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Full Length Article

Synthesis of Ce-doped In_2O_3 nanostructure for gas sensor applications

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ABSTRACT

Nanostructured materials with advantages in large surface-to-volume ratio and high specific surface area have demonstrated great potential in improving the gas sensing property because these structural and morphology features provide improved surface sensing activities. In this work, porous Ce-doped In_2O_3 nanospheres have been successfully prepared using a facile hydrothermal method, and their morphology, microstructure, and gas-sensing properties were characterized by X-ray diffraction (XRD), X-ray photoelectron spectra (XPS), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM) and gas sensing testing (GST). Ce doping not only enhances the response value and reduces response-recovery time but also lowers the operating temperature and retains good stability. The possible reasons for enhanced sensing properties of as-prepared Ce-doped In_2O_3 sensors were also proposed.

1. Introduction

With the increasing concern about energy efficiency and emission control, household security, food processing and detection of toxic, flammable, and explosive gases [1,2], metal-oxide semiconductor-based gas sensors (MOSBGS) have attracted continually increasing interest for their ease of fabrication, fast response, good reproducibility and high sensitivity to a wide range of target gases [3,4]. Metal oxide based sensing nanotechnology has been considered a breakthrough technology that is expected to have a great impact on the scientific community and industrial revolution [5]. Nanostructured materials with advantages in large surface-to-volume ratio and high specific surface area have demonstrated great potential in improving the gas sensing property because these structural and morphology features provide improved surface sensing activities, such as sufficient surface reactions and fast gas diffusion, based on their porous structure and high surface permeability, which allow more gas exposures and easy gas sensing [6]. As a significant *n*-type wide band gap semiconductor material [7–9], indium oxide (In_2O_3) has been explored for gas sensors owing to its wide variety of structures or morphologies such as nanoparticles [10], hexagons [11], nanocubes [12], nanoflower [13], nanosheets [14], nanowires [15], hierarchical and hollow structures [16,17]. Designing and constructing In_2O_3 nanomaterials with the novel morphology and porous structure still have important scientific and practical significance for the promotion of gas sensing performances and the development of gas sensors. Furthermore, it has been established that the surface states of In_2O_3 could be easily regulated in various ways, such as oxide composites [18], doping [19] and heterojunction forming [20], among which doping of metal elements is of advantage for their gas-sensing enhancement, which makes it possible to obtain an ideal gas sensor with outstanding sensitivity, good selectivity, and low cost [21].

Glycol is an intermediate volatility organic compound frequently utilized in various fields, including the oil, gas, resin synthesis, and paper industries. In the atmosphere, glycol can be oxidized either in the gas phase or in the aqueous phase following uptake to a cloud, fog, or wet aerosol particle. It exhibits great damage to health, such as respiratory difficulty and pulmonary edema. It also affects the nervous system and even causes death. However, as far as we know, there are few studies using the In_2O_3 nanoporous structures for glycol gas-sensing applications. Here in our work, we demonstrated a simple novel hydrothermal method to synthesize Ce-doped In_2O_3. The effect of Ce doping on structures and morphologies of as-synthesized In_2O_3 sample were investigated. Furthermore, the gas-sensing properties of Ce-doped In_2O_3 and pristine In_2O_3 for glycol gas have been performed. The results indicated that the as-obtained Ce-doped In_2O_3 porous nanospheres exhibited significantly enhanced gas-sensing performance to glycol gas, including high response, good selective and short response and recovery times, which is due to the high surface area, abundant active sites. The gas-sensing mechanism of as-prepared Ce-doped In_2O_3 sensors was also proposed.

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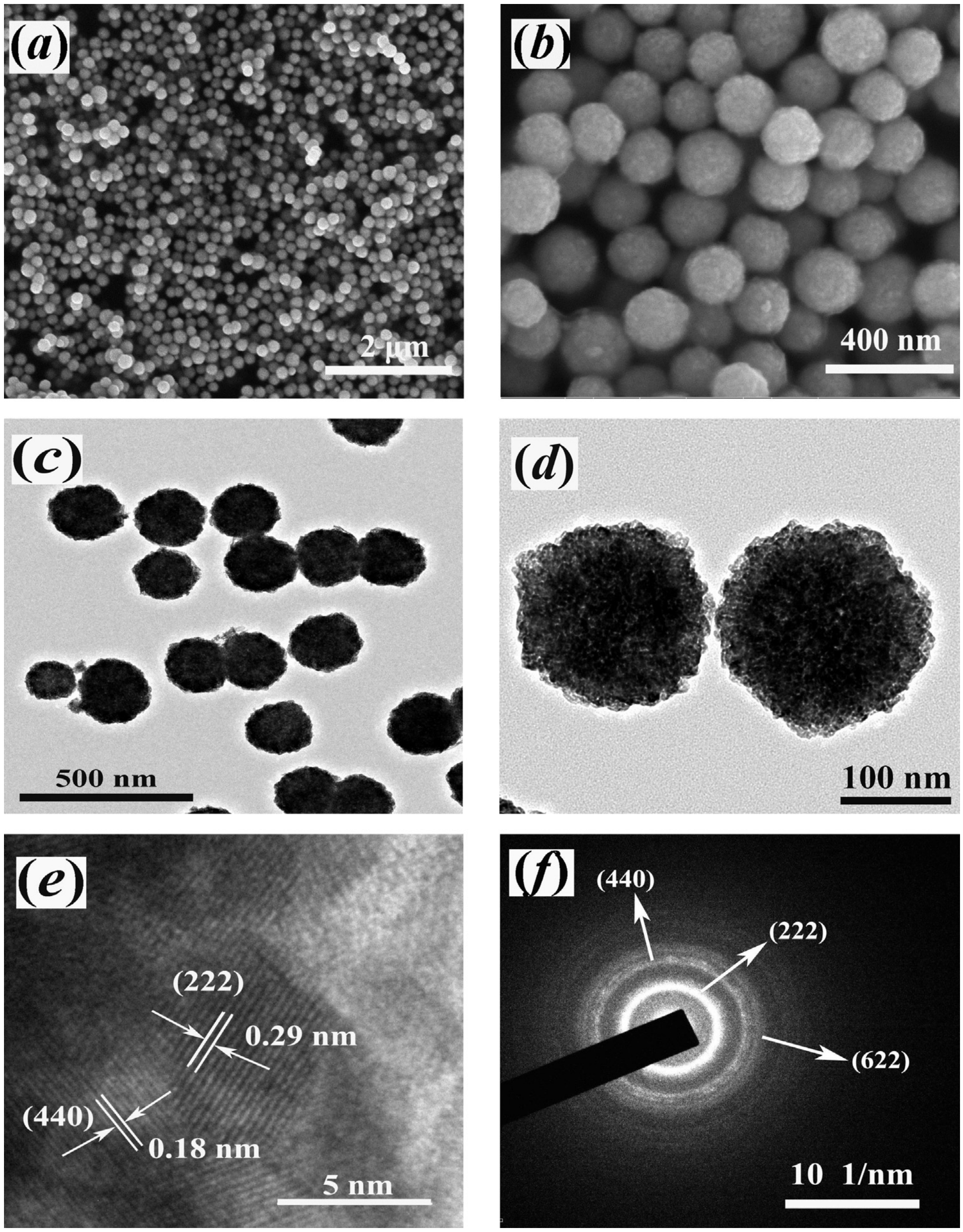

Fig. 1. (a and b) Low and high magnification SEM images; (c and d) TEM images; (e) HRTEM image with their SAED pattern (f) of Ce-doped In_2O_3.

2. Experimental procedure

2.1. Materials preparation and characterization

Ce-doped In_2O_3 microspheres were synthesized by using a simple hydrothermal method. In a typical experiment procedure, details of the experiment were as follows: 2 mmol $InCl_3{\cdot}4H_2O$, 0.08 mmol $Ce(NO_3)_3{\cdot}6H_2O$, 5 mmol citric acid and 30 mmol urea were dissolved in the mixed solution of 30 mL deionized water and 30 mL ethylene glycol to form a homogeneous solution under magnetic stirring for 50 min, which was then transferred into a 100 mL Teflon-lined stainless steel autoclave and under heat treatment at 160 °C for 24 h. When the autoclave cooled down to the room temperature naturally, the products were collected by centrifuging at 9000 rpm and sequentially washing with distilled water and ethanol for several times. Finally, the Ce-doped In_2O_3 samples were dried at 60 °C overnight and annealed at 400 °C for 4 h in muffle furnace. Undoped In_2O_3 porous nanospheres was obtained by the same process with free addition of $Ce(NO_3)_3{\cdot}6H_2O$.

The samples were characterized by using X-ray diffraction (XRD, D8-Advance, Bruker) with Cu K_α radiation, a field emission scanning electron microscope (FESEM, FEI QUANTA FEG250) equipped with energy dispersive X-ray spectroscopy (EDX, INCA MAX-50), a high-resolution transmission electron microscope (HRTEM, JEM-2100F). X-ray photo-electron spectroscopy (XPS) was performed on a Thermo ESCALAB 250XI electron spectrometer equipped with Al K_α X-ray radiation ($h\nu = 1486.6$ eV) as the source for excitation. The average pore size, pore volume, and specific surface area of the samples were examined through measuring N_2 adsorption-desorption isotherm with a Micromeritics ASAP2020 apparatus.

2.2. Gas sensing tests

The details of gas sensor fabrication have been reported in our previous work [22]. After the homogeneous paste of the obtained