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Lotus pollen derived 3-dimensional hierarchically porous NiO microspheres for NO_2 gas sensing

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ABSTRACT

Hierarchically porous NiO microspheres with interconnected nano-pores were prepared with chemical bath deposition by using lotus pollens as bio-templates. The NiO microspheres thus derived have a specific surface area of 95.58 m^2/g and the average pore size is 20.98 nm, such a nanostructure is ideal for gas sensing. To enhance the performances, the NiO microspheres were further decorated with Pd/PdO, and the sensor based on the Pd-decorated NiO microspheres demonstrated a high sensitivity ($S = 203$), fast response/recovery (73 s/169 s) and excellent selectivity to 1.8 ppm NO_2 gas at 250 °C. Compared with the other NO_2 gas sensors based on NiO reported in previous works, the sensitivity of the NO_2 sensor of this work is the highest and the response/recovery is among the fastest.

1. Introduction

NO_2 is highly toxic and causing acid rain and photochemical smog. According to the American Conference of Governmental Industrial Hygienist (ACGIH) and the Occupational Safety and Health Administration (US), the threshold limit values (TLV) for NO_2 is 3 ppm and the permissible exposure is 1 ppm for short-term exposure (<15 min) [1,2]. Therefore, NO_2 gas sensors of high sensitivity and selectivity for detecting low concentrations of NO_2 gas (below 3 ppm) are urgently needed.

Metal oxide semiconductors, e.g., SnO_2 [3,4], ZnO [5,6], In_2O_3 [7,8], NiO [9,10] and WO_3 [11,12], are commonly used as sensing materials to detect NO_2 gas. Among these oxides, NiO, a p-type semiconductor with a band gap of 3.6–4.0 eV, is very attractive, mainly owing to its high chemical stability and considerable electrical conductivity change along with chemical reactions on the surface [13–15].

Common NO_2 gas sensors based on NiO is the Nernstian planar type, consisting of an yttria-stabilized zirconia (YSZ) substrate and a NiO sensing electrode (SE), which can selectively detect NO_2 at 900 °C under wet condition [16–18]. But these NO_2 gas sensors usually need high operation temperature that will cause high power consumption and potential safety hazards. Chemiresistor gas sensors based on NiO exhibit good performance towards low concentrations of NO_2 at low operating temperatures; sensing properties of typical NO_2 sensors based on NiO are listed in Table 1. However, most of them suffer from relatively low sensitivity.

The morphology of material is key to improve gas sensing properties; the structure with a large specific surface area and many active sites is especially favorable [19]. Various morphologies with different dimensional structures have been synthesized to improve the performance of the NO_2 gas sensors based on metal oxide semiconductors, including nanowires [20], nanorods [21,22], nanofibers [23], nanobelts [24], nanotubes [25], nanosheets [26], nanoflowers [27,28], nanoparticles [29], and hollow microspheres [30]. In particular, hierarchical and mesoporous oxide nanostructures have attracted great attention due to their high surface area and nano-porous structures. Generally, the preparation of these nanostructured morphologies needs special conditions, such as complicated equipment, high temperature or high pressure. To develop a simple and low cost approach to product novel nanostructures with high surface area is highly desirable for fabricating highly sensitive NO_2 gas sensors.

In this work, NO_2 gas sensors based on 3D hierarchically porous NiO microspheres were prepared with chemical bath deposition by using lotus pollens as bio-templates. The bio-template approach is very versatile in synthesizing advanced materials

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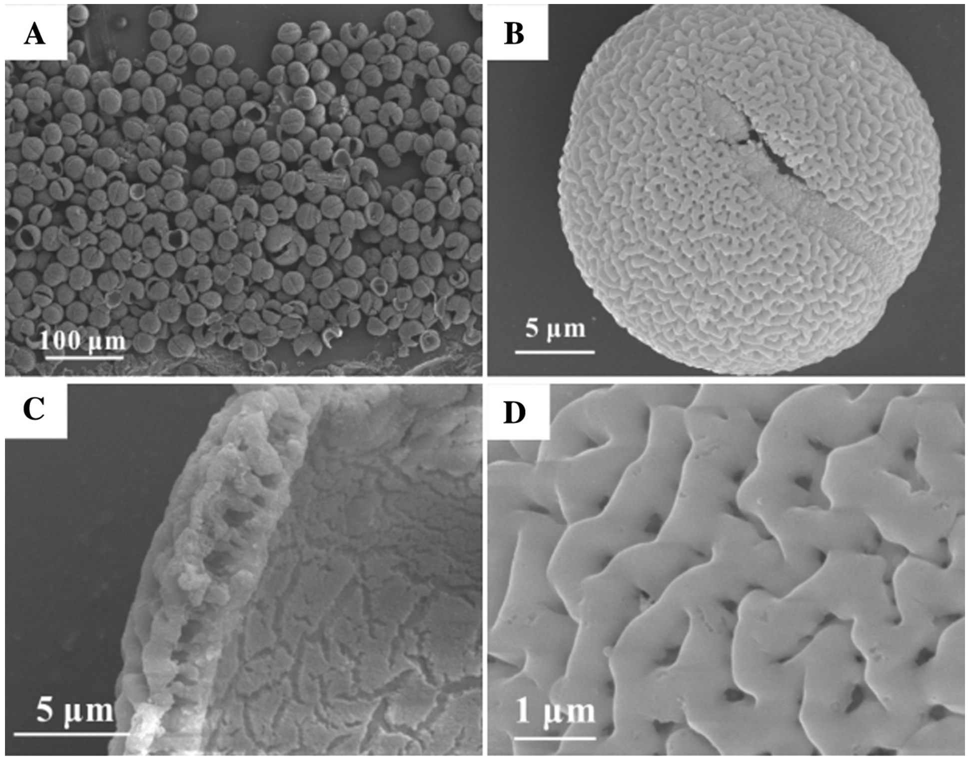

Fig. 1. SEM images of lotus pollens: (A) low-magnification image, (B) high-magnification image, (C) cross-section, and (D) surface.

Table 1
Comparison of the sensing properties of various NO_2 sensors based on NiO.

Material	NO_2 (ppm)	T (°C)	Response	t_{resp}/t_{reco} (s)	Refs.
NiO nanosheets	1	250	~1.2	–/–	[30]
NiO NS/RGS	1	200	3	~80/120	[32]
NiO nanoflowers	5	150	20	–/–	[33]
NiO nanowalls	1	150	~2	~120/~400	[34]
NiO–Pd microspheres	**1.8**	**250**	**203**	**73/169**	This work
NiO–Pd microspheres	**1.8**	**50**	**1.33**	**430/936**	This work

with unique nano/microstructures and desired functions. As the 3D hierarchically porous NiO microspheres have a high specific surface area (95.58 m^2/g) and good surface permeability, they demonstrated excellent gas sensing performance. To further enhance the gas sensing performance, Pd/PdO was decorated to the NiO microspheres. Owing to the fantastic nanostructure of the NiO microspheres and the noble metal catalyst, the gas sensor based on the Pd-decorated NiO microspheres exhibited high sensitivity (S = 203), fast response/recovery (73 s/169 s) and excellent selectivity to 1.8 ppm NO_2 gas at 250 °C. At a low temperature of 50 °C, the sensor's performance was also reasonably good (S = 1.33).

2. Experimental

2.1. Preparation and characterization of NiO microspheres

Bio-templates of lotus pollen were prepared as follows: 10 g pollen grains were immersed into 70 mL ethanol with ultrasonic treatment for 1 h, then filtered and cleaned with deionized water, and later immersed into a mixed solution of formaldehyde and ethanol (1:1 in volume) with vigorous stirring for 10 min, which was followed by another filtering and cleaning with deionized water. The dehydration of the pollen grains were carried out in 50 mL 12 M sulphuric acid at 80 °C for 4 h. After dehydration, the pollen grains were filtered again and cleaned with ethanol and deionized water several times. The final products were dried at 60 °C overnight.

NiO microspheres were prepared by chemical bath deposition according to the following procedure. 3 g dehydrated pollens were firstly immersed into a mixed solution prepared by mixing 40 mL

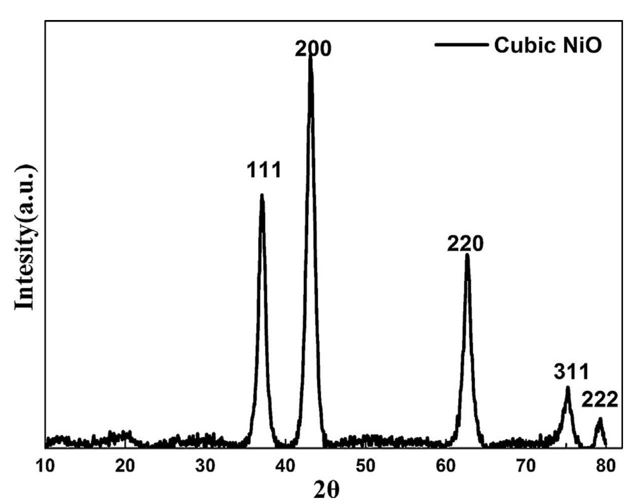

Fig. 2. XRD pattern of NiO microspheres.