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Facile fabrication of chromium oxide micro/nanospheres and enhanced ethanol gas sensing performances

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ABSTRACT

Chromium oxide (Cr_2O_3) micro/nanospheres are skillfully designed and successfully synthesized by a facile route without any templates or surfactants. Morphology and structure characterizations reveal that Cr_2O_3 micro/nanospheres are assembled by irregular nanoparticles as primary building blocks and present loose hierarchical architecture. The Cr_2O_3 micro/nanospheres sensors exhibit rapid response and recovery kinetics (5 s and 6 s), good selectivity and remarkable repeatability to ethanol gas at 220 °C, and the sensitivity to 100 ppm ethanol is about 4 times higher than that of the collapsed Cr_2O_3 micro/nanospheres based sensors. The enhanced gas sensing performances are predominantly attributed to the synergistic effect of the unique sphere-like architecture and highly loose structure, thus providing beneficial conditions to greatly improve gas diffusion, adsorption and surface reaction.

1. Introduction

Metal oxide semiconductors based gas sensors have been investigated extensively owing to their controllable preparation, facile integration and excellent gas sensing performances in the detection of toxic, harmful, flammable and explosive gases [1,2]. The morphology, structure and chemical composition of oxide semiconductors play significant roles in determining their gas sensing properties. In order to improve gas sensing performances, various methods and routes have been employed to engineer and fabricate multifarious novel architectures [3,4]. Among these advanced structures, three dimensional hierarchically loose architectures comprised of much low dimensional nanobuilding blocks can provide substantial performance boosts for gas sensors because of large specific surface area, good surface permeability, low density and well stability [5].

Cr_2O_3, as an important functional material, has been investigated in many fields [6,7]. In gas sensing application, p-type Cr_2O_3 nanomaterials have exhibited the ability of catalyzing the oxidation of many volatile organic compounds. If the as-prepared Cr_2O_3 materials are of hierarchical loose architectures, it can be expected that the sensor based on Cr_2O_3 materials shows a superior gas sensing performance.

Herein, we skillfully design a facile synthesis route for the preparation of Cr_2O_3 micro/nanospheres. The as-prepared Cr_2O_3 micro/nanospheres are assembled by irregular nanoparticles and present rough surfaces and loose hierarchical structures. The sensors based on Cr_2O_3 micro/nanospheres exhibit enhanced ethanol gas sensing properties.

2. Experiments

In a typical procedure, first, 0.2g chromium nitrate ($Cr(NO_3)_3\cdot 9H_2O$) and 0.8g sodium hydroxide (NaOH) was dissolved to 15 mL and 10 mL deionized water under stirring to form a uniform solution, respectively. Subsequently, 10 mL NaOH solution was added into 15 mL $Cr(NO_3)_3$ solution under magnetic stirring. After magnetic stirring for 5 min at room temperature, 100 mL ethanol was slowly added into the above mixed solution. After being stirred for further 1 h, the light blue precursors precipitates were collected by centrifugation, washed several times with deionized water, dried in air at 60 °C for 6 h. Subsequently, the as-prepared precursors and 20 mL deionized water were added into a Teflon-lined stainless steel autoclave, maintained at 120 °C for 3 h and cooled down naturally after the reaction. The light blue precipitates were collected by centrifugation, washed several times with deionized water, dried in air at 60 °C for 6 h and then calcined at 400 °C for 10 min to obtain final Cr_2O_3 micro/nanospheres. The collapsed Cr_2O_3 micro/nanospheres were synthesized for comparison by the same approach only without the hydrothermal treatment. SEM

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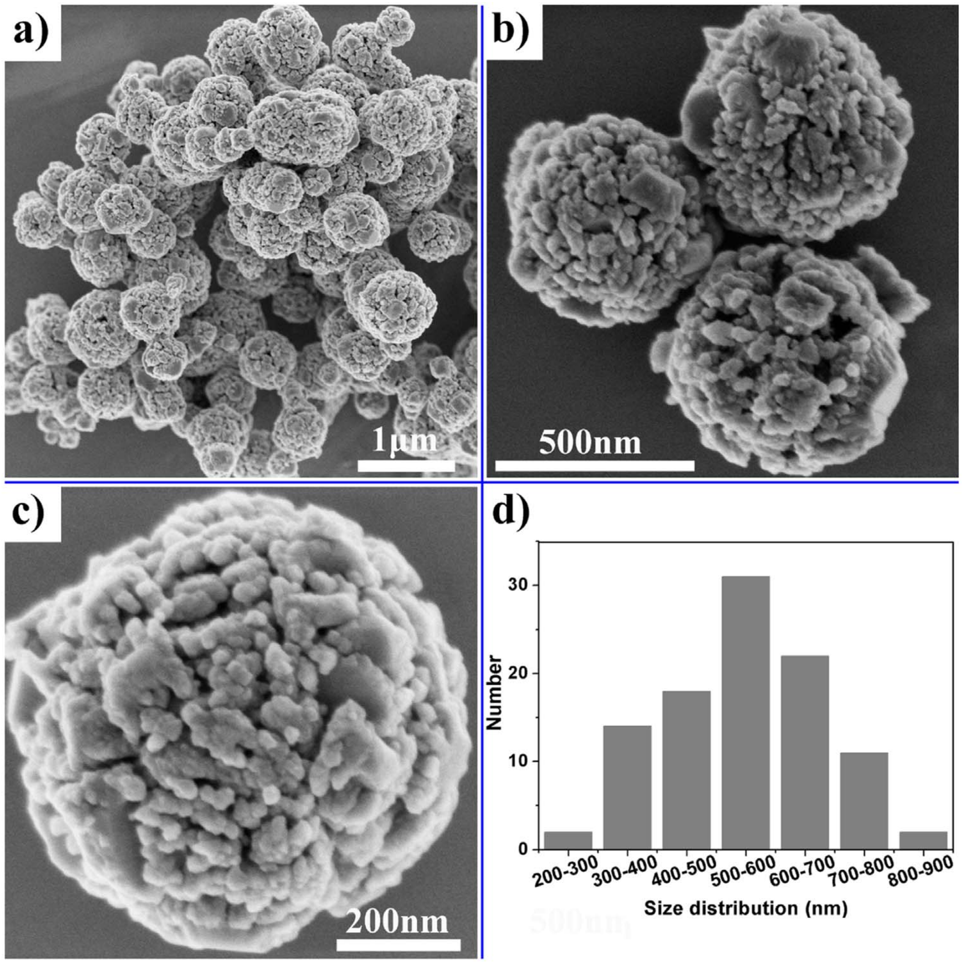

Fig. 1. (a–c) Different magnifications FESEM images and (d) the diameter distribution of Cr_2O_3 micro/nanospheres.

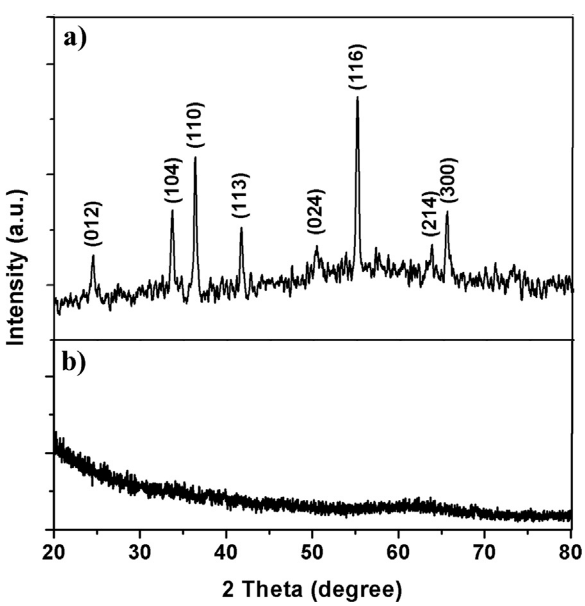

Fig. 2. XRD patterns of (a) Cr_2O_3 micro/nanospheres and (b) Cr_2O_3 precursors.

images of precursors (Fig. S1) and collapsed Cr_2O_3 micro/nanospheres (Fig. S2) were provided in Electronic Supplementary Information.

FESEM images were obtained using a JEOL JSM-6700F microscope. TEM images were obtained on a JEOL JEM-2200FS microscope. The crystal phases of the synthesized samples were characterized by X-ray powder diffraction (XRD, Rigaku D/max-Ra). The fabrication detail of the gas sensor could be found in our previous report [8]. The sensor response was defined as $S = (R_g - R_a)/R_a * 100\%$ for reducing gases. Here, R_a and R_g were the resistance of the sensors in the air and target gas, respectively. The response and recovery time was defined as the time taken by the sensors to achieve 90% of the total resistance change in the case of adsorption and desorption, respectively.

3. Results and discussion

Fig. S1 presents the typical morphology of as-prepared Cr_2O_3 precursors. The products consist of a large number of micro/nanospheres with smooth surfaces and no other morphologies can be observed. After the hydrothermal and annealing treatment, the final Cr_2O_3 micro/nanospheres are obtained. As shown in Fig. 1a, the Cr_2O_3 products are composed of numerous micro/nanospheres. Enlarged FESEM images in Fig. 1b–c clearly indicate that Cr_2O_3 micro/nanospheres are assembled by irregular nanoparticles with dimensions of tens of nanometers as primary building blocks. The obvious spaces among the neighboring nanoparticles can be clearly discerned, indicating the loose structure of Cr_2O_3 micro/nanospheres. Fig. 1d is the size distribution of Cr_2O_3 micro/nanospheres. The diameters of all micro/nanospheres imaged range from 200 nm to 900 nm, and the diameters of most micro/nanospheres concentrate in 500–600 nm.