Nanoseed-assisted rapid formation of ultrathin ZnO nanorods for efficient room temperature

NO₂ detection

Yi Xia^{a, b}, Jing Wang^{b, c}, Xian Li^d, Dan Xie^d, Dali Zhou^{a*}, Lan Xiang^{b*}, Sridhar Komarneni^{c*}

^a College of Material Science and Engineering, Sichuan University, Chengdu 610065, China

^b Department of Chemical Engineering, Tsinghua University, Beijing 100084, China

^c Materials Research Institute, Materials Research laboratory, The Pennsylvania State University,
University Park, PA 16802

^d Institute of Microelectronics, Tsinghua University, Beijing 100084, China

Abstract

The influence of ZnO nanoseeds on the formation of ZnO nanorods from ϵ -Zn(OH)₂ in NaOH solution at 80°C was investigated, using ZnO nanoparticles with a diameter of 4-10 nm as the seeds. The experimental results indicated that the presence of ZnO nanoseeds promoted the rapid heterogeneous formation of ultrathin ZnO nanorods. Compared with the ZnO submicron rods with a diameter of 0.5-1.0 μ m, the ultrathin ZnO nanorods with a diameter of 10-15 nm were found to be more sensitive for detecting NO₂ at room temperature owing to their higher variation of channel conduction to the diameter.

Keywords: ZnO, sensors, seed,

* Corresponding author.

E-mail: zdl@scu.edu.cn (D. Zhou); xianglan@mail.tsinghua.edu.cn (L. Xiang);
sxk7@psu.edu (S. Komarneni), Fax: +1-814-865-2326, Tel: +1-814-865-1542.

1. Introduction

Ultrathin ZnO nanorods are promising candidates for optics and opto-electronics [1-3]. Many former studies revealed that ultrathin ZnO nanorods exhibited highly improved performances for various applications such as luminescent device, field emitters and gas sensors, owing to the unique quasi one-dimensional morphology, high surface area as well as abundant surface states [4-6]. A great number of solutions, including solvothermal and nanoseed-assisted approaches have been developed to synthesize ultrathin ZnO nanorods owing to the mild synthesis condition and the easy tailoring of properties by morphology control. ZnO nanorods with the diameters of 2-10 nm were fabricated via solvothermal approaches in which organic solvents such as methanol or ethanol and surfactants such as sodium dodecylbenzenesulfonate were used to inhibit the radial growth of ZnO nanorods [7, 8]. Ultrathin ZnO nanorods with diameters less than 20 nm were produced in bulk solution or on substrate via the surfactant-free nanoseed-assisted aqueous route [9-11]. However, a long reaction time (8.0-24.0 h) was needed due to the slow growth rate in dilute solutions of 0.1-10 mmol·L⁻¹. Using ϵ -Zn(OH)₂ as the precursor, ZnO nanorods with a length of 10-15 μ m and a diameter of 100-500 nm were formed quickly within 30.0 min via the solution pathways [12-14]. However, up to now, rapid formation (within 30 min) of ultrathin ZnO nanorods (diameter < 20 nm) could not be accomplished and remains as a challenge.

Seeded growth has been previously demonstrated as an effective method for diameter control of ZnO nanorods [15-20]. Herein, a facile nanoseed-assisted method was developed for the quick

formation of ultrathin ZnO nanorods (diameter: 10-15 nm) at 80 °C within 10.0 min, using ϵ -Zn(OH)₂ as the Zn precursor, NaOH solution as the reaction medium and ZnO nanoparticles as the seeds. The influence of ZnO nanoseeds on the morphology of ZnO nanorods was investigated and the synthetic ZnO nanorods were tested for NO₂ detection.

2. Experimental

2.1 Samples preparation

ϵ -Zn(OH)₂ was prepared by drop-wise addition of 50 ml of 2.0 mol·L⁻¹ ZnSO₄ into 50 ml of 4.0 mol·L⁻¹ NaOH at 25 °C under stirring, then the precipitate was filtrated, washed and dried at 25 °C for 24.0 h. ZnO nanoseeds were prepared by mixing 0.004 mol Zn(Ac)₂ and 0.1 mol NaOH in 200 ml of ethanol solution at 25 °C for 2 h, then precipitation was centrifuged, washed and dried at 25 °C for 24.0 h.

ZnO nanorods were synthesized by mixing 0.035 mol of ϵ -Zn(OH)₂ and 0 to 2 mmol of ZnO nanoseeds in 40 mL of 4 mol·L⁻¹ NaOH solution followed by aging at 80 °C for 0 to 50.0 min. The slurries of synthesized products were centrifuged, washed and dried at 25 °C for 24.0 h.

2.2 Characterization

The soluble zinc in solutions were detected by EDTA titration method. To get the molar ratio of ZnO and ϵ -Zn(OH)₂ in the solid products, 0.1 g sample was dissolved in 10 mL of 1 mol·L⁻¹ hydrochloric acid and then buffered to pH 5-6 with an ammonia-ammonium chloride buffer. The total amount of zinc was analyzed by EDTA titration, then the molar ratio of ZnO could be calculated based

on the titration results. The structures of the samples were identified by powder X-ray diffraction (XRD) using an X-ray diffractometer (XRD, D8 Advance, Bruker, Germany) with $\text{CuK}\alpha$ radiation ($\lambda=0.154178$ nm). The morphology of the samples was characterized by a field emission scanning electron microscope (FESEM, JSM7401F, JEOL, Japan) and a high-resolution transmission electron microscope (HRTEM, JEM-2010, JEOL, Japan).

2.3. Gas sensor fabrication and measurements

For fabrication of gas sensor, N-type (100) oriented silicon wafer was used as the substrate. A 300 nm thick silicon dioxide (SiO_2) dielectric-layer was thermally-grown on the silicon wafer. The inter-digital Ti/Au electrodes with finger width of 10 μm and gap width of 10 μm were patterned by standard photolithography and the titanium/gold (Ti/Au, 20 nm/100 nm) electrodes were deposited by RF sputtering and lift-off processes. ZnO was dispersed in ethanol to achieve a concentration of 0.04 $\text{mol}\cdot\text{L}^{-1}$. The suspension was drop-casted onto the substrate and dried at 90 $^{\circ}\text{C}$ for 30 min. The fabricated sensors were placed in a homemade chamber with air inlet and outlet. The dry air was used as the carrier gas, the input concentration of NO_2 was 1 to 10 ppm and the flow rate of the mixing gas was 200 $\text{mL}\cdot\text{min}^{-1}$. The resistances of the films were measured by Keithley 2700 Multimeter/Data Acquisition System at 25 $^{\circ}\text{C}$. The sensitivity (S) of the sensor is defined as $(R_g - R_a)/R_a \times 100 (\%)$, where R_a and R_g are the resistances in air and NO_2 , respectively.

3. Results and discussion

3.1. Formation of ultrathin ZnO nanorods

Fig. 1 shows the XRD patterns and morphology of the precursor and nanoseeds. The XRD peaks of the precursor and nanoseeds were indexed to ϵ -Zn(OH)₂ (JCPDS 38-0385) and ZnO (JCPDS 36-1451), respectively. ϵ -Zn(OH)₂ octahedral microparticles were of a primary diameter of 5-7 μ m and ZnO nanoparticles were of poor crystallinity with a primary diameter of 4-10 nm.

Fig. 2 shows the variation of the molar ratios of ZnO in products and the soluble Zn in solutions with reaction time. The samples prepared using 0, 0.2 and 2.0 mmol of ZnO nanoseeds were denoted as P1, P2 and P3, respectively. The increase of ZnO nanoseeds from 0 to 2.0 mmol accelerated the conversion of ϵ -Zn(OH)₂ to ZnO, leading to the decrease of the reaction time from 30.0 min to 5.0 min (Fig. 2a). The data in Figure 2b revealed an initial increase but a subsequent decrease of the soluble Zn with reaction time in all cases, suggesting the conversion of ϵ -Zn(OH)₂ to ZnO via mainly the dissolution-precipitation route[14].

Fig. 3 presents the morphology of the products formed at different reaction times. Both the length and the diameter of the ZnO nanorods increased with the increase of reaction time in all cases. The presence of ZnO nanoseeds promoted the formation of ZnO nanorods with small diameters and short lengths. For example, ZnO nanorods with a length of 0.5-1.0 μ m and a diameter of 10-15 nm were formed within 10.0 min in the case of 2.0 mmol ZnO nanoseeds and remain unchanged with time. The presence of ZnO nanoseeds apparently acted as the nuclei for the heterogeneous precipitation of ZnO, thus promoting the quick formation of ZnO nanorods with small diameters [21].

3.2 Gas sensing performances and mechanism

Fig. 4 shows the dynamic response curves and the sensitivities of the sensors for NO₂ detection at room temperature. S1, S2 and S3 represent the sensors composed of the ZnO nanorods formed at 30.0 min in the presence of 0, 0.2 and 2.0 mmol of ZnO nanoseeds, respectively. The sensitivities increased with the decrease of the diameters of ZnO nanorods. For instance, the sensitivity of S3 to 10.0 ppm NO₂ was ca. 336%, much higher than those of S2 (125%) and S1 (35%). Furthermore, S3 exhibited a sensitivity of up to 100% to 1.0 ppm NO₂ while little response was detected for S1.

The depletion layer modulation model was employed to explain the mechanism for sensing NO₂ (Fig. 5). The adsorption of oxygen on ZnO nanorods in air captured the free electrons from the nanorods ($O_2 + e^- \rightarrow O_2^-$), forming a depletion layer with low-conductivity. The depth of depletion layer increased while the channel conduction decreased when ZnO nanorods were exposed to electrophilic NO₂ due to electron transfer from ZnO to NO₂ ($2NO_2 + O_2^- + 2e^- \rightarrow 2NO_3^-$) [22]. The sensitivity for NO₂ sensing depended on the variation of channel conduction in air and NO₂. The depletion depth of ZnO nanorods was relatively constant with ZnO diameters if the temperature, the nature of sensing material and atmosphere were kept constant [23]. A decrease in radius of the ZnO nanorods would enlarge the channel conduction difference in air and NO₂ due to the higher ratio of the depletion layer to the diameter, which favored the increase in sensitivity. Therefore, the present ultrathin ZnO nanorods exhibited higher NO₂ sensitivities in comparison to the submicron ZnO rods.

A comparison of NO₂ sensing performance at room temperature between the present sensor made with ultrathin ZnO nanorods and the previously tested ZnO-based sensors operating at different temperatures is summarized in Table 1. The previously reported ZnO-based films, which were

fabricated by ZnO nanostructure or hybridization of ZnO nanostructure with conducting polymers or carbon nanomaterials, exhibited sensitivities of 2.2–95% with 1–20 ppm of NO₂, while the ultrathin ZnO nanorods film in the present work demonstrated high sensitivities up to 100 and 336% with 1 and 10 ppm of NO₂, respectively. Therefore, the presently synthesized ultrathin ZnO nanorods provides a novel alternative route to prepare ZnO films to potentially fabricate low-cost room temperature NO₂ sensors.

4. Conclusion

In summary, a facile nanoseed-assisted method has been developed to synthesize ultrathin ZnO nanorods with a diameter of 10–15 nm from ϵ -Zn(OH)₂ octahedral microparticles, using ZnO nanoparticles of 4–10 nm in diameter as the seeds. The presence of ZnO nanoseeds promoted the heterogeneous formation of ZnO nanorods within 10 min. Compared with the submicron ZnO rods with a diameter of 0.5–1.0 μ m, the ultrathin ZnO nanorods exhibited a higher sensitivity for NO₂ detection owing to the higher variation of channel conduction to the diameter.

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Fig. 1 XRD patterns and SEM morphology of precursor (a) and TEM morphology of nanoseeds (b).

Fig. 2 Variations of molar ratios of ZnO in products (a) and soluble Zn (b) with reaction time. P1, P2

and P3 are samples formed with 0, 0.2 and 2.0 mmol of ZnO nanoseeds.

Fig. 3 Morphology by SEM and TEM of products formed at different reaction times: (a-c) P1, (d-f)

P2 and (g-i) P3; reaction time (min): (a, d, g) 3.0, (h) 5.0, (b, e, i) 10.0 and (c, f) 30.0.

Fig. 4 Dynamic response curves (a) and sensitivities (b) of sensors.

Fig. 5 Schematic illustration for NO₂ detection

Table 1. Comparison of room-temperature NO₂ sensing performance with the previously reported gas sensors.

Morphology	NO ₂ conc. (ppm)	Temperature (°C)	S(%)	Ref.
Ultrathin ZnO nanorods	1	RT	100	This work
	10		336	
ZnO hierarchical nanostructure	20	RT	32	24
ZnO nanowires	20	225	95	25
ZnO nanowires	20	225	92	26
Nanopatterned polycrystalline ZnO	20	RT	2.2	27
Co ₃ O ₄ -decorated ZnO nanowire	5	200	45.4	28
ZnO nanosheets/porous silicon	1	RT	<6	29
ZnO hierarchical nanostructure/P3HT	4	RT	59	30
ZnO nano particles/rGO	5	RT	25.6	31