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Importance of Hierarchical Nano-Morphology for High Performance Potentiometric Sensors

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Abstract

Hierarchical nanostructured materials have been widely studied in many fields like semiconducting gas sensors due to the peculiar properties arising from the large surface/volume ratio. Nevertheless, similar studies have been rarely conducted for mixed-potential gas sensors. The response of such sensors is governed jointly by the rate of electrochemical reactions at the three phase boundary and of the heterogeneous reaction at the electrode surface, and thus closely related with the morphology and microstructure of the electrodes. In this work, a planar mixed-potential sensor was prepared based on SnO_2 sensing electrode of hierarchical porous hollow nanofibers. As compared with a similar sensor with sensing electrode of SnO_2 nanoparticles, the nanofiber sensor exhibited much superior H_2 sensing performance, achieving 5 times larger response values and 2.6 times shorter response time at 450 ºC for 1000 ppm H_2. Moreover, excellent selectivity, long-term stability, and repeatability were also achieved. The morphology-dependent sensing behavior will be discussed in terms of the diffusion-reaction process. These results highlight the importance of morphology to mixed-potential gas sensors, and show that hierarchical nanofiber electrode is desirable for achieving high gas sensing performance.

Key words: Hierarchical nanostructure, mixed-potential, gas sensor, morphology, diffusion-reaction.

Introduction

Mixed potentiometric gas sensors have attracted great interest recently. The sensing performance of mixed potentiometric sensor is closely related to the microstructure of the electrode [1]. Hierarchical nanostructured materials have been widely studied in many different fields such as semiconducting gas sensors [2]. Nonetheless, so far there is very limited research on mixed potential sensors with nanostructured morphologies.

Herein, two sensors attached with SnO_2 nanofibers (NFs) and SnO_2 nanoparticles (NPs) were prepared, respectively. The sensing performance of the sensors was systematically studied.

Preparation and Characterization

SnO_2 nanofibers were synthesized via electrospinning on a home-built setup. SEM and TEM images of SnO_2 NFs, NPs, and the different sensing electrodes were presented in Figure 1. It can be clearly seen that the SnO_2 nanofibers were highly porous with numerous pores on the wall of the fiber and had a hollow core. The hollow NFs were randomly but evenly

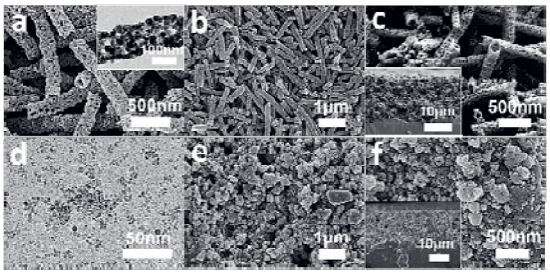

Fig.1. (a-c) SEM images for (a) pristine SnO_2 nanofibers and (b) surface and (c) cross-section of the NFs SE; inset in (a) is the TEM image of a nanofiber. (d) TEM image of pristine SnO_2nanoparticles, (e, f) SEM images for (e) surface and (f) cross-section of NPs SE.

stacked upon each other after sintering, forming a highly porous scaffold architecture. In contrast to the NFs, the pristine NPs in the powder form had much smaller grain sizes and secondary particles formed by aggregation of the nanoparticles. As a result of the wide particle size distribution, the NPs SE appeared more compact with much lower porosity and generally much smaller pores which is expected to

significantly increase the resistance for gas transport.

Sensing performance

Figure 2 compares the response (in absolute values) and response time as a function of H_2 concentration for the NFs and NPs sensors. The NFs sensor exhibited markedly higher response than the NPs sensor, which were 10 and 5 times higher for 100 ppm and 1000 ppm H_2 at 450°C, respectively. A linear relationship was observed between the response value with either H_2 concentration or its logarithm. Moreover, the NFs sensor exhibited distinctly smaller response time than the NPs sensor, which were 5 s and 13 s at 1000 ppm, respectively, corresponding to a 2.6-fold reduction. The response time was found to decrease with increasing H_2 concentration, following a power-law behavior.

Figure 3 displays the cross-sensitivities of the sensors to 100 ppm various gases at 450 ºC. The NFs sensor was most responsive to H_2 and more selective H_2 sensing was achieved for the NFs sensor compared to the NPs sensor.

Diffusion-reaction process

The excellent sensing performance of the NFs SE can be attributed to the unique electrode microstructure of 3D scaffold architecture, which allows fast gas diffusion and depresses the heterogeneous reaction.

The present work showed that electrode morphology is of crucial importance to the gas sensing performance of mixed potential sensor.

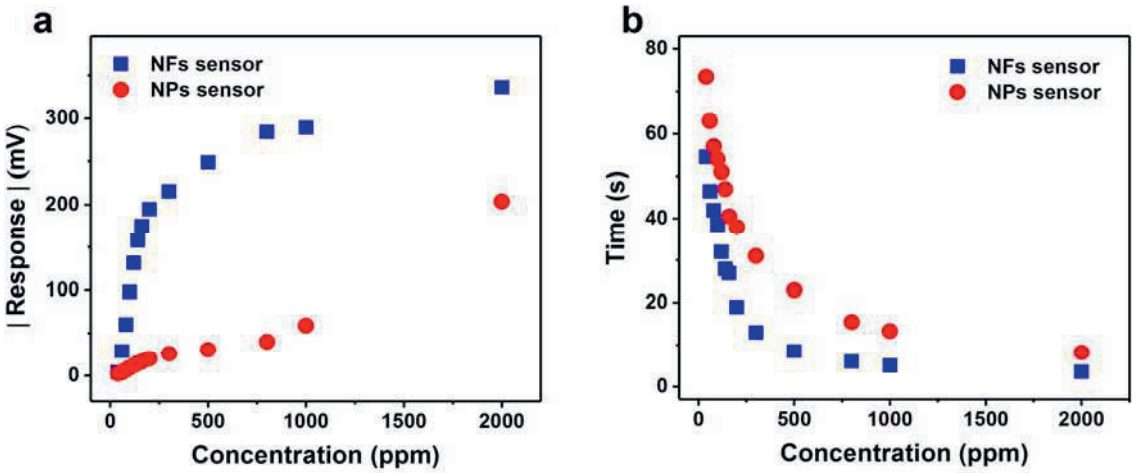

Fig.2. (a) (Absolute) Response values and (b) response time of NFs sensor and NPs sensor as a function of hydrogen concentration at 450 °C.

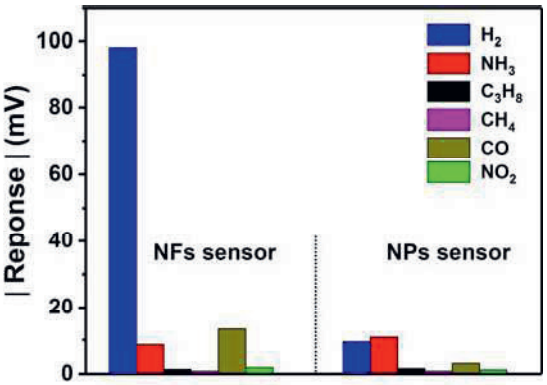

Fig.3. Cross-sensitivities of NFs sensor and NP sensor to 100 ppm various gases at 450°C.

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