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High-selective sensitive NH_3 gas sensor: A density functional theory study

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ABSTRACT

P-type metal oxide semiconductor with extraordinary surface reactions is highly active for gas sensing reactions. However, presenting large active sites in materials surface for sensing reactions is a great challenge. Here, we report a strategy to fabricate Co_3O_4 hexagonal platelets and characterize the adsorption of ammonia (NH_3) by using density-functional theory (DFT) calculations. The as-prepared Co_3O_4 hexagonal platelets exposed by (112) crystal plane shows high selectivity and sensitivity to NH_3 at room temperatures. In addition, fantastic reproducibility of the device is also demonstrated. Such alluring sensing performances can be attributed to unique size, structure, and surface arrangement on the Co_3O_4 platelets that facilitate the NH_3 adsorption and interface interaction. The present studies provided a new insight into improving the selectivity of gas sensors by designing special crystal-facets exposure in the nanomaterials surface matrix.

1. Introduction

Gas sensors are of critical importance for security and environmental applications during the past years [1,2]. There is a growing demand for gas sensors that are easy to fabricate, high sensing performances and low cost. In particular, attention is given to the excellent selectivity and high sensitivity of gas sensors, because high selectivity is predicted to exclusively respond to a certain target gas and high sensitivity can usually enhance the limit of detection, which are enable to widespread use in practical applications [3–6]. Current gas sensors are dominated by metal oxide semiconductors (MOSs)-based sensing layers, such as stannic oxide (SnO_2) [7,8], ferric oxide (α-Fe_2O_3) [9,10], and zinc oxide (ZnO) [11,12] and show high performance. Despite significant developments over the past few decades, their intrinsic high working temperature, poor selectivity and rescovery behaviours limits the widespread use of these materials. Therefore, the key challenge in this field is the development of materials with as many new properties and functions as possible.

Nanomaterials with high energy facet which have large coordinatively unsaturated active sites, can exhibit higher catalytic activity for gas absorptions [3,13]. P-type MOSs Co_3O_4 with a multiple oxidation states and the possible defect effect shows high catalytic activity and excellent conductivity than conventional n-type metal oxides [14]. In addition to its unique structural, devisable surface arrangement render it a promising sensing materials to detection target gases in sensing reactions [15]. Several works have recently been demonstrated that the high energy facet in MOSs exhibit high recognition property in detection toxic and hazardous gases [3,16–18]. For instance, Wang and co-workers demonstrated that the NiO with (101) facet, are highly active and stable in TiO_2 nanofibers matrix, which exhibits selective sensing CO gas at low temperatures [3]. Research concerning the surface adsorption of the SnO_2 (110) surface for ethanol, acetic acid, water, and oxygen has been reported by Zhou's group, which demonstrated SnO_2 (110) surface with the oxygen bridging site plays an important role in the absorption of the O–H group within these molecules [16]. Therefore, one efficient method to preparing MOSs with high-energy crystal facets is was essential to enhance the selectivity of gas sensors.

Here, we report one strategy to prepare p-type Co_3O_4 platelets with high-energy crystal facets via a simple chemical method. As the result, the hexagonal Co_3O_4 platelets with exposed {112} facets exhibit a high selective sensitivity to NH3 gas at room temperature. This experimental results and the density-functional theory (DFT) calculations confirm that high-energy crystal facets of Co_3O_4 platelets has a high active to monitoring NH_3 gas. The findings of this work provide a novel insight into understanding the selectivity of gas sensors.

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2. Experimental

The Co_3O_4 platelets were prepared following reported methods with minor modification [19]. In this work, $CoCl_2{\cdot}6H_2O$ (5 mM) was dissolved in 180 mL distilled water and 20 mL of ethanol. Subsequently Hexamethylenetetramine (HMT) was added into above mixture solution. Then, the pink solution was heated at 90 °C with a moderate stirring for 2 h. The obtained precipitates were collected and washed using deionized water and ethanol via centrifugation process. In order to remove the organic impurities, the obtained products were annealed at 350 °C for 1 h to obtain Co_3O_4 samples with hexagonal platelets structure.

The crystal structure and morphology features and interior structure of the samples were conducted via X-ray diffractometer XRD (Cu Kα radiation, λ = 1.54 Å), field emission scanning electron microscope (FESEM, 5.0 kV), transmission electron microscopic (TEM, 120 kV and HRTEM, 200 kV) and selected area electron diffraction (SAED). X-ray photoelectron spectroscopy (XPS) was carried out using a UPS/XPS system (Thermo-Fisher, ESCLAB 250, USA). Electro-sensing properties were recorded using a computer-controlled Keithley 2636 B System SourceMeter (Keithley).

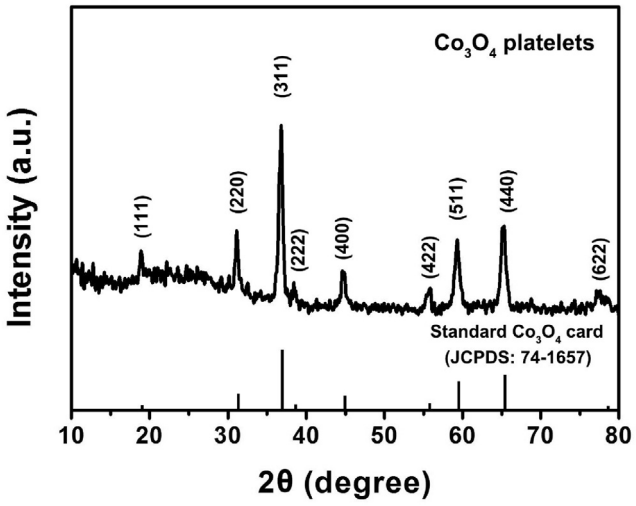

Fig. 1. XRD patterns of Co_3O_4 platelets and standard card (JCPDS: 74-1657) of Co_3O_4 nanomaterials.

3. Results and discussion

The crystal phase of the calcined product-Co_3O_4 hexagonal platelets was investigated by using XRD (Fig. 1). The primary diffraction peaks of Co_3O_4 hexagonal platelets at 19.044, 31.345, 36.935, 38.641, 44.92, 55.796, 59.508, 65.406, and 78.623° are ascribed to the (111), (220), (311), (222), (400), (422), (511), (440), and (622) planes, respectively, which are perfectly match the spinel Co_3O_4 structure with face-centered cubic (FCC) phase (JCPDS card, No. 74-1657).

The morphologies and crystalline characteristics of $Co(OH)_2$ and Co_3O_4 hexagonal platelets were further characterized by FESEM, TEM and HRTEM. Fig. 2a–b exhibits the FESEM images of the samples before and after calcined, respectively. The $Co(OH)_2$ and Co_3O_4 products both have a highly well-regulated plate-like shapes of approximately 3-4 um in lateral sizes and 50–60 nm in thicknesses (Fig. S1, Supporting information). The structure and size of the samples before and after calcined is similar. Low magnification TEM image (Fig. 2c) shows that the structure and size of Co_3O_4 hexagonal platelets is consistent with observation of FESEM image (Fig. 2b). Notably, the enlarged view of the single Co_3O_4 hexagonal platelets exhibits that the surface is rough and have some concave pores, which is benefit for adsorption and diffusion of target gases (inset Fig. 2c) [20].

Further, Fig. 2d shows a typical high-resolution TEM (HRTEM) image and selected area electron diffraction (SAED, inset) that take form the single Co_3O_4 hexagonal platelets. Lattice fringes were obtained with 0.29 nm/0.47 nm in distance, respectively, which corresponded to the (220) and (111) lattice planes of the Co_3O_4 nanomaterials (Fig. 2d). The corresponding SAED pattern (inset of Fig. 2d) combine with the analysis of HRTEM image showed as-obtained Co_3O_4 nanomaterials could possess hexagonal struc-

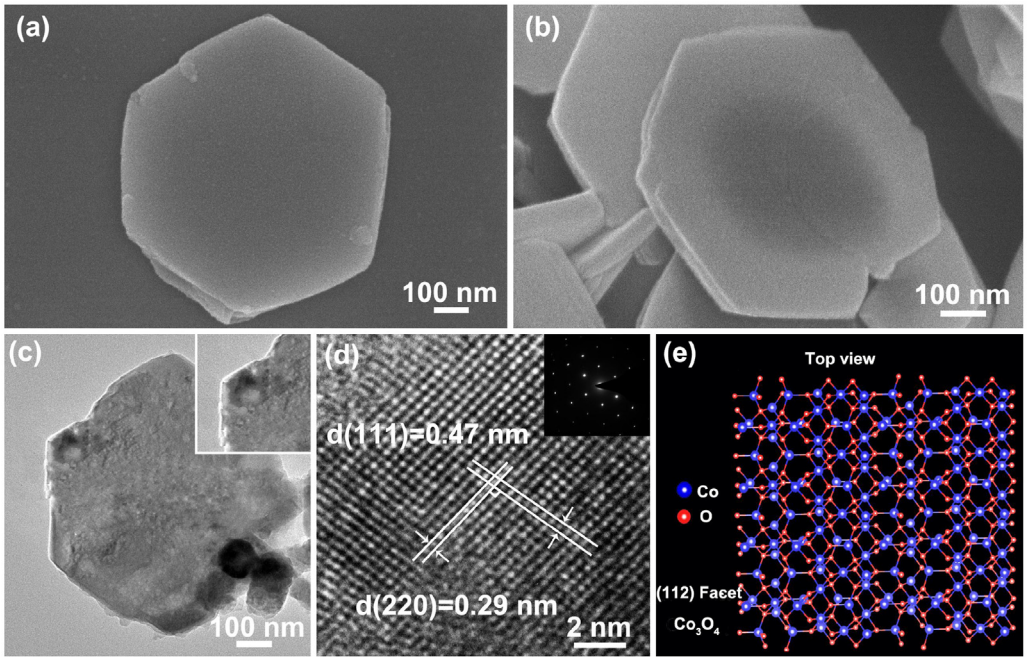

Fig. 2. FESEM images of (a) $Co(OH)_2$ and (b) Co_3O_4 hexagonal platelets. (c) TEM, (inset d) SAED, and (d) HRTEM images of Co_3O_4 hexagonal platelets calcined at 350 °C. (e) Atomic configurations of Co_3O_4 hexagonal platelets.