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Growth of porous ZnO single crystal hierarchical architectures with ultrahigh sensing performances to ethanol and acetone gases

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ABSTRACT

Three-dimensional (3D) porous ZnO hierarchical architectures have been fabricated through annealing the zinc hydroxide carbonate precursor, which was obtained by a one-pot hydrothermal process with the assistance of carbon nano-fiber and cetyltrimethyl ammonlum bromide (CTAB). The ZnO hierarchical architectures are assembled from porous single crystal ZnO nanosheets. Experiment evidence reveals that carbon nano-fiber plays an important role in the formation of 3D hierarchical architectures. The growth mechanism of the 3D porous ZnO hierarchical architectures has been proposed based on control experiments. Gas sensing test results show that as prepared 3D porous ZnO hierarchical architectures exhibit superior sensing performance to ethanol and acetone. The sensor response to 100 ppm ethanol and acetone are 340 and 362 at the optimum operating temperature of 370 °C and 300 °C, respectively. The superior gas sensing performances are attributed to the unique 3D porous hierarchical architectures structure, the single crystal nature and the exposed polar crystal faces of ZnO nanosheet.

1. Introduction

As a typical n-type semiconductor, zinc oxide (ZnO) has been extensively investigated and widely applied in various areas, such as gas sensor [1], nano-generators [2], field emission [3–5], catalyst [6–8] and photodetectors [9,10]. In particular, ZnO has been used as one of the predominant sensing materials because of its excellent sensing performance. So far, ZnO based gas sensors are considered have potential applications in industry safety and environment monitoring system [11–15]. Recently, gas sensors are reported have potential application in disease diagnosis through detecting the disease-related volatile organic compounds (VOCs) [16–18]. Therefore, until recent years, great efforts still devoted to further improving its gas sensing properties including high sensitivity, low optimum operating temperature and fast response rate.

Previous research indicates that the gas sensing performance of the devices is greatly influenced by the morphology and microstructure of sensing materials, such as shape, particle size and specific surface area [19]. Until now, intensive efforts have been directed to prepare ZnO sensing materials with novel morphology and microstructure, including nanoparticles [20], nanorods [21], nanowires [22], nanosheets [23] and flowers [24]. Among those nano and mirco-structures, three dimensional (3D) porous ZnO structures have drawn remarkable attentions in gas sensing research areas due to the fact that the hierarchical architectures structure can provide large contacting surface area for sensing reaction and abundant channels for gas diffusion. For example, Wang et al. reported 3D porous ZnO foam structures with trace level detection ability of triethylamine and ethanol [25]. Ge and co-authors fabricated 3D porous ZnO microspheres with excellent gas sensing performance to acetone [26]. Li et al. reported multilayered ZnO nanosheets with 3D porous architectures with excellent gas sensing properties than ZnO nanocrystals [27]. Our previous works also displays that the nest-like 3D porous ZnO structure show high sensor responses and fast response and recover rate to acetone and ethanol detection [28]. All of the above reports confirm that the 3D porous hierarchical architectures structure have great benefit for enhancement of their gas sensing properties.

In addition of morphology and microstructure, the exposed crystal plane of ZnO is considered as another main influencing factor to its physic and chemical properties. ZnO crystal exposed {0001} facets are desired enhancement in various areas such as luminescent devices [29], photocatalytic decomposition [30,31], solar cells [32], catalyst [33] and so on. Especially, the gas sensing performance of ZnO is relative to its exposed planes. Previous researches display that ZnO nanodisk networks with an exposed polar {0001} surfaces have enhancement gas sensing properties to ethanol than that of sample exposed other crystal faces [34]. Tian et al. reported that the effect of exposed facet is dominant rather than the size effect and the gas

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sensing properties of ZnO crystal facets is {0001} > {10$\bar{1}$0} [35]. Silva and co-workers reported ZnO exposed polar facets used for high performance UV activated gas sensors [36]. All the above reports confirm that the exposed crystal facets is an dominant factor to the gas sensing performance of ZnO because the polar face provide more active sites for oxygen adsorption and the subsequent reaction than other crystal facets.

It is believed that the gas sensing properties are related to the gas diffusion, active site and electronic transmission. 3D porous ZnO hierarchical architectures may provide abundant gas diffusion transports, the exposed polar facets provide a mass of active site and the single nature promotes the electronic transmission. Herein, we report a facile approach to prepare ZnO porous hierarchical architectures assembled from nanosheets with single crystalline nature exposed {0001} polar crystal face, in which the precursor is prepared through a hydrothermal process using zinc acetate, urea, cetyl trimethyl ammonium bromide (CTAB) and carbon nano-fiber as raw materials. The ZnO porous hierarchically structures were obtained by thermal-decomposing the precursor, and the growth process was investigated on the base of the control experiments. The gas sensing test results showed that the obtained porous ZnO hierarchical architectures showed a superior sensor response to ethanol and acetone.

2. Materials and methods

2.1. Materials

All reagents were of analytical grade and used as received and without any further purification. Zinc acetate $(CH_3COO)_2 \cdot 2H_2O$, urea $(CO(NH_2)_2)$, cetyl trimethyl ammonium bromide (CTAB) were purchased from Sinopharm Chemical Reagent Co., Ltd. Carbon nano-fiber (Fig. S1) with diameter of about 50–100 nm was purchased from Nanjing XFNANO Materials Tech Co., Ltd. The surface of carbon nano-fiber is smooth.

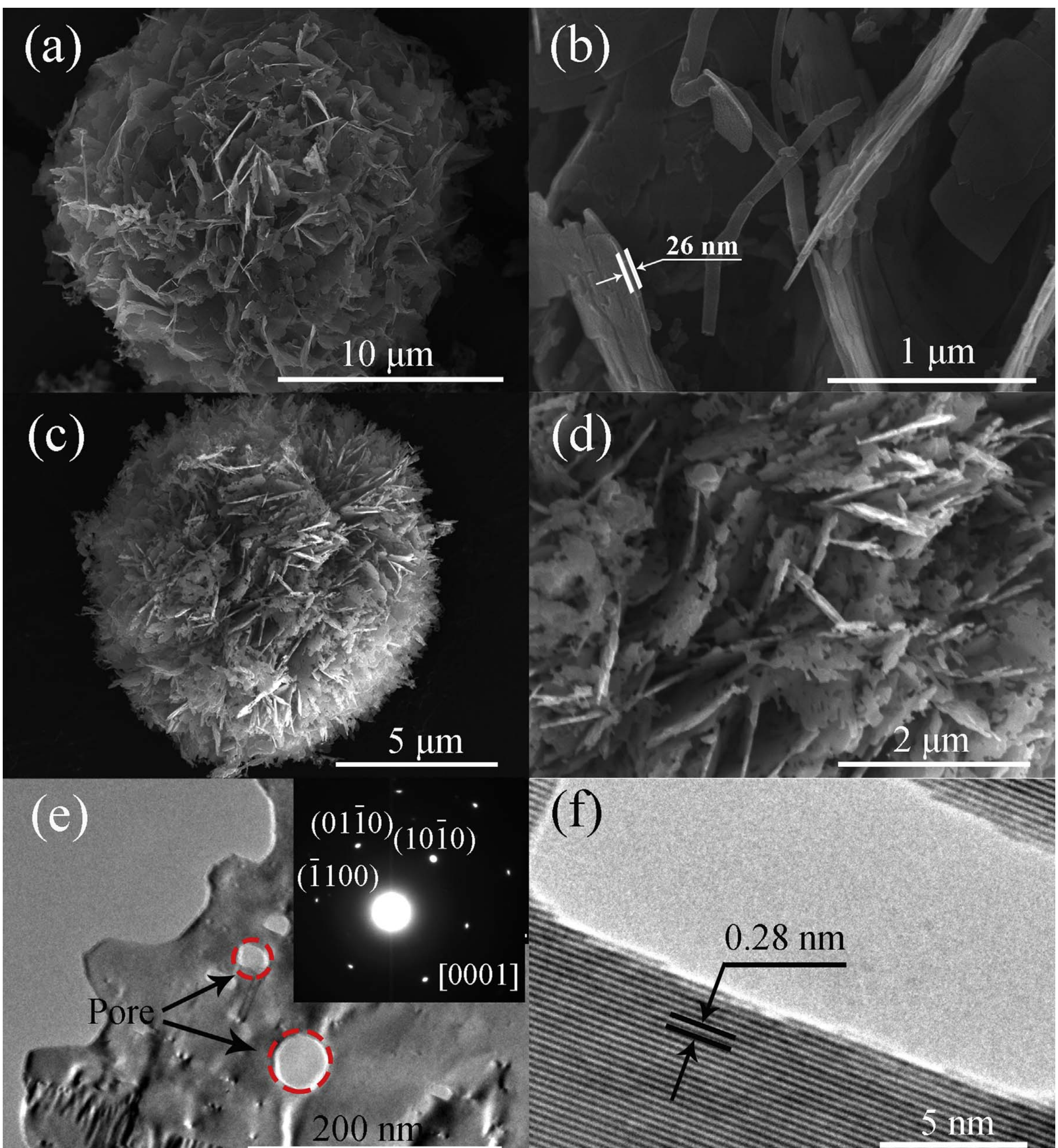

Fig. 1. (a, b) SEM images of precursors at different magnifications, (c,d) SEM and (e, f) TEM images of porous ZnO hierarchical architectures. The inset of (e) is the selected area electron diffraction (SAED) pattern.