxysilane (MPTS), (3-aminopropyl)trimethoxysilane (ATPMS), and 4-Mpy were purchased from Sigma Aldrich. $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, benzene, chloroform, acetone, concentrated sulfuric acid, hydrogen peroxide, acetic acid were obtained from Shanghai Chemical Reagents Co. All of chemical were of A.R. grade and used without further purification.

2.2. Pretreatment of ITO and Quartz Wafer Substrates

The ITO conductive glass and quartz wafer were immersed in Piranha solution ($\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2 = 7:3$, v/v) at 90°C for 30 min to make hydroxy radicals on their surfaces. Then the substrates were carefully rinsed with demonized water and dried in the air condition.

2.3. Preparation of Thiol Group-terminated SAMs on the Substrate

The as-pretreated substrates were immersed in dehydrated cyclohexane solution containing 0.5 mmol/L of MPTS for 6 h. In order to remove other physically adsorbed ions or molecules, the substrates were cleaned in turn ultrasonically with chloroform, acetone, and ultrapure water.

2.4. Preparation of Sulfonic Group-terminated SAMs

MPTS SAMs on the substrate was put in a solution of 30% $\text{H}_2\text{O}_2/\text{HOAc}$ (1:5 v/v) and maintained at 45°C for the oxidation of thiol group to generate sulfonic group-terminated SAMs. The substrate was withdrawn after 60 min and cleaned with chloroform, acetone, and ultrapure water.

2.5. Preparation of Amino Group-terminated SAMs

The pretreated substrates were immersed in dehydrated methyl alcohol solution containing 0.3 mmol/L of ATPMS for 6 h. In order to remove other physically adsorbed ions or molecules, the substrates were cleaned with methyl alcohol.

2.6. Preparation of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ crystals

The undersaturated $\text{Zn}(\text{NO}_3)_2$ solutions were prepared by dissolving 140 g of $\text{Zn}(\text{NO}_3)_2$ in 100 mL of demonized water at 40°C in the water bath. The solutions were precisely dissolved for 1 h and then the solutions cooled down to 30°C , which of supersaturated solutions were obtained. Then the SAMs modified substrates and hydroxyl substrate were vertically inserted into the above solution at 30°C . After a soaking time of 8 h, the substrates were drawn from the solution and dried for the test.

2.7. Preparation of ZnO Micro-nano Structures via an Annealing Treatment

ZnO micro-nanostructures were obtained via an annealing treatment of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ crystals grown on the surface of SAMs modified substrates and hydroxyl substrates at 450°C for 4 h.

2.8. Characterization

The morphologies of the products were characterized by a field-emission scanning electron microscope (JEOL JSM-6700F). The X-ray diffraction (XRD) measurement was recorded with a D/Max-RA X-ray diffractometer using Cu K α ($k = 1.5406$) radiation. All Raman spectra were measured by a Jobin Yvon/HORIBA LabRam ARAMIS Raman spectrometer equipped with a HeNe laser (633 nm). The typical exposure time for each measurement in this study was 10 s with one time accumulation.

3. Result and Discussion

When different groups-terminated SAMs modified substrates and hydroxyl substrates are vertically soaked in the $\text{Zn}(\text{NO}_3)_2$ solution, the induced nucleation and growth of crystals occur on the surface of substrates. Then, the ZnO micro-nanostructures have been prepared via an annealing treatment of the prepared $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ crystals at 450°C for 4 h. The SEM images in Fig. 1a and b reveal the formation of rectangular micro-nanotubes with smooth surface of ZnO on the hydroxyl group-terminated SAM modified substrates. The diameters of the nanotube channel are in the range of 100–500 nm, and the surface of nanotube is smooth. As shown in Fig. 1c, the SEM image shows that the feathery ZnO aggregates have been formed on the amino group-terminated SAM modified substrate. And the corresponding

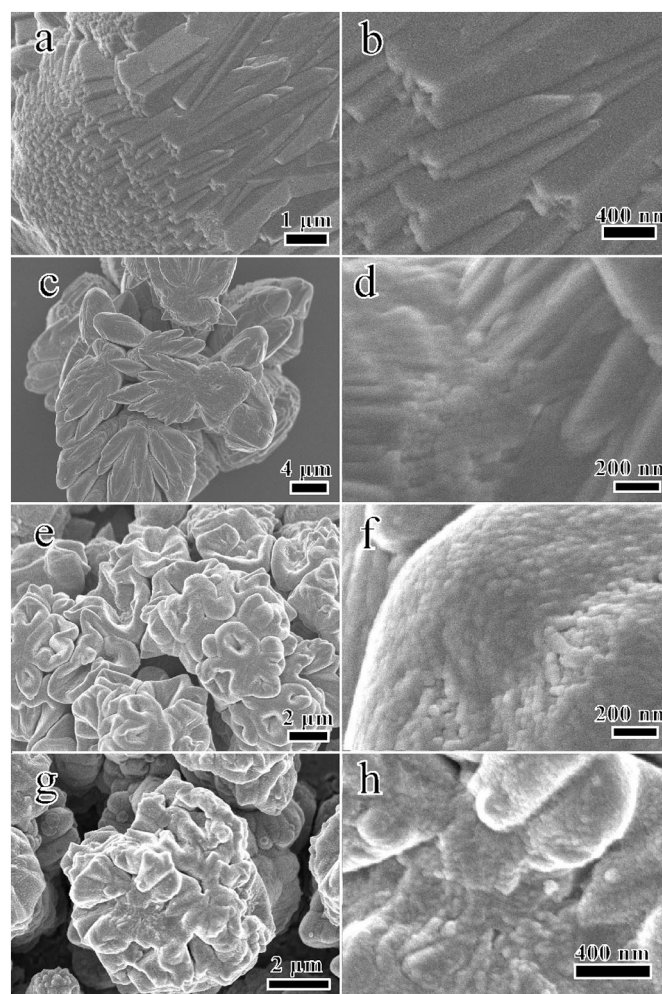


Fig. 1. SEM images of ZnO microcrystals prepared by calcine of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ grown on the SAMs template with the ending groups (a) hydroxyl-group; (c) amino group; (e) sulfonic group; (g) thiol group; (b, d, f, h) the corresponding larger versions of (a, c, e, g).

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