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Experimental and theoretical studies of gold nanoparticle decorated zinc oxide nanoflakes with exposed $\{10\bar{1}0\}$ facets for butylamine sensing

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ABSTRACT

The exposed surface facets play an important role in determining the gas-sensing performance of nanostructured materials. This study reports the facile hydrothermal synthesis of zinc oxide nanoflakes with exposed $\{10\bar{1}0\}$ facets, as confirmed by the high resolution transmission electron microscopy (HRTEM) and the corresponding selected area electron diffraction (SAED) analysis. The gas-sensing properties of the ZnO nanoflake sensor were investigated toward toxic *n*-butylamine, an important marker compound in food and medical industries. The pure ZnO nanoflake sensor exhibits a response of 23.9–50 ppm of *n*-butylamine at an optimum operating temperature of 300 °C. Density Functional Theory (DFT) simulations were used to study the adsorption behavior of *n*-butylamine on the ZnO$(10\bar{1}0)$ surface. The results show that *n*-butylamine chemically adsorb on the ZnO$(10\bar{1}0)$ surface through the formation of a bond between the nitrogen atom of the *n*-butylamine ($C_4H_{11}N$) and the surface Zn atom of ZnO. To further improve the gas-sensing properties, the as-prepared ZnO nanoflakes were subsequently loaded with three different quantities of Au (1.37, 2.82, and 5.41 wt% Au). The gas-sensing measurements indicate that the Au nanoparticle-decorated ZnO nanoflakes display superior sensing performance to non-modified ZnO nanoflakes by exhibiting 4–6 times higher response and an improved selectivity toward *n*-butylamine gas, along a decreased optimum operating temperature of 240 °C. Moreover, the response and recovery properties of the ZnO nanoflake sensor are improved by a factor of 1.5–2.5 depending on the Au loading. The enhanced sensing performance of the Au nanoparticle-decorated ZnO nanoflakes to *n*-butylamine gas can be attributed to the excellent catalytic activity of Au nanoparticles (NPs) which promotes a greater adsorption of oxygen molecules on the surface of ZnO and the presence of multiple electron depletion layers, specifically at the surface of ZnO and at the ZnO/Au interface, which greatly increases their conductivity upon exposure to the gas.

1. Introduction

Detection and monitoring of hazardous gases in food, chemical and manufacturing industries have received increasing attention recently due to the growing awareness about public health safety [1]. Many studies have been carried out to develop high-performance gas sensors with excellent response, selectivity and stability. Among the various forms of gas sensors, semiconducting (chemiresistive) gas sensors are particularly attractive for the sensing of harmful gases, because of the low manufacturing cost, easy processing, and reliable performance. Semiconducting gas sensors usually consist of metal oxide materials, such as zinc oxide (ZnO), tin dioxide (SnO_2), iron oxide (Fe_2O_3), tungsten oxide (WO_3), and indium oxide (In_2O_3) [2].

Among these oxides, ZnO, is an important n-type semiconductor with a band gap of $E_g = 3.3$ eV, and has been widely applied for different applications including gas sensors [3,4], photocatalysts [5,6] solar cells [7,8], and lithium-ion batteries [9]. ZnO exhibits excellent thermal and chemical stability and high electrical conductivity, which makes it highly attractive for gas-sensing application [10]. However, pure ZnO sensors typically suffer from low selectivity and high optimum operating temperatures of ≥300 °C, which

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may impede their broader applications [11,12]. To reduce such problems, many efforts have been devoted in this area aiming to controlling particle size and morphology [13], maximizing the exposure of active crystal facets [14,15], and introducing transition metal dopants [11,15–19], metal oxide additives [1,17] or noble metal sensitizers [11,17,20–23].

Organic amines (e.g., *n*-butylamine) are important marker compounds for quality control in food industries and medical diagnosis [24]. *n*-Butylamine is also frequently used as a vulcanizing accelerator and reaction initiator in the polymer industries, a chemical intermediate in the production of emulsifying agents, rubber chemicals, tanning agents and special soaps. Furthermore, it is also utilized in the manufacture of pharmaceuticals, dyes, insecticides and textiles. *n*-Butylamine is toxic and is easily absorbed through skin. Direct exposure of *n*-butylamine vapor can cause eye, skin and upper respiratory tract irritation [25]. Therefore, it is necessary to develop sensor material(s) to detect *n*-butylamine gas with excellent response, selectivity, and stability. To date, atmospheric *n*-butylamine has been quantified by isotachophoresis, and by high pressure liquid chromatography (HPLC), however, these techniques require expensive equipments [26]. To date, there were few limited reports on the use of solid state semiconductor nanosensors for detection of *n*-butylamine, with only sensors based on WO_3, V_2O_5 and AgV_xO_y nanostructures have been reported so far [27–29]. The reported responses of these sensors to *n*-butylamine, however, are relatively low and require further improvement.

A clear understanding of the sensing mechanism of ZnO nanosensors is crucial for ensuring the successful application of these sensors in real life monitoring applications. Theoretical simulation studies have been carried out to investigate the adsorption of oxidizing (e.g., NO_x, SO_x) and reducing gases (CO, NH_3, ethanol) on different ZnO surfaces [30–33]. The DFT study by Breedon et al. [30,34] found that NO_2 and NO interacted weakly with ZnO$(1\,0\,\bar{1}\,0)$ and $(2\,\bar{1}\,\bar{1}\,0)$ crystal without generating any significant surface distortions. Prades et al. [32] expanded the study further by examining the adsorption of NO_2 on ZnO$(1\,0\,\bar{1}\,0)$ and $(1\,1\,\bar{2}\,0)$ crystal planes with 12.5% O vacancy and found that NO_2 was strongly adsorbed on the surface Zn atoms, in the presence of oxygen vacancies. Moreover, the DFT investigation by An et al. on the adsorption of several reducing and oxidizing gases on defect-free, single-walled ZnO nanotube reveal that O_2 and H_2 molecules were physisorbed on the sidewall of the ZnO nanotube while CO, NH_3, and NO_2 were molecularly chemisorbed. Despite some successes, theoretical simulation studies of the adsorption of organic amine (e.g., *n*-butylamine) on the ZnO surface were not yet reported. Hence, there exists a lack of clear understanding of the atomic scale interactions that occur between organic amine gas molecules and ZnO surface during the gas-sensing process, particularly in terms of: (i) the effect of the interaction on the bond length and bond angle of the amine gas molecules, and (ii) the adsorption mechanism of the amine gas molecules on the ZnO surface.

This study reports the facile hydrothermal synthesis of ZnO nanoflakes with $\{1\,0\,\bar{1}\,0\}$ facets under mild hydrothermal conditions and the subsequent modification with different Au contents (1.37, 2.82, and 5.41 wt% Au) for gas-sensing application. The morphology and composition of the as-prepared ZnO/Au nanocomposites were characterized by various analytical techniques, including transmission electron microscopy (TEM), high resolution TEM (HRTEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and inductively coupled plasma atomic emission spectroscopy (ICP-AES). The effect of the different Au loading on the sensing properties of ZnO nanoflakes toward *n*-butylamine and other gases and the important parameters such as response, selectivity and stability were evaluated. Additionally, density functional theory (DFT) simulations were also conducted for achieving a clear atomic-scale understanding of the interaction between *n*-butylamine gas (along with other gases e.g. ethanol, *n*-butanol, and acetone) and ZnO$(1\,0\,\bar{1}\,0)$ surface of the nanoflakes during the gas-sensing process.

Table 1
Summary of the synthesis conditions used for the preparation of Au-decorated ZnO samples.

Samples	V ($HAuCl_4 \cdot 3H_2O$) (μL)	V ($NaBH_4$) (μL)	Au loading (wt%—ICP)
ZnO NF/Au (1)	203	121	1.37
ZnO NF/Au (2)	508	303	2.82
ZnO NF/Au (3)	1016	606	5.41

2. Experimental

2.1. Chemicals

Zinc chloride ($ZnCl_2$, 99%), sodium hydroxide (NaOH, 99%), gold(III) chloride trihydrate ($HAuCl_4.3H_2O$, 99.99%), sodium borohydride ($NaBH_4$), *n*-butylamine ($C_4H_{11}N$, 99%) acetone (C_3H_6O, 99.9%), *n*-butanol ($C_4H_{10}O$, 99.8%), ethanol (C_2H_6O, 99.8%), methanol (CH_4O, 99.9%), and heptane (C_7H_{14}, 99%) were purchased from Sigma–Aldrich and used as received without further purification. All the chemicals were of analytical grade. Ultra-pure water was used throughout the experiments.

2.2. Synthesis of porous ZnO nanoflakes

The porous ZnO nanoflakes were prepared according to our previous report with minor modifications [2]. In a typical procedure, a mixture solution was first prepared by mixing a 40 mL solution of 0.15 M sodium hydroxide (NaOH) and a 2 mL solution of 0.3 M $ZnCl_2$. Next, the white-colored suspension was subsequently transferred into a 50 mL Teflon-lined stainless-steel autoclave and heated at 150 °C for 16 h and allowed to cool to room temperature naturally. The resulting precipitate was collected by centrifugation, washed thoroughly with deionized water and ethanol several times and finally dried at 60 °C for 5 h before further use.

2.3. Synthesis of Au nanoparticle-decorated ZnO nanoflakes

Briefly, three steps are involved in the synthesis process. Firstly, 30 mg of ZnO nanoflakes was well-sonicated in 10 mL of deionized water for 20 min. Secondly, varying quantities of a 0.01 M solution of $HAuCl_4 \cdot 3H_2O$ were added into the ZnO suspension under magnetic stirring to achieve ZnO/Au nanocomposites with three different Au loading (labeled as ZnO NF/Au (1), ZnO NF/Au (2), and ZnO NF/Au (3)). Finally, different amounts (depending on the Au loading) of freshly made 0.05 M $NaBH_4$ solution (Au^{3+}:BH_4^- = 1:3) were added into the ZnO suspension and allowed to react for 15 min under stirring. The purplish products were thoroughly washed with water and ethanol several times until the supernatant was clear and then dried in an oven at 60 °C for 5 h. The details regarding the quantities of $HAuCl_4$ and $NaBH_4$ solutions used during the synthesis process can be found in Table 1. The final Au contents in the samples of ZnO NF/Au (1), ZnO NF/Au (2), and ZnO NF/Au (3) were determined by ICP-AES to be 1.37, 2.82, and 5.41 wt%, respectively.

2.4. Characterization

The phase composition and purity of the synthesized ZnO nanoflakes were examined using Phillips X'pert Multipurpose X-ray Diffraction System (MPD) equipped with graphite monochromatized Cu-Kα radiation (λ = 1.54 Å) in the 2θ range of 20–70°. The particle morphologies were observed on a FEI Nova NanoSEM 230 field emission scanning electron microscope (SEM). TEM