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Enhancing ethanol detection by heterostructural silver nanoparticles decorated polycrystalline zinc oxide nanosheets

Liyang Lin[a,b], Tianmo Liu[a,*], Yu Zhang[a], Xiaobin Liang[b], Rong Sun[b], Wen Zeng[a], Zhongchang Wang[b,*]

[a]College of Materials Science and Engineering, Chongqing University, Chongqing 400030, China
[b]Advanced Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan

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Abstract

Noble metals decorated two-dimensional nanostructures with a large surface-to-volume ratio raise substantial promise for many technological applications particularly for high-performance chemical sensing. Here, we design and synthesize a hierarchical heterojunction comprising ultrathin two-dimensional polycrystalline ZnO nanosheets on a large scale, which serve as reaction positions for reduced gases, and uniformly dispersed Ag nanoparticles to enhance reaction activity. We find that the Ag nanoparticles in the heterostructural system act as strong electron acceptors, inducing remarkable surface space charge layers. As a result, the heterostructural system shows significantly improved gas-sensing performance to ethanol as compared to pure ZnO. Such metal nanoparticles decorated two-dimensional polycrystalline ZnO nanosheets can be applied in not only as gas-sensing but also catalytic and photocatalytic fields.

Keywords: Polycrystalline ZnO two-dimensional nanosheets; Ag nanoparticles; Heterostructure; Ethanol sensors; Ultrahigh sensitivity

1. Introduction

Decorating transition metal oxides (TMOs) with metal nanoparticle is currently a subject of intensive study in that the formation of metal–semiconductor heterojunction holds substantial promise for a wide range of technological application, e.g. in sensing, electrochemical, catalytic, and photovoltaic fields [1–6]. In such heterostructural systems, the morphology of ZnO and metal nanoparticle of choice are of fundamental scientific relevance because their surface states and charge transfer can be remarkably modified, thereby mediating property shift. In particular, Schottky barriers might form between the transition metal oxides and metal nanoparticles, causing Fermi level of the whole system to shift upward, influencing much functionality of the heterojunctions [7,8].

Zinc oxide (ZnO) represents such *n*-type semiconductor (3.37 eV), which shows excellent performances in gas sensing, photocatalysis, piezoelectricity, and so on. In all these applications, ZnO gas sensors have attracted a great deal of attention because they can meet the demands of industrial production and people's daily life due to their outstanding performances. To further improve its gas-sensing functionality, two ways are often adopted. One is to enhance electron mobility by designing a heterostructural system, such as ZnO–SnO_2 [9], ZnO–TiO_2 [10], and ZnO–Au–Pd [11]. Of these systems, noble m"bodyetal doped systems show better flexibility in morphology and more marked electron transfer than metal oxide doped ones. The other way is to increase surface-to-volume ratio by fabricating nanostructures with well-designed morphologies. To date, a series of ZnO nanostructures have been reported such as the one-dimensional (1D) nanorods, nanowires, and nanotubes [9,12–14], the 2D nanosheets [15] and nanocombs [16], and the assembled 3D nanostructures [17–22]. Among these nanostructures, ultrathin 2D nanosheets can

*Corresponding authors.
E-mail addresses: tmliu@cqu.edu.cn (T. Liu), zcwang@wpi-aimr.tohoku.ac.jp (Z. Wang).

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increase significantly surface-to-volume ratio due to their confined thickness, thus increasing the effective reaction surface regions by several orders of magnitude [23–25]. Nevertheless, it remains challenging to fabricate the ultrathin 2D TMO nanosheets on a large scale [26], especially the ultrathin ZnO nanosheets.

Here, we combine these two technical routes to fabricate ultrathin polycrystalline ZnO 2D nanosheets (ZnO-PNSs) decorated with ultra-small Ag nanoparticles using a simple yet efficient hydrothermal method. The metal Ag is selected purposely because it is a cheap noble metal, yet shows excellent gas sensitivity. We demonstrate that the ZnO-PNSs have a small thickness of ~10 nm and a grain size of ~10 nm, on which Ag nanoparticles of 10 nm are homogeneously dispersed. We also prepare the Ag-doped ZnO-PNSs with various Ag concentrations and probe systematically their gas-sensing properties. The Ag-decorated ZnO-PNSs are found to have excellent gas sensitivity even at an ultralow ethanol gas concentration, offering evidence to the fundamental impact of the sheet-particle heterojunction on gas-sensing functionalities.

2. Experimental section

2.1. Sample preparation

All chemicals were used as-received with no further purification, including zinc acetate dihydrate ($C_4H_{10}O_6Zn$, AR, 99.0%), hexamethylenetetramine (HMTA, AR, 99.0%), silver nitride ($AgNO_3$, AR, 99.8%), ultrapure water, and ethanol (C_2H_6O, AR, 95.0%). The ZnO precursors were synthesized with the hydrothermal method. The 0.5 mmol Zinc acetate dihydrate (0.12 g) and 0.3 mmol HMTA (0.042 g) were first added into 40 mL H_2O to form a solution under stirring for 30 min. The transparent solution was then transferred into a Teflon liner stainless-steel autoclave (50 mL) and heated at 110 °C for 15 h. The ZnO precursors were finally washed with ethanol and water and dried at 60 °C for 12 h. The harvested white products were subsequently annealed at 400 °C for 2 h. To synthesize Ag-doped ZnO, the as-prepared ZnO (60 mg), $AgNO_3$ and PVP (1.8 mg) were dispersed into the DMF solution (30 mL) under stirring for 1 h, in which a variety of weight ratios were adopted for the Ag, i.e. 2%, 5%, 10%, 15%, and 25%. The suspension

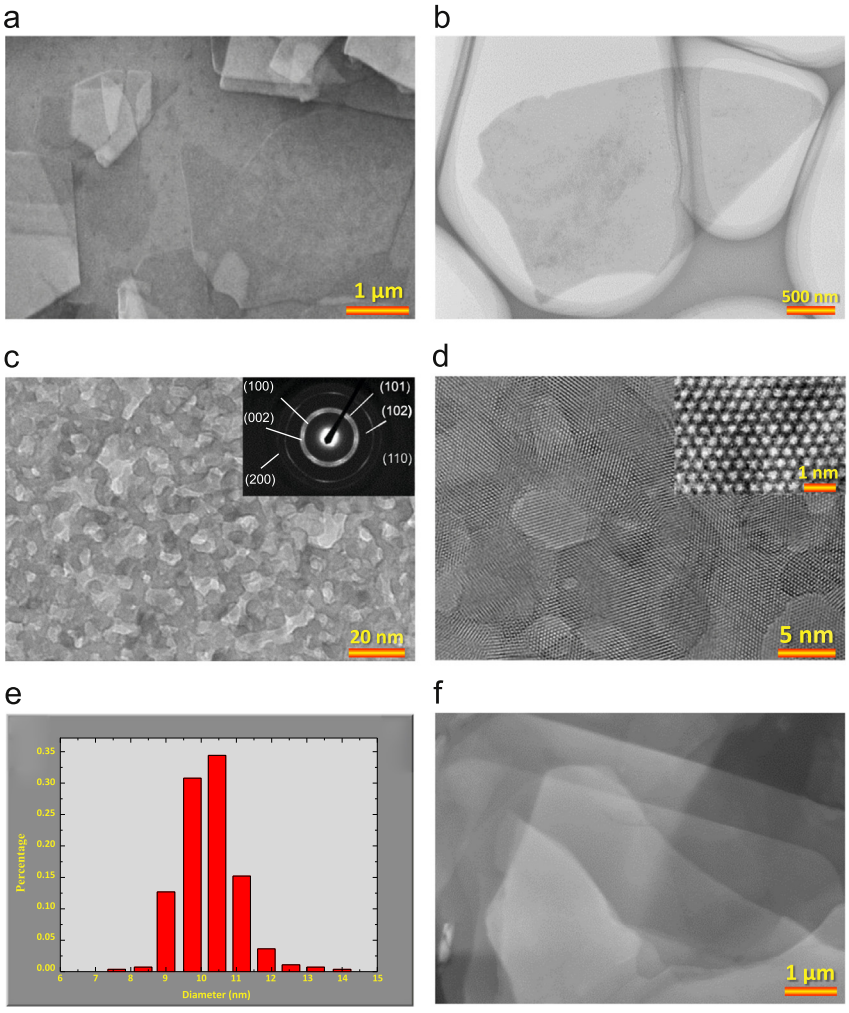

Fig. 1. Identifying two-dimensional polycrystalline ZnO nanosheets. (a) SEM image of the nanosheet. (b) Low-magnification TEM image of a nanosheet. (c) Magnified TEM image of the nanosheet. The inset shows the selected-area diffraction pattern (SADF). (d) Aberration-corrected high-resolution TEM image of the nanosheet. The inset gives a magnified HRTEM image of a local region. (e) Diagram of the size distribution of the monocrystalline ZnO particles. (f) SEM image of the precursor.