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In-situ generation of highly dispersed Au nanoparticles on porous ZnO nanoplates via ion exchange from hydrozincite for VOCs gas sensing

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ABSTRACT

The indoor volatile organic compounds (VOCs) have caught much attention because millions of people are suffering from indoor air pollution. To detect VOCs, various gas sensors with fast response, high sensitivity and high stability have been fabricated by nanocomposite technology. In this study, highly dispersed Au nanoparticles are deposited on porous ZnO nanoplates (Au@ZnO) via ion exchange method from hydrozincite [$Zn_5(CO_3)_2(OH)_6$] without the addition of any surfactants. By immersing hydrozincite precursors into 0.1%–5% $HAuCl_4$ solutions and followed by annealing, several Au@ZnO sensors with size-limited Au nanoparticles are fabricated for the detection of nine types of VOCs. Comparing with pure ZnO nanoplates, the as-prepared Au@ZnO sensors show enhanced sensitivity by 2–9 times at 400 °C toward all nine types of VOCs. Also, fast response/recovery time and fine repeatability in the gas-sensing tests are attained. More oxygen species and active sites to the adsorbed VOCs molecules are generated by Au@ZnO hybrids, which lead to the improvement of ZnO-based gas sensor limitation.

1. Introduction

Volatile organic compounds (VOCs) are emitted to the atmosphere from various industrial and natural sources. VOCs can be classified into seven groups, which are oxy hydrocarbons, halogenated hydrocarbons, aromatic hydrocarbons, aliphatic hydrocarbons, terpenes, esters and aldehydes [1,2]. The concentration of VOCs is much higher in indoors compared to outdoors, which not only pollutes the environment but also affects human health in both acute and chronic ways through breathing and skin contamination. VOCs present in several household products such as air fresheners, paints, cleansers and disinfectants, wood preservatives and automotive products etc., contribute to indoor air pollution [3]. In modern society, most of the people spend 80%-90% of their time indoors, therefore, there is an urgent need to develop fast, sensitive and cost-effective gas sensors for the detection of VOCs [4–6].

Among various types of gas sensors, the semiconductor oxides sensors hold a central position due to their unique properties such as high reproducibility, thermal stability, high surface-to-volume ratio and low tendency to form agglomerates. Metal-oxides based semiconductors such as tin oxide, indium oxide, zinc oxide and tungsten oxide have been extensively studied for their gas-sensing properties in the past years [7–14]. Among them, ZnO has been considered as one of the most potential sensing materials. Many efforts have been focused on the development of gas sensors based on ZnO nanostructures with various morphologies and composition for the detection of VOCs. Recently, hierarchical ZnO nanostructured materials have been reported with enhanced sensitivity and rapid response compared to the mono-morphological ZnO [15–18]. However, utilizing pure ZnO as sensing material are very limited to enhance response, shorten response/recovery time and extend detectable VOCs, which requires further improvement in the rational design and preparation methods [19,20]. To develop highly sensitive sensors, various strategies such as loading of noble metals, doping of transition metals, employment of core-shell structures, doping of catalytic metal oxides, use of filtering layers and altering the operating temperature have been attempted to obtain highly sensitive sensor response [21–23]. Many research groups have used noble metals (Pd, Pt, Au and Ag) for either doping or loading on metal oxide nanostructures to explore the possibility of enhancing the gas-sensing characteristics [24–29]. Recent works have dealt with Au modified ZnO nanostructures for gas sensing, which show variously effective gas-sensing improvement [30–33]. But still more investigations are needed, especially to increase the

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response and stability of the ZnO-based gas sensors toward various VOCs [34,35].

Herein, we report a highly dispersed Au loaded porous ZnO nanoplates prepared through ion exchange from hydrozincite [$Zn_5(CO_3)_2(OH)_6$] in 0.1%-5% $HAuCl_4$ solution. The porous ZnO support showed excellent control over the size and dispersity of Au nanoparticles. The synthesized Au loaded ZnO nanoplates (Au@ZnO sensors) were applied for the detection of nine types of VOCs. The as-fabricated Au@ZnO gas sensors exhibited higher sensitivity than that of pure ZnO nanoplates. The gas-sensing properties of Au@ZnO sensors were studied systematically. Finally, the gas-sensing mechanism and explanation to understand the excellent sensing performance were also discussed.

2. Experimental

2.1. Materials

Urea ($CO(NH_2)_2$), zinc acetate dihydrate ($Zn(CH_3COO)_2·2H_2O$), and chloroauric acid ($HAuCl_4·4H_2O$) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). All the reagents were analytically pure and used without any further purification.

2.2. Characterization techniques

The morphologies of the samples were examined by high-resolution transmission electron microscopy (HRTEM, Japan, JEM-2100). The phase and crystallinity of the samples were analyzed by Bruker D8 advanced X-ray powder diffractometer (XRD) with graphite monochromatized Cu K_α radiation ($\lambda = 0.15418$ Å) operated at room temperature. The oxidation state and relative chemical composition of the samples were evaluated by X-ray photoelectron spectroscopy (XPS) using a Thermo ESCALAB 250 (USA) with monochromatic Al K_α (1486.6 eV) as the X-ray excitation source. Gas-sensing properties of samples were measured using a static system controlled by a computer (HW-30A, Hanwei Electronics Co. Ltd.) under a humidity of 30%. N_2 adsorption-desorption (BET) data were recorded using micromeritics ASAP2020 HD88.

2.3. Synthesis of porous Au@ZnO nanoplates

In a typical experiment, 20 mL $Zn(CH_3COO)_2$ solution (0.2 mol L^{-1}) was added into 20 mL urea solution (0.4 mol L^{-1}), followed by ultrasonication for 10 min. Subsequently, the mixture was transferred into a 50 mL Teflon-lined stainless-steel autoclave and kept in an oven at 120 °C for 5 h. After cooled down to room temperature naturally, the precipitates were collected by centrifugation and washed three times with deionized water and ethanol before being dried at 60 °C for 12 h in air. The as-prepared products (hydrozincite [$Zn_5(CO_3)_2(OH)_6$] precursors) were calcined at 400 °C for 2 h to obtain pure ZnO.

Au@ZnO nanocomposites with different amount of Au were synthesized via ion exchange method, which can be described briefly as follows: 0.2 g of Hydrozincite [$Zn_5(CO_3)_2(OH)_6$] was suspended in 20 mL of solution containing 0.002457, 0.01229, 0.02457, 0.07372 and 0.1229 mmol $HAuCl_4$ (corresponding mass concentration were 0.1%, 0.5%, 1%, 3% and 5%, respectively) and stirred for 12 h at room temperature. The resulting precipitates were separated by centrifugation and dried at 60 °C for 12 h in air. Finally, the products were calcined at temperature of 400 °C for 2 h, and labelled as 0.1% Au@ZnO, 0.5% Au@ZnO, 1% Au@ZnO, 3% Au@ZnO and 5% Au@ZnO.

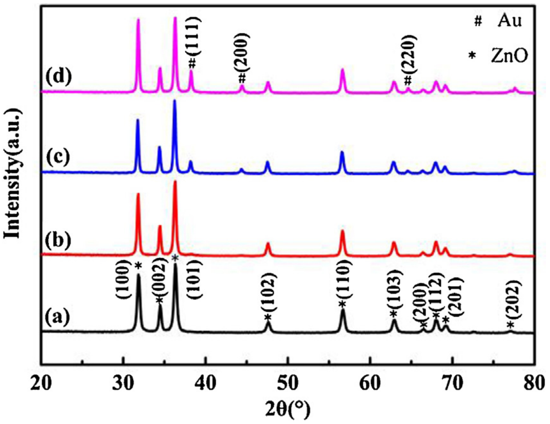

Fig. 1. XRD patterns of (a) pure porous ZnO nanoplates, (b) 1% Au@ZnO, (c) 3% Au@ZnO, (d) 5% Au@ZnO.

2.4. Gas-sensing measurements

The calcined ZnO and Au@ZnO samples were mixed with a suitable amount of ethanol to form a paste, followed by being printed onto alumina tubes with a Ni-Cr heating wire placed inside. In a typical method, 0.04 g Au@ZnO powder was mixed with 0.5 mL ethanol in mortar to form a paste, and then was printed onto alumina tubes of the component with brush. After natural drying, the component was welded onto the test platform of gas-sensing instrument by the Pt joint, and a Ni-Cr heating wire placed inside was also contacted with the test platform by welded joint. Hereto, the sensor device fabrication was finished. In order to improve the stability and repeatability, the tubes were aged at 450 °C for 120 h. The target gases (acetone, methylbenzene, formaldehyde, chlorobenzene, ethanol, ether, butyl acetate, isoprene and decane) with calculated concentration were introduced into the testing chamber on the gas-sensing test system by a microsyringe. The operating temperature could be adjusted precisely through the current flow across the Ni-Cr heater. The sensor response (R_s) was calculated by $R_s = R_a/R_g$, where R_a is the resistance in air and R_g is the resistance in target gas.

3. Results and discussion

3.1. Structure, morphology and surface species

The phase and crystal structure of the obtained materials were characterized by XRD. The XRD patterns are given in Fig. 1(a–d). As shown in Fig. 1(a), the XRD patterns of pure ZnO nanoplates match well with the standard spectrum of JCPDS 36-1451. No characteristic peaks of any other impurities are observed, which indicates the good phase purity of the obtained ZnO nanoplates. The XRD patterns of Au@ZnO materials in Fig. 1(b)–(d), suggest that all the additional three peaks are attributed to Au (111), (200) and (220) lattice planes, which can be indexed to the JCPDS No. 04-0784. A comparison among all the patterns suggests that the formation of Au particles in the deposition process has no influence on the crystal structure of ZnO. When increasing the deposition amount of Au, more crystalline Au nanoparticles are observed in the Au@ZnO heterostructures.

TEM images of the products are presented in Fig. 2(a–g). The TEM image (Fig. 2(a)) reveals that the pure ZnO nanoplates show random porous structures. Highly dispersed nanoparticles on porous ZnO nanoplates can be clearly seen in Fig. 2(b)–(d). It can also be observed in Fig. 2(b) that the Au nanoparticles are small and scarce in 1% Au@ZnO sample. The size of the Au nanoparticles on porous ZnO nanoplates increases with an increase in the amount of Au. The