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Zinc oxide nanotetrapods with four different arm morphologies for versatile nanosensors

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ABSTRACT

The structural morphology of metal oxide nano- and microstructures plays a crucial role in the performances of sensors and especially of nanosensors. Here, a simple approach on the synthesis of three-dimensional (3D) highly porous ZnO nano- and microstructure networks with four different arm morphologies in the same process is reported. Systematic studies about the growth of micro- and nanotetrapods were performed and the corresponding mechanism has been discussed in detail. The difference in the morphologies of the obtained structures was understood on the basis of synthesis temperature variations, content of Zn vapor and oxygen in the furnace at different locations, which result in different growth rates along the ZnO *c*-axis. The approach developed in this work gives the possibility to simultaneously grow the interconnected networks of nano-ZnO-tetrapods (T), ZnO-T, with complex arm morphologies, ZnO-T-nanosheets, and ZnO nanowires (NW)-T. The obtained free-standing network material was integrated in an electronic device for gas/vapor sensing investigations. The individual structures with different morphologies (NW with a diameter down to 30 nm, two interconnected NWs, microsheets, and nanotetrapods with a diameter of the arms in the range of 40–80 nm) were integrated into nanosensor devices in order to investigate the influence of the morphology on the electrical and gas sensing properties. The results showed higher ($S \approx 510$–2500 ppm) ammonia vapor sensing properties of ZnO-T compared to ZnO-T-nanosheets and ZnO-NW-T, revealing the importance of nano-junctions in nanosensor devices. The presented approach offers the possibility to understand the importance of exposed facets and junctions on the sensing properties of such nanostructures. These results offer new opportunities for further experimental and fundamental studies of oxide morphologies in the context of nanosensor applications for environmental monitoring.

1. Introduction

Nano- and microstructures of semiconducting metal oxides with various morphologies are desirable for many applications in the fields of gas sensing, biosensing, visible-blind UV photodetectors, photocatalysis, nanosensors, etc. [1–3]. In general, the performance of nanomaterial critically depends on its size and morphology [4–8]. Several experimental studies have demonstrated the importance of a higher surface-to-volume ratio for obtaining the enhanced gas sensing performances utilizing nanostructures [5,9]. However, the decrease in the size of the semiconducting oxide nanostructures leads to different critical issues such as agglomeration, which impacts the porosity [9]. The surface is the most relevant aspect with respect to gas sensing applications in materials with low porosity. A larger fraction of the material cannot participate in chemical processes as it remains inaccessible to gaseous and biological analytes during tests or device operations. In conventional gas sensing devices, the sensor nanostructures are usually fabricated via paste deposition or by using simple drop casting of the free-standing sensing material, i.e. nano- or microstructures of the semiconducting oxides. But in such arrangements, the entire

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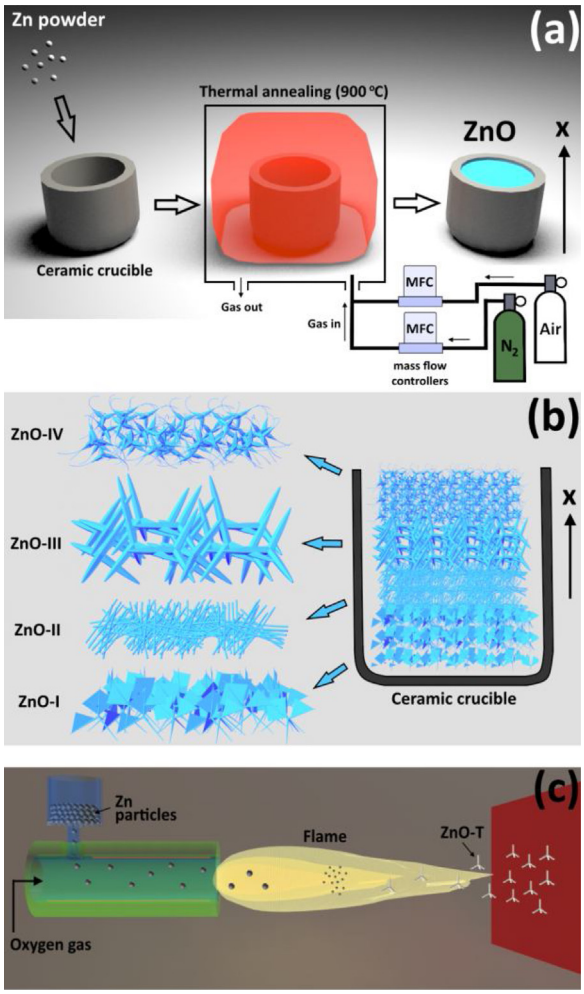

Fig. 1. (a) Schematic representation of the synthesis process for the hierarchical ZnO nanotetrapodal structures using a simple ceramic crucible and a muffle furnace. (b) The morphological distributions of tetrapodal ZnO nano- and microstructures in the ceramic crucible after the synthesis process. Schematic representation of the synthesis process for the hierarchical structures: (c) ZnO nano- and microstructures continuous synthesis process with the miniJet or burner transport synthesis (BTS) approach.

surface of the involved sensing nanomaterial is unexposed to the reference gas molecules and hence a moderately low sensing performance is achieved [9].

In this context, the variety of ZnO morphologies is one of the most impressive among other metal oxides, as well as the diversity of synthesis methods [1,3,9,10]. Among all morphologies, the ZnO tetrapods attracted special interest due to their unique physico-chemical performances and self-assembly properties for applications in gas sensing, biosensing, optoelectronics, piezoelectricity, nanoelectronics, and more [7,9–12]. Another important advantage of 3D tetrapods compared to one-dimensional nano- and microstructures is the possibility to fabricate multiterminal devices based on individual structures to extend the family of electronic devices and explore their functionalities [7,11,12]. Several methods were reported for synthesis of ZnO tetrapods, including the thermal-evaporation method [13,14], the aqueous solution method [11,15], and the flame transport synthesis [7,9,10,16,17]. However, reliable cost-effective methods providing the possibility to easily and essentially change the morphology of ZnO nano- and microstructures are desirable.

In this work, we report on a simple one-step method for synthesizing highly porous ZnO nano- and microstructure networks with different morphologies for ammonia vapor (25% NH_{3aq}) sensing applications at room temperature. Structures with four different arm morphologies were synthesized in one single step process demonstrating excellent room temperature ammonia sensing properties. Structural (XRD, TEM), morphological (SEM) and vibrational (micro-Raman) properties were studied in detail. The growth mechanism of different morphologies during the same process has been proposed and discussed. The sensing investigations demonstrated that the ZnO tetrapods networks with long wire-like tips exhibit the highest performances due to formation of more potential barriers within the interconnected 3-D network. For a better understanding of the influence of such parameters as most exposed crystalline planes, the diameter of the NW and the role of the junctions in the core of the tetrapod, as well as between individual NWs, the individual nano- and microstructures of ZnO were integrated into sensor devices and their sensing properties were studied. The obtained results demonstrate the importance of the morphology and porosity of versatile ZnO nanostructures for sensing applications of ammonia which is a corrosive, bio-hazard, and dangerous for environment reagent.

2. Experimental section

The synthesis method of highly-porous and self-assembled ZnO nano- and microstructure networks is based on direct thermal oxidation of Zn metal powder in a furnace. A defined amount of Zn powder (Sigma Aldrich, <10 μm, ≥98%, CAS#: 7440-66-6), usually about 2 g, is distributed inside a ceramic crucible. The crucible is put into a furnace (Nabertherm LE2/11) which is preheated to 900 °C and is continuously flushed with Nitrogen gas (N_2). The N_2 flow is regulated to around 150–200 l/h. After two minutes process time the gas flux is changed from N_2 to pressured air to supply oxygen to the system. The process is stopped after another ten minutes by either switching off the furnace and letting it cool off or by taking out the crucible. In both cases, the process yielded a white cotton-like product with a very low density. The overall synthesis process takes only ≈12 min and is presented in a schematic shown in Fig. 1a. Scanning electron microscopy (SEM) investigations demonstrated that the observed morphologies of tetrapod arms mainly depend on the locations in the crucible from where they have been harvested, as indicated in Fig. 1b. Four major different regions were distinguished and the samples taken from the bottom (I), lower mid (II), upper mid (III), and top (IV) of the ceramic crucible are identified as ZnO-I, ZnO-II, ZnO-III, and ZnO-IV, respectively.

Morphological investigations were performed by SEM (Ultra 55 Zeiss FEG at 7 kV). Structural properties were investigated using a high-resolution X-ray diffractometer (Siemens D5000) operated at 40 kV and 10 μA using the CuKα_1 radiation (λ = 1.5406 Å). Structural investigations in real and reciprocal space were performed by methods of transmission electron microscopy (TEM) on a FEI Tecnai G^2 Twin microscope operating at 300 kV, as was described previously [9,18]. Micro-Raman spectra were measured with a Raman WITec Alpha300 RA spectrometer in a backscattering configuration interfaced with a digital photometer and data acquisition processor. A 532 nm line from Nd-YAG laser was used for excitation.

Gas sensing measurements were performed at room temperature (≈25 °C) as described previously [6,18]. The test gas was mixed with ambient air (30% RH) in order to obtain the necessary concentration and the total flow rate was maintained at 500 sccm. All nanosensors demonstrated typical *n*-type electrical behavior, i.e., an increase in current of the device under exposure to reducing gases. Liquor ammonia (25%) was used as a source of ammonia vapor. The RH of ammonia vapors was measured to be ≈ 50%. The gas response was defined as the ratio of current under exposure to gas (I_{gas}) and in the air (I_{air}). The response (t_r) and recovery