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Experimental and theoretical studies on noble metal decorated tin oxide flower-like nanorods with high ethanol sensing performance

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ABSTRACT

This study reports a facile solvothermal method for the synthesis of tin oxide (SnO_2) flower-like nanorods with dominant (1 1 0) crystal surface, which could be further decorated with varying amounts of noble metals, (gold (Au) and palladium (Pd)) to enhance the gas-sensing properties. Analysis of the gas-sensing results reveal that the decoration of Au and Pd nanoparticles on the surface of the SnO_2 nanorods is advantageous in: (i) enhancing the sensitivity towards ethanol (9–15 times); (ii) reducing the response/recovery time (by 15–40 s), and (iii) significantly decreasing the optimum operating temperature (from 250 to 175 °C). Beyond physical experiments, molecular dynamics (MD) method was also conducted to quantify diffusivity, adsorption and reaction capabilities of ethanol on SnO_2(1 1 0) plane and to better understand the role of noble metals in enhancing the gas-sensing performance of SnO_2. The findings in this study will be useful for future design of metal oxide nanocomposites with specific crystal surface for achieving high performance in surface-governed applications.

1. Introduction

Tin oxide (SnO_2), an *n*-type semiconductor with a wide band-gap of $E_g = 3.4$ eV, has attracted much interest in the fields of photocatalysis [1,2], lithium-ion batteries [3,4], solar cells [5,6] and gas sensors [7,8]. SnO_2 has been widely researched as a gas sensing material because of its low cost, high response, excellent stability and potential for miniaturization for integration into micro-machined substrates [9]. Numerous efforts have been conducted to enhance the gas-sensing performance of SnO_2-based sensors by means of shape and size control [7,10] and more recently through crystal surface engineering.

In order to improve the response and selectivity of SnO_2 sensors, nanocomposites composed of SnO_2 with other metal oxides such as α-Fe_2O_3 [11], ZnO [12], TiO_2 [13] and CuO [14] or with noble metals (Au [15], Pt [16], or Pd [17]) have been investigated. For example, Pt-decorated SnO_2 was shown to exhibit enhanced response towards methane (CH_4) at 200–450 °C compared to pure SnO_2 nanocrystals [18]. Kolmakov et al. [17] reported an enhancement in the response of SnO_2 nanowires towards oxygen (O_2) and hydrogen (H_2) gases at 200–270 °C by addition of Pd nanoparticles (NPs).

Beyond physical experiments, theoretical studies have been also performed using such as density functional theory (DFT) method to understand the surface-dependent sensing mechanism of SnO_2. The DFT simulation has been also used to investigate the adsorption of carbon monoxide (CO) [19], nitric oxide (NO) [20], water (H_2O) [21], and hydrocarbon molecules [22]. For instance, Bredow and Pacchioni [20] studied the adsorption of NO molecules on the SnO_2(1 1 0) plane and found that the interaction was mainly covalent and the interaction strength was significantly increased by the presence of oxygen defects. The DFT study by Viitala et al. [22] revealed that the chemisorption of acetylene, ethylene and ethane on SnO_2(1 1 0) surface is dependent mainly on the ionic and covalent bonding, while the weak adsorption of CO on SnO_2(1 1 0) occurred though an electrostatic effect [19]. However, the theoretical study of the adsorption of H_2O, O_2 and ethanol gases on the SnO_2(1 1 0) plane, particularly after decoration with noble metals, is rarely reported [23]. Furthermore, issues such as high operating temperatures (usually >200 °C), poor selectivity or stability, and incomplete understanding of the sensing mechanisms, have impeded further applicability of these materials [18].

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This study aims to develop facile strategies for the preparation of Au and Pd-decorated SnO_2 flower-like nanorods with dominant (1 1 0) crystal surface which can highly enhance the gas sensing performance. The phase composition and morphological features of the noble metal-decorated SnO_2 nanocomposites will be characterized. The influence of the pertinent variables, especially the Au and Pd contents on the sensing performance of SnO_2 nanorods towards ethanol will be examined. Furthermore, molecular dynamics (MD) simulations will be employed to understand the interactions between ethanol, water (moisture), oxygen and SnO_2(1 1 0) surface with or without Au or Pd decorations. This work will be useful for the design and construction of metal oxide nanocrystals with crystal surface control for achieving enhanced gas sensing and/or catalytic performance.

2. Experimental

2.1. Chemicals

Tin(IV) chloride pentahydrate ($SnCl_4{\cdot}5H_2O$, 98%), ammonium hexachloropalladate(IV) ($(NH_4)_2PdCl_6$, 99.99%), gold(III) chloride trihydrate ($HAuCl_4{\cdot}3H_2O$, 99.99%), sodium borohydride ($NaBH_4$, 99.9%), sodium hydroxide (NaOH, 97%), methanol (CH_4, 99.8%), ethanol (C_2H_6O, 95%), absolute ethanol (C_2H_6O, 99.9%), hexane (C_6H_6, 99%), toluene (C_7H_8, 99.8%), isopropanol (C_3H_8O, 99.7%), formaldehyde (HCHO, 37.5 wt% in H_2O), and acetone (C_3H_6O, 99.9%) were purchased from Sigma Aldrich and used as received without further purification. Ultra-pure water was used in all the synthesis processes.

2.2. Synthesis of SnO_2 flower-like nanorods

The SnO_2 flower-like nanorods were prepared according to a previous report with modifications [24]. Typically, 0.5259 g of $SnCl_4{\cdot}5H_2O$ was added to 20 mL of NaOH solution (0.81 M) and stirred until fully dissolved. Subsequently, 20 mL of absolute ethanol was poured into this mixture solution and stirred for 15 min to produce a white suspension. Finally, the resulting suspension was transferred into a 50 mL stainless-steel Teflon-lined autoclave, sealed and heated at 200 °C for 48 h. The greyish product was washed with deionized water and ethanol several times, and then dried at 60 °C.

2.3. Synthesis of Pd and Au-decorated SnO_2 flower-like nanorods

Briefly, 30 mg of SnO_2 flower-like nanorods was well-sonicated in 10 mL of deionized water for 10 min. Then, varying quantities of 0.01 M $(NH_4)_2PdCl_6$ solution were added into the SnO_2 suspension under magnetic stirring to obtain Pd loading of 2, 5 and 10 wt% (Table S1). Finally, different amounts (depending on the Pd loading) of freshly made 0.05 M $NaBH_4$ solution (Pd^{4+}:BH_4^- = 1:4) were added into the SnO_2/Pd suspension and allowed to react for 15 min under gentle stirring. The greyish-black products were thoroughly washed with water and ethanol several times and then dried in an oven at 60 °C for 5 h. Similar procedures were performed to prepare SnO_2/Au nanocomposites, in which varying amounts of 0.01 M $HAuCl_4{\cdot}3H_2O$ solution were added to the SnO_2 suspension under magnetic stirring, followed by the addition of different volumes of freshly made 0.05 M $NaBH_4$ solution (Au^{3+}:BH_4^- = 1:3) to achieve Au loading of 2, 5, and 10 wt% (Table S2).

2.4. Characterization

The phase composition of the products were analysed using a Phillips X'pert multipurpose X-ray diffraction (MPD) system equipped with graphite mono-chromatized Cu-Kα radiation (λ = 1.54 Å), operated at 40 kV and 40 mA. The XRD patterns were collected over a 2θ range of 10°–70°, with a step-size of 0.02°. The morphological characterization of the products was conducted using a Tecnai G^2 20 transmission electron microscope (TEM) with an accelerating voltage of 200 kV. High resolution transmission electron microscopy (HRTEM) images of the samples were obtained using a Phillips CM200 field emission gun transmission electron microscope operated at 200 kV. X-Ray photoelectron spectroscopy (XPS) analysis of the products was carried out using an ESCALAB250Xi X-ray photoelectron spectrometer, with Al-Kα radiation as the excitation source.

2.5. Gas sensor fabrication and measurements

The gas sensors in this study were prepared using similar steps described in our previous reports [25,26]. The gas-sensing tests were performed with a computer-controlled WS-30A gas-sensing measurement system and more details regarding the gas-sensing tests can be found in the Supporting Information (Fig. S1). The response or sensitivity (S) of the sensor is defined as $S = R_a/R_g$, where R_a and R_g are the resistance of the sensor in air and in the tested gas atmosphere, respectively. The tests were performed at a relative humidity of 50–65%. Digital photographs of the fabricated sensors are given in Fig. S2.

2.6. Numerical simulation

The commercial software: Material Studio (Version 4.3, Accelrys Inc, 2007) was used to perform Molecular Dynamics simulations using the Discover module. The periodic canonical ensemble (NVT) with the COMPASS (Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies) force-field was used to calculate the potential energy of the system. This particular force-field is especially useful for this system because its parameters are derived from ab initio data, which can be applied to predict organic and inorganic materials in both gas and condensed phases [27,28]. The SnO_2 lattice ($a = b = 4.737$ Å, $c = 3.186$ Å, $\alpha = \beta = \gamma = 90°$) was cleaved according to previous studies to create the SnO_2(1 1 0) slab surface with dimensions of ~30 Å × 30 Å and thickness of 12 Å [29–31]. The exposure of the top atoms of each surface was chosen as was the case of previous studies where these atoms were seen to exhibit the highest stability [32,33]. Further details regarding the simulation of the adsorption of ethanol on the SnO_2(1 1 0) surface are given in the Supporting Information.

3. Results and discussion

3.1. Composition and morphology

The phase composition of the as-prepared samples with or without metallic decoration was characterized using XRD technique. Fig. 1 shows the XRD patterns of pure SnO_2 and Au or Pd-decorated SnO_2 products. All of the diffraction peaks in the original SnO_2 product (Fig. 1a) can be fully indexed to rutile SnO_2 (JCPDS. No. 36-1451), with lattice constants of $a = 4.738$ Å and $c = 3.187$ Å. Compared to pure SnO_2, the Au-decorated SnO_2 products show a number of additional peaks at 38.3°, 44.6°, and 64.7°, which can be indexed to the (2 0 0), (1 1 1) and (2 2 0) planes of cubic gold (JCPDS No. 04-0784). Furthermore, the intensities of Au(2 0 0), (1 1 1), and (2 2 0) peaks are found to increase with increasing Au loading. In comparison, the XRD patterns of Pd-decorated SnO_2 nanocomposites show additional peaks at 40.1°, 46.6° and 66° as shown in Fig. 1a. These peaks can be ascribed to (1 1 1), (2 0 0), and (2 2 0) peaks of face-centre-cubic (fcc) palladium, respectively, with $a = b = c = 3.97$ Å (JCPDS No. 04-0802).