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PtO_2-nanoparticles functionalized CuO polyhedrons for n-butanol gas sensor application

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ABSTRACT

The CuO polyhedrons functionalized with different amounts of PtO_2 nanoparticles were synthesized by simple two-step method. The gas sensing properties of the sensors prepared by PtO_2 functionalized CuO polyhedron were studied and compared with pure CuO sensors. The electrical sensitivity values show that the response of S2-CuO ($3.5\%_{wt}$ PtO_2-CuO) polyhedron is higher than that of pure CuO polyhedron in n-butanol/air atmosphere. The sensor showed excellent reproducibility and good selectivity to n-butanol gas, and its working temperature was relatively low (180 °C), and the reaction time quickly reached 2.4 s. The enhanced properties are attributed to the structure of the CuO polyhedron and the synergistic effect of CuO and PtO_2.

1. Introduction

Metal organic frameworks (MOFs) is a coordination polymer composed of multidentate organic ligands (mostly aromatic and polyacids) containing oxygen, nitrogen and the like, and self-assembled with transition metal ions [1,2]. At present, a large number of MOFs materials have been synthesized, and most of these MOFs have high porosity and good chemical stability. Because it can control the structure of the hole and the specific surface area, MOFs than other porous materials have a wider application prospects, such as adsorption separation, catalyst, magnetic materials and optical materials [3–5]. Recently, MOFs materials have often been used as templates for the preparation of metal oxide gas sensitive materials.

Metal oxide semiconductor sensor is the use of test gas adsorption change the conductivity of the semiconductor, to stimulate the alarm circuit. Because of its very sensitive response, so the field is widely used to measure the phenomenon of gas leakage. CuO is a p-type semiconductor with a narrow band gap (Eg = 1.2 eV), which has good electrochemical and catalytic properties [6,7]. The various nanostructure of CuO materials, such as nanowires [8,9], nanorods [10], nanotubes [11,12], nanoflowers [13,14] and nanoparticles [15,16] have been synthesized and studied its gas sensitivity characteristics. W. Z. Song et al. reported prepared hierarchical CuO microspheres by a simple reflux technique combined with proper calcination , which showed great sensing performance to NO_x at room temperature in the air [17]. Y. D. Wang et al. fabricated hollow CuO fibers via a facile solution combustion method, and the CuO fibers-based sensor showed n-propanol sensing performance at 200 °C [18]. Since the CuO gas sensor has low sensitivity and slow response/recovery time, it is necessary to prepare CuO structure with loose structure and high surface activity to improve the sensitivity and speed up the reaction rate [19].

In order to improve the gas-sensing properties of CuO gas sensors, the most effective method is to introduce transition metals (Pd, Pt, Ni, etc.) [20]. For example, Ag additives as precious metals are favorable for electron transfer, and Pt is a good catalyst that can significantly increase the sensitivity of gas sensitivities [21]. Precious metal doping of oxide materials remains a challenge, mainly because it is difficult to evenly dopants in metal oxides [22–24]. There are many studies on the field of gas-sensitive materials for precious metal-modified CuO materials, but few reports of platinum functionalized CuO gas-sensing materials.

In this work, we synthesized a series of direct PtO_2-doped CuO polyhedron via simple two-step method. The structure and morphology of as-synthesized PtO_2 functionalized CuO polyhedron was studied using various characterization tools such as SEM, TEM, XRD, XPS and BET. To demonstrate the potential applications, the gas-sensing properties of the pure and S2-CuO polyhedron were investigated. It was found that PtO_2 not only improved the sensitivity to n-butanol but also

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decreased the operating temperature at which the sensitivity was maximized. The sensing mechanism was deduced in this paper. The sensors are accurate and selective to n-butanol, thus, they might be considered for practical production.

2. Experimental

2.1. Synthesis of CuO polyhedron

All of the chemical reagents used in this study were of analytical grade and were used directly without further purification. CuO polyhedrons were prepared by solvothermal and thermal annealing methods as previously reported [25,26]. 0.248 g $Cu(CH_3OO)_2{\cdot}H_2O$ and 0.148 g benzene-1,3,5-tricarboxylic acid (H_3BTC) were dissolved in a mixed solvent (36 mL) of ethanol, dimethylformamide (DMF) and H_2O in to a volume ratio of 1:1:1. This solution was transferred to a 50 mL autoclave, heated to 75 °C, and maintained at that temperature for 20 h. After the reaction, the product was washed three times with acetone and methylene chloride and dried at 60 °C for 12 h. The dried samples were annealed at 400 °C for 2 h to transformed Cu-MOF (HKUST-1) into CuO polyhedron.

2.2. Synthesis of PtO_2 functionalized CuO polyhedron

The PtO_2 nanoparticle functionalized CuO polyhedron was obtained as below. Firstly, 50 mg of the HKUST-1 was dispersed in 10 mL ethanol. Next, 1.5 mL $HPtCl_6$ (0.077 mol/L) aqueous solution was introduced into the above mixture under stirring about 4 h. The precipitate was collected by centrifugation, and washed with deionized water and absolute ethanol several times, dried at 60 °C, the dried samples was annealed at 300 °C for 2 h to obtained PtO_2/CuO polyhedron. The CuO polyhedrons with different PtO_2: 0%, 2%, 3.5% and 10% denoted as S0-CuO, S1-CuO, S2-CuO and S3-CuO, respectively.

2.3. Characterization of as-prepared powders

The powder X-ray diffraction pattern of all samples was measured on a Rigaku X-ray diffractometer with CuK1 radiation (λ = 0.15406 nm) operating at 40 kV and 150 mA. Study on the chemical composition of nanostructured surface using ESCALAB250Xi X-ray photoelectron spectroscopy. The morphology and microstructure of the samples were observed by scanning electron microscopy (FESEM JEOL JSM-7500F) and transmission electron microscopy (FEI TECNAI G2). The accelerating voltage was 120 and 200 kV. BET surface area and the corresponding Barrett-Joyner-Halenda (BJH) pore size were obtained using a micron ASAP 2010M instrument.

2.4. Fabrication of sensor

The preparation and measurement of the sensor are similar to those depicted in our previous report [27]. A suitable amount of the as-obtained materials were mixed with a few drops of ethanol to form a paste. The paste was then coated onto an alumina tube with a diameter of 1 mm and length of 4 mm. The temperature of the coating tube was controlled by adjusting the heating current using a Ni-Cr alloy wire inserted into the tube as a heater, as shown in Fig. 1. The manufactured sensor was then aged at 200 °C for 12 h to improve thermal stability and reduce response fluctuations. The gas sensing performances was measured on a commercial NMDOG Multifunctional Precision Sensor Analysis Tester (Changsha Dingcheng Scientific Instrument Co., Ltd., Hunan, China). The response is defined as Rg/Ra in which the resistors in the clean air and the target gas are recorded as Ra and Rg, respectively. The response and recovery times are defined as the time it takes for the sensor to reach 90% of the total resistance change, respectively.

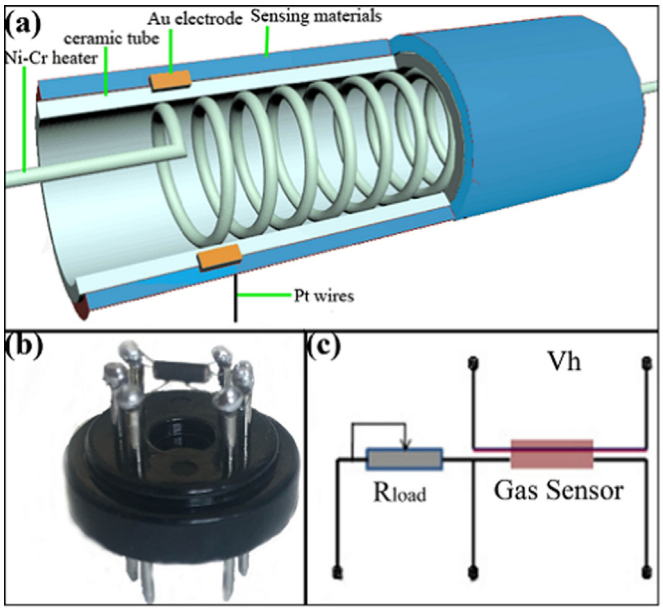

Fig. 1. The schematic structure of (a) the alumina tube, (b) sensor and (c) test circuit.

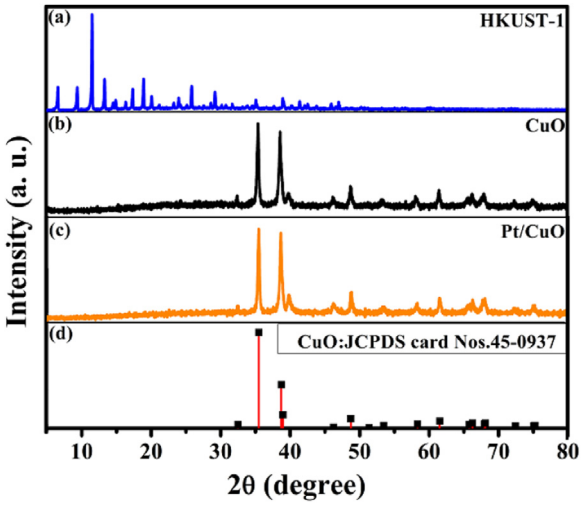

Fig. 2. X-ray diffraction patterns of the HKUST-1, CuO and PtO_2/CuO samples.

3. Results and discussion

3.1. Materials characterization

The phase composition of the as-synthesized samples was confirmed by X-ray diffraction (XRD) pattern, Fig. 2 shows the X-ray diffraction patterns of the HKUST-1, CuO and PtO_2/CuO samples. It can be seen from XRD Fig. 2(a) that the main peaks of the composites are 11.6°, 13.4° and 19.0° corresponding to HKUST-1 [26]. After the post-deposition annealing treatment, broad and well defined XRD peaks were observed for sample at 2θ = 35.49°, 38.73°, 48.72° and 61.53° (Fig. 2(b)) corresponding to (0 0 2), (1 1 1), (−2 0 2) and (−1 1 3) planes of the rutile structure of CuO (JCPDS-45-0937) [28]. However, the XRD pattern of PtO_2-CuO composites (Fig. 2(c)) does not have any other phase, such as PtO_2, suggesting the ratio of Pt content is very small [29]. To evaluate the elemental composition of as-synthesized samples, the EDS analysis of 3.5 wt% S2- CuO in Fig. 5(d) was done and three elements (O, Cu and Pt) existed at the selected region. The Pt signal in the EDS spectrum indicates that Pt ions are present in the complex.

XPS measurements were then carried out to probe the valence state

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