Preparation of high aspect ratio nickel oxide nanowires and their gas sensing devices with fast response and high sensitivity

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NiO p-type semiconducting nanowires with high aspect ratios up to approximately 2000 have been prepared by chemical reduction under assistance of magnetic fields and subsequent heat treatment method. The diameter of NiO nanowires is about 150 nm and the length can be up to 300 μm. Ni nanowires have been prepared from a structure of Ni nanospheres at atmospheric pressure. Transformation from Ni nanowires to NiO semiconducting nanowires via in situ chemical oxidation process in open air have been conducted by undergoing a process of an amorphous oxidation. Heat treatment results in significant influence on the grain size in the NiO nanowire structure. NiO nanowires with crystalline grain size of about 12 nm is characteristic with a band gap energy of about 4.20 eV, which is larger than the bulk NiO material (3.65 eV). Meanwhile, we find that the optical band gap energy gradually increases with the decrease of the crystalline grain size. NiO nanowires with different grain sizes have been used to fabricate arrays for a gas sensor under an external magnetic field. NH3 gas sensing capability at room temperature by NiO nanowire arrays is characteristic for its high sensitivity, fast response, rapid recovery and good reproducibility.

Introduction

Metal oxide semiconducting nanomaterials have attracted considerable attention because of their potential applications in areas such as energy harvesting,1 memories,2 nonvolatile memories,3 light emitting diodes,4 field effect transistors,5 and so on. As a typical p-type semiconducting nanomaterial, nickel oxide (NiO) nanowires possess stable wide band gap energy in the range of 3.6–4.0 eV (depending on the crystallinity and preparation method) and cubic rock salt structure with a lattice parameter of 0.4195 nm, which is considered to be an interesting and prosperous functional nanomaterial.6 A number of template-assisted methods have been successfully demonstrated for the synthesis of low-dimensional p-type semiconducting materials with regular morphologies, and the most typical example is the porous anodic aluminum oxide (AAO) templates. Take for example the case of NiO nanowires, which are usually synthesized in the nanopores of the AAO templates.7 Although template-assisted approaches towards the synthesis of NiO nanowires have been very successful, they still have some limitations. For instance, the ordered AAO templates often need multi-step procedures to be prepared and process parameters such as the temperature, voltage, concentration of acid need to be carefully controlled. The separation of pure NiO nanowires from the as-synthesized products is both complex and tedious.

In contrast, the solution-based chemical methods that involve no physical templates can easily bypass these difficulties. To this end, the chemical approach has been actively explored to process NiO into low-dimensional nanostructures.8 For example, Zhan et al. have successfully synthesized NiO nanowires with diameters of about 40–100 nm and lengths up to 10 μm by the microemulsion and annealing methods.9 However, the as-synthesized products obtained upon precursor compound annealing are very often amorphous, and additional treatment protocols are required in order to achieve well-defined morphology and structure, both of which are closely related to the electronic, magnetic, gas-sensing and catalytic properties of materials.10,11 Moreover, the final products of all these methods are characteristic with issues such as low aspect ratio, irregular morphology, and low yield. To overcome such drawbacks, the hydrothermal method and the oxidation method have been combined together for NiO crystal growth, which ensures the synthesis of nanowires with high aspect ratio. For instance, Liu et al. have produced NiO nanowires with different aspect ratios by a hydrothermal reaction of NiCl2 with NaC2O4 and H2O in the presence of ethylene glycol and subsequent annealing at 400 °C in air.12

To date, nanoplates,13 hexagonal nanodisks,16 nanowires,9 nanotubes,7 concave polyhedrons,14 and nanowalls15 of NiO have been synthesized by template methods or solution-based...
chemical methods. However, it is still a big challenge to develop a synthetic strategy to prepare NiO nanowires with high aspect ratio in a large scale as well as at low cost. Nanowires with a high aspect ratio could benefit overall integration by facilitating interconnection of nanoelectronic device arrays. In addition, NiO is one of the most widely applied gas sensing oxide materials with good environmental stability. Moreover, NiO is one of the most widely applied gas sensing oxide materials with good environmental stability. The prior gas sensors based on NiO films have been shown to possess significant sensing properties. Recently, the gas sensors based on porous NiO nanotubes and nanowires have been fabricated by placing a fraction of the NiO nanomaterials on interdigitated electrodes on a silicon substrate. In this report, we have demonstrated a template-free, surfactant-free, magnetic-field-assisted, and high-yield method that allows for the production of NiO nanowires with uniform diameters and high aspect ratios at atmospheric pressure. Meanwhile, we assemble nanowire arrays on the Si/SiO2 wafer substrate under the assistance of external magnetic fields. By combining lithography and lift-off processes, gas sensors based on ultralong NiO nanowires have been made. This sensor shows high sensitivity toward the detection of NH3 gas, which is comparatively analyzed vis-a-vis other gases at room temperature.

Experimental section

Preparation of the NiO nanowires

All the chemicals used in our experiments were of analytical reagent grade and were directly used without further purification. In a typical procedure, 1.19 g of NiCl2·6H2O (Sinopharm Chemical Reagent Co., Ltd, China) was dissolved into 50 mL ethylene glycol (EG, Shanghai Chemical Reagents Company, China) under continuous magnetic stirring at room temperature. Half an hour of continuous magnetic stirring was carried out to ensure that Ni2+ ions were dispersed homogeneously in the solution. Then 200 mL EG solution of NaOH (12.0 g, Shanghai Chemical Reagents Company, China) and 150 mL EG solution of NH4H2O (100 mL, 85 wt%, Sinopharm Chemical Reagent Co., Ltd, China) were added dropwise into the above solution containing Ni2+ ions. This reaction mixture was stirred constantly to obtain a homogeneous navy blue solution and subsequently transferred into a flask. The flask was then placed in a magnetic field and heated to 70 °C at atmospheric pressure. The strength of the magnetic field in the flask was 0.4 T at the temperature of 70 °C. After about 60 min, the reaction was completed and a grey-black fluffy solid was adsorbed on the inner surface of the flask. The products were separated from the solution using a magnetic field and washed three times with distilled water and ethanol, respectively, and then the products were dried in a vacuum oven at 60 °C for 12 h. The as-prepared products were heated at 400 °C, 600 °C, 800 °C, respectively, for 3 h in a heat treatment furnace in open air. After the heat treatment, the furnace was cooled to room temperature naturally. The resultant samples were then collected for characterization. Fig. 1 (A), (B) and (C) show the flowchart, home-made magnetic field device and heat treatment furnace of nanowires preparation, respectively.

Preparation of the gas sensors

The Si substrate with 300 nm SiO2 layer was ultrasonically rinsed with acetone, ethanol and distilled water in turn. The as-prepared NiO nanowires were ultrasonically dispersed in distilled water for half an hour. The pre-treated Si substrate was immersed in the NiO nanowire-water suspension for 45 min under an external magnetic field to form nanowire arrays, and then rinsed with ethanol and distilled water repeatedly, and blown dry with N2. Next, the wafer substrate deposited with Ni nanowires was heated at 400 °C, 600 °C, and 800 °C, respectively, for 3 h in a heat treatment furnace in open air. Using standard micro-fabrication procedures, the NiO nanowires-based gas sensor was fabricated. Briefly, the interdigitated electrodes were made by sputtering 30 nm Ti and 170 nm Au onto a patterned photoresist mold, and a lift-off technique was used to remove the photoresist. Finally, the electrodes were sonicated in ethanol, washed with distilled water thoroughly and then dried with N2. Fig. 1 (D) shows the schematic diagram of nanowire arrays assembly process and sensor fabrication.

Characterization

The crystalline phases of the as-synthesized samples obtained were characterized by X-ray powder diffraction (XRD) using a 18 kW advanced X-ray diffractometer (D8 ADVANCE, Bruker, Germany) in a 2θ range from 35 to 98 degree with Cu-Kα radiation (λ = 0.154056 nm). The size and surface morphology measurements were performed by using an emission scanning electron microscope (SEM, Zeiss Ultra 55, Germany) at an accelerating voltage of 5 kV. The inner microstructure of the samples was investigated by transmission electron microscopy (TEM, JEM-2100, JEOL, Japan). High-resolution transmission electron microscopy (HRTEM) images were recorded with a JEM-2010 transmission electron microscope operating at 200 kV. Thermogravimetric analyses of the samples prepared were carried out on a thermal gravimetric analyzer (TGA, Pyris 1, USA) at 400 °C in flowing air. UV-visible absorption spectra were recorded using a UV-vis spectrophotometer (Lambda 950, PerkinElmer, America) with a wavelength range of 170–700 nm at room temperature.

Sensor testing system

Measurements on gas sensitivity were performed on the home-made sensor testing system (see Fig. 2), and the relative humidity of the environment during the experiments was about 35–45%. To generate and dilute the NH3 gas, nitrogen was used as the carrier gas, flowing through a glass tube containing ammonia water to form NH3 gas. The flow ratio of NH3 gas in our experiment was controlled by mass flow controllers (MFC, Beijing Qixing Co., Ltd, China) from 1 to 30 mL min⁻¹. Then this NH3 gas was mixed with diluting nitrogen in a stainless steel mixing chamber, and the output flow ratio of the diluted NH3 gas was controlled by MFC. The different concentrations of NH3 gas were produced by regulating the flow rate of the dilution gas with that of the flow rate of the carrier gas. The NH3 gas was delivered at a flow rate of 2 L min⁻¹ into the testing chamber to test the sensor performance. The sensor was illuminated with an IR lamp and the testing chamber was evacuated to desorb the NH3 gas from the NiO nanowire.
surface after each testing cycle, and all the gas sensing measurements were carried out at room temperature (300 K). The electrical signal of the gas sensor was monitored using a precision semiconductor parameter analyzer (Agilent 4156C). The sensor response was evaluated by the resistance change at a sampling voltage of 1 V.

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**Fig. 1** (A) Flowchart and (B, C) devices for the sample preparation, showing the specific method of the synthesis of NiO nanowires, which contained two steps. The Ni nanowires were prepared by chemical reduction route in a (B) thermostatic water-bath device at 70 °C for 60 min with a 0.4 T magnetic field. The second step was the heat treatment of as-synthesized Ni nanowires at different temperatures for 3 h in a (C) heat treatment furnace to obtain NiO nanowires. Schematic diagrams of the nanowire arrays assembly process and sensor fabrication (D): (D1) assembly of nanowire arrays under assistance of magnetic field, (D2) heat treatment (Ni → NiO conversion), (D3) photoresist patterning, (D4) sputtering Au electrode and (D5) removing the photoresist.

**Fig. 2** Schematic diagram shows the gas testing system.
Results and discussion

Structure and morphology analysis

In the first stage of the synthesis of NiO nanowires with high aspect ratio, a controlled hydrazine reduction route has been developed to prepare ultralong Ni nanowires at low temperature. The exact mechanism for the formation of ultralong Ni nanowires via this chemical reduction route in ethylene glycol solution assisted by an external magnetic field is still under investigation by our group. The specific chemical reactions for the synthesis can be expressed as follows:

\[ \text{Ni}^{2+} + 2\text{OH}^{-} \rightarrow \text{Ni(OH)}_2 \downarrow \]  \hspace{1cm} (1)

\[ 2\text{Ni}^{2+} + \text{N}_2\text{H}_4 + 4\text{OH}^{-} \rightarrow 2\text{Ni} \downarrow + \text{N}_2 \uparrow + 4\text{H}_2\text{O} \]  \hspace{1cm} (2)

\[ \text{Ni(OH)}_2 + \text{N}_2\text{H}_4 \rightarrow 2\text{Ni} \downarrow + \text{N}_2 \uparrow + 4\text{H}_2\text{O} \]  \hspace{1cm} (3)

Fig. 3 (A1) presents the scanning electron microscopy (SEM) image of the as-prepared ultralong Ni nanowires assisted with a 0.4 T magnetic field. The morphology of the sample have been identified as one-dimensional acicular Ni nanowires, with an average length of 300 μm and a diameter of about 100 nm. Fig. 3 (A4) clearly shows a single ultralong Ni nanowire with the uniform diameter and high aspect ratio. In order to better understand the surface structure of the Ni nanowires, further observation at higher magnification (Fig. 3 (A2)) has revealed that each nanowire has been formed via the aggregation of Ni nanoparticles drawn together, and not by the nucleation and growth under the attractive magnetic forces. To further investigate the exact role of the external magnetic field, an experiment in the absence of the magnetic field has been carried out. Fig. 3 (B1) and Fig. 3 (B2) show the SEM images of Ni nanochains obtained without magnetic field applied. These Ni nanochains with an average length of 4 μm are formed via the connection together of these nanospheres with about 100 nm in diameter, hence illustrating that magnetic field plays an important role in the formation of Ni nanowires with high aspect ratio (up to 2000).

The corresponding XRD patterns of the Ni nanowires were shown in Fig. 3 (A3). All the diffraction peaks of the sample match well with the Ni face-centered cubic (fcc) structure (PDF standard cards, Joint Committee on Powder Diffraction Standards (JCPDS) card No. 04-0850, space group, fccm (225)). These peaks at the scattering angles (2θ) of 44.62°, 51.94°, 76.58° and 93.02° correspond to crystal planes of (111), (200), (220) and (311) of crystalline Ni, respectively. From the XRD patterns, no other characteristic peaks, such as for nickel oxide or nickel hydroxide, were detected, indicating that pure ultralong Ni nanowires have been obtained using this magnetic-field-assisted chemical reduction method at atmospheric pressure. The average crystalline grain size of the sample has been calculated from the XRD patterns according to the Scherrer formula. The average crystalline grain size of the ultralong Ni nanowires was 10.08 nm, which is obviously smaller than the diameter of Ni nanowires in SEM images (Fig. 3 (A2)), illustrating that Ni nanowires have been assembled from many crystalline grains under the magnetic field assistance. The XRD patterns of the Ni nanochains prepared without applying a magnetic field are similar, and the average crystalline grain size was 10.12 nm.

The evolution of the surface morphology, crystalline phase and average grain size of the NiO nanowires under different heat treatment conditions have been investigated and shown in Fig. 3. The XRD patterns of the ultralong NiO nanowires prepared after heat treatment at 400 °C, 600 °C, or 800 °C, for 3 h in open air appear similar. The sharp and strong peaks of the XRD patterns in Fig. 3 (C3), (D3) and (E3) indicate that the final products are well crystallized, in which all the diffraction peaks can be well indexed to NiO with a cubic structure according to the JCPDS card No. 47-1049 (space group, fccm (225)). However, the diffraction peak intensities of the samples prepared at (D3) 600 °C and (E3) 800 °C are stronger than the ones at (C3) 400 °C, indicating the increase of the crystallinity of NiO nanowires under the higher heat treatment temperature. Furthermore, the average crystalline grain sizes are about 12.22 nm (400 °C, 3 h), 16.71 nm (600 °C, 3 h), 24.03 nm (800 °C, 3 h), respectively, calculated by Scherrer’s equation from the FWHM of (200), (111), (220), (311), (222), and (400) reflections, illustrating that the average crystalline grain sizes of the NiO crystals are getting bigger with the increase of heat treatment temperature. Meanwhile, we also observe that the color of the NiO samples changes from light-green (heat treatment at 400 °C for 3 h) into dark-green (heat treatment at 800 °C for 3 h). The SEM images of the ultralong NiO nanowires obtained after heat treatment at 400 °C, 600 °C, 800 °C, respectively, for 3 h in open air are shown in Fig. 3 (C1 and C2, D1 and D2, E1 and E2, respectively), indicating that the ultralong NiO nanowires consisted of small crystals with an average size of 12–24 nm. It is also observed that the morphology of as-synthesized ultralong NiO with uniform linear structures is about 150 nm in diameter, 300 μm in length, with an aspect ratio of 2000. Moreover, we observe that the surface of NiO nanowires becomes smoother (without acicular structure) with the increase of heat treatment temperature.

Formation mechanism

From the above experimental results with ultralong Ni nanowires and nanochains, we propose that the formation mechanism of the ultralong Ni nanowires induced by the magnetic field is as follows (as shown in Fig. 4 (A1)): initially, nickel ions were reduced by hydrazine hydrate and generated nickel atoms. The small nickel primary atoms acted as seeds to allow more metal atoms to be reduced and inclined to aggregate into larger spheres for the sake of decreasing surface energy. Afterwards, due to the application of an external magnetic field, the nickel magnetic spheres aligned along the lines of the magnetic force in this process. The linear chains were formed by the joining of these nanospheres with the increase in the reaction time. The nickel chains strongly enhance the local magnetic field and increase in length to form ultralong nanowires, until the nickel ions are completely consumed. At the same time, the strong magnetic dipole interactions between crystalline grains improved the structural intensity of the nanowires. After ultrasonic treatment for 2 h, the nanowires remain intact, indicating that the nanowires were rather stable as a result of strong magnetic interactions. Fig. 4 (B1) clearly shows two adjoining grains having different crystallographic orientations in a single nanowire, which further illustrates that Ni nanowires are assembled by many crystalline grains under the magnetic field assistance.
In order to illustrate the detailed transformation process from ultralong Ni nanowires to NiO semiconducting nanowires, we investigate the condition of constant temperature (400 °C, 210 min) of the thermogravimetric analysis (TGA) on the as-prepared ultralong Ni nanowires under air flow. Fig. 4 (C) shows the TG curve of the as-synthesized Ni nanowires obtained using the chemical reduction, magnetic-field-assisted route. We observe that the total weight gain was about 23.5%, which was close to the theoretical weight gain value of 21.3% calculated for the change of pure Ni to NiO crystals. This thermogravimetric result indicates that the oxidation process from Ni nanowires to NiO nanowires would last for around 3 h at 400 °C. To further verify the oxidation mechanism of NiO, we perform TEM characterization of the nanowires prepared through oxidation about 30 min of ultralong Ni nanowires. The nanowire has an average diameter of about 130 nm (see Fig. 4 (B31)) and an amorphous NiO layer with a thickness of about 3 nm (see Fig. 4 (B3)). Fig. 4 (B3) is an HRTEM image of part of the nanowires, which shows the crystalline Ni and amorphous NiO structures. Therefore, NiO diffraction peaks have not been detected in the XRD patterns, as shown in Fig. 4 (B32). Energy-dispersive X-ray spectrum (EDS) analysis (see Fig. 4 (B33)) of the amorphous

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**Fig. 3** Evolution of the surface morphology, crystalline phase and average grain size of the samples: Ni products were prepared via chemical reduction route in ethylene glycol solution with (A1, A2, A3 and A4) and without (B1, B2 and B3) a 0.4 T magnetic field applied. NiO products were obtained through the heat treatment of the Ni nanowires at 400 °C (C1, C2 and C3), 600 °C (D1, D2 and D3), 800 °C (E1, E2 and E3), respectively, for 3 h in open air.
NiO shows that the atomic ratio between Ni and O is about \(1:0.91\), indicating the presence of the oxygen vacancies in the amorphous NiO layer. Since the NiO layer is formed by oxidation of the Ni nanowire surface, and the oxidation is processed in a Ni-rich condition, a large number of oxygen vacancies are expected to exist in the NiO layer. This means that the generation of vacancies in the amorphous oxide layer is faster than the diffusion of vacancies away from the oxide layer.

Fig. 4 (B4) shows the HRTEM image of the nanowires synthesized through oxidation for about 180 min. A spacing of the crystallographic planes measured from the HRTEM image is about 0.20 nm, which corresponds to the interplanar distance of (200) lattice planes of cubic NiO. On the basis of the above results, a possible oxidation mechanism from ultralong Ni nanowires to NiO semiconducting nanowires could be schematically described as follows. Initially, oxygen molecules absorb onto the surface of the as-prepared Ni nanowires and decompose into oxygen atoms (see Fig. 4 (A2)), forming an adsorption layer of oxygen atoms. On further heat treatment in the second stage, the atoms of the Ni nanowire lost two electrons to form Ni\(^{2+}\) ions and the oxygen atoms obtained the two electrons removed from the Ni atom, forming a negatively charged oxygen ion. This will create an electric field in the surface of nanowires, facilitating the transport of Ni\(^{2+}\) ions. The tendency to form a NiO phase is small at the beginning of the oxidation, since the localized reaction of oxygen with an underlying metal substrate exerts a very strong influence on the free energy barrier of oxide nucleation. This results in the formation of an amorphous NiO layer on the surface of the Ni nanowires. In the third stage, the NiO grains formed on the surface layer of the nanowires and oxidation layer grew from the outer surface of Ni nanowires to the interior of the nanowires at high temperature with the increase of the oxidation time. The Ni atom lost two electrons to form Ni\(^{2+}\) ions at the interface between Ni and NiO, and oxygen atom obtained the two electrons which were removed from the Ni atom to form O\(^{2-}\) ions at the interface between NiO and air. Afterwards, the positively charged Ni\(^{2+}\) ions diffused outward along the grain boundaries of oxidation layer and the
negatively charged O\(^{2-}\) ions diffused inward toward to meet the Ni\(^{2+}\) ions, forming NiO, increasing the thickness of the oxidation layer.

**Spectroscopy analysis**

UV-vis absorption spectroscopy is one of the important methods to reveal the energy structures and optical properties of the semiconducting nanocrystals. Fig. 5 shows the UV-visible absorption spectra of the as-synthesized NiO nanowires by ultrasonically dispersing in absolute ethanol. The strong absorptions in the UV region are observed at wavelengths of about 271 nm, 284 nm and 320 nm for the samples as-synthesized after magnetic heat treatment at 400 °C, 600 °C and 800 °C, respectively, for 3 h in open air, indicating that the NiO nanowires prepared via this method could be promising optical p-type semiconducting nanomaterials. These absorptions in the UV region can be attributed to the electronic transition from the valence band to the conduction band in the NiO semiconducting nanocrystals. Meanwhile, we also observe that the strong absorption peak of sample “a” (at 271 nm, crystalline grain size of 12.22 nm) reveals a slight blue shift (about 49 nm) in comparison with the sample “c” (at 320 nm, crystalline grain size of 24.03 nm). This phenomenon of the blue shift is evidence of the quantum confinement effect and implies that the strong absorption wavelength of semiconducting nanocrystals becomes smaller with the decrease of crystalline grain size. R. Rosetti et al. believe that when the semiconducting crystalline grain size is sufficiently small and the radius of the crystalline grain approaches the radius of the first excited-state orbital of the conduction band electrons, the so-called quantum-size effects are observed. With a reduction in crystalline grain size, there is a concomitant blue shift in the absorption spectrum and the band gap energy of the semiconductor becomes larger.

The direct optical band gap energy (\(E_g\)) can be calculated on the basis of the optical absorption spectra by the following equation:

\[
(ahv)^2 = B(HV - E_g)
\]

where \(h\) is the incident photon energy, \(\alpha\) is the absorption coefficient and \(B\) is a constant relative to the material, respectively. Therefore, the optical band gap for the absorption peak can be quantitatively estimated by extrapolating the linear portion of the \((ahv)^2–hv\) curve to the energy axis. Fig. 6 demonstrates the typical \((ahv)^2\) versus \(hv\) curve for as-synthesized NiO nanowires at different heat treatment temperatures. The corresponding band gap energies of NiO nanowires with different crystalline grain sizes were about 4.2 eV, 4.0 eV and 3.8 eV, respectively. The sample “a” with a crystalline grain size of 12.22 nm shows a band gap energy of about 4.2 eV, which is increased by 0.55 eV in comparison with the bulk NiO material (3.65 eV). The band gap energy of sample “c” (grain size is 24.03 nm) is about 3.8 eV, which is smaller than sample “a” (grain size is 12.22 nm), indicating the band gap energy gradually increases with the decrease of the crystalline grain size.

**Gas sensing properties**

Fig. 7 (A) shows the schematic diagram of the as-prepared gas sensor. In this gas sensor, the ultralong NiO nanowires are used as conducting channels in the interdigitated electrodes. The interdigitated arrays of electrodes had a finger length of 600 μm and line width of 10 μm. The arrays of NiO semiconducting nanowires with high aspect ratio are formed between these interdigitated electrodes, as shown in the SEM image (see Fig. 7 (A1)). A conductance between two electrodes is measured to investigate the sensory response. We fabricated three kinds of gas sensors by using as-prepared NiO nanowires obtained via heat treatment of Ni nanowires at (sample “a”), crystalline grain size of 12.22 nm) 400 °C, (sample “b”), crystalline grain size of 16.71 nm) 600 °C and (sample “c”), crystalline grain size of 24.03 nm) 800 °C for 3 h in open air. In our experiments, the sensor response \(R_t\) in conductance is defined by equation:

\[
R_t = \frac{\Delta G}{G_0} = \frac{(G - G_0)}{G_0}
\]

where \(G_0\) is the conductance of the gas sensor before exposure to the target gas, and \(G\) is the conductance of the sensor after exposure. The plots of \((ahv)^2\) versus \(hv\) for as-synthesized NiO nanowires. The optical band gaps of NiO nanowires with crystalline grain sizes of 12.22 nm, 16.71 nm and 24.03 nm were about 4.2 eV, 4.0 eV and 3.8 eV, respectively.

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where $G_0$ and $G$ are the conductance of the NiO nanowires before and after exposure to the testing gas. Fig. 7 (B) shows gas sensing measurements performed using ultralong NiO nanowires with different grain sizes. The linear slope of current–voltage ($I$–$V$) curves for NiO nanowires (sample “a”) with crystalline grain of 12.22 nm is found to be higher than that for other NiO nanowires with larger grain size (sample “b” or “c”). Since the change in conductivity is related to the overall surface area and the concentration of negatively charged chemical species, such as $O_2^-/C_0$, $O_2^-/C_0$, and $O^-/C_0$, absorbed on the surface, it is likely that the coverage of oxygen is higher in NiO nanowires with smaller grain size.

Three sensing cycle experiments with different concentration of NH$_3$ gas from 50 ppm to 200 ppm have been investigated, as shown in Fig. 7 (C). The results show that the gas sensor exhibits a fast response and is sensitive to the presence of NH$_3$ gas at room temperature. For instance, when the sensor is exposed to 50 ppm of NH$_3$ gas for about 36 s without the need for pre-concentration step, the conductance change is about 19%. Meanwhile, it is obvious that the change in the conductance increases with the increasing NH$_3$ gas concentration. Importantly, we find that after three sensing cycle experiments, it takes less than 10 min to completely recover by blowing the reference gas together with illumination using an IR lamp, which is important for practical ultralong NiO nanowire sensor applications.

In addition, the conductance change for NiO nanowires increases with the increasing grain size (see Fig. 7 (C)) (the sensor response in 50 ppm to 200 ppm: $R_t$ (sample “a”) > $R_t$ (sample “b”) > $R_t$ (sample “c”); grain size: $D$ (sample “a”, 12.22 nm) < $D$ (sample “b”, 16.71 nm) < $D$ (sample “c”, 24.03 nm)), due to the smaller grains having more grain boundaries. Previous reports have demonstrated that the grain boundaries or grain junctions are considered as the active sites to adsorb gas molecules, and can affect the electron transport through the nanowire arrays, resulting in the conductance changes. In order to investigate H$_2$O vapor interaction on NH$_3$ gas sensing results, the gas sensor was only exposed to H$_2$O vapor under the same flows that are used to measure NH$_3$ gas. The measurement results are shown in Fig. 7 (C). At a concentration of 100 ppm, the H$_2$O vapor did not give appreciable signals, whereas the conductance change of the sensor upon exposure to NH$_3$ gas was about 30% (see Fig. 7 (C)). When H$_2$O concentration was 200 ppm, the conductance change of the sensor was less than 1%, compared with 51% for NH$_3$ gas. This makes NH$_3$ sensing results relative precision in our measurements.

To further investigate the reproducibility of the sensor, the gas sensor is repeatedly exposed to 50 ppm NH$_3$ gas, as shown in Fig. 7 (D). The change of the conductance is maintained, and the recovery abilities are not reduced after four sensing cycles, which indicates that the NiO nanowire-based sensor is characterized by an outstanding repeatability and reproducibility. The selectivity of the sensors to a variety of flammable, toxic and corrosive gases including chloroform, hexane, dichloromethane, acetone, ethanol, formaldehyde, toluene, and ammonia have been investigated. Fig. 7 (E) shows that the NiO nanowire-gas sensor exhibits excellent selectivity to NH$_3$ gas when exposed to those interfering vapors. For example, the conductance change of the sensors upon exposure to 200 ppm of NH$_3$ gas is 51%, whereas that change is less than 7% upon exposure to 1000 ppm of other gases (such as chloroform, hexane, dichloromethane, acetone, ethanol, formaldehyde, and toluene). This excellent selectivity for NH$_3$ gas can be explained as follows: in the first place,
ammonia is a strong electron donor, and the electrons could be transferred from ammonia to the p-type NiO nanowires, resulting in a significant change in the conductance of sensor. In the second place, selective physisorption to ammonia is also one of the key factors. A variety of active sites available for ammonia molecule sorption exist on the ultralong nanowire arrays. This selective physisorption to ammonia affects electron transport through the nanowire arrays, resulting in excellent selectivity for NH3 gas.

Conclusions

In summary, we have demonstrated a chemical reduction and a subsequent oxidation during heat treatment, resulting in a large-scale synthesis of NiO nanowires with high aspect ratio, having uniform diameters of about 150 nm and a length up to about 300 μm. Our investigation demonstrates that the external magnetic field and heat treatment can significantly influence the structure as well as crystalline grain size of semiconducting nanowires formed in open air. Based on the UV-visible absorption spectra characterization, we find that the ultralong NiO nanowires with a crystalline grain size of 12.22 nm have a characteristic band gap energy of about 4.20 eV, with an increase of 0.55 eV in comparison with the bulk NiO material (3.65 eV).

Significantly, this high aspect ratio NiO nanowire-based sensor exhibits a fast response, rapid recovery and good reproducibility toward NH3 gas over other organic gases. It is suggested that the approach we demonstrated here can also be extended to other one-dimensional ultralong semiconducting nanomaterials for corresponding gas sensing applications.

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