Hierarchically Assembled ZnO Nanorods on TiO2 Nanobelts for High Performance Gas Sensor

Zhenhuan Zhao1,2, Dongzhou Wang1, Xueliang Kang1, Yuanhua Sang1, and Hong Liu1,2,*

1State Key Lab of Crystal Materials, Shandong University, Jinan, 250100, China
2Beijing Institute of Nanoenergy and Nanosystems, Chinese Academy of Sciences, Beijing, 10085, P. R. China

ABSTRACT

Gas sensors based on semiconductors have wide applications. In this study, TiO2 nanobelts prepared from alkali-hydrothermal process were used to hierarchically assemble ZnO nanorods to form a surface heterostructure. The as-synthesized hierarchical heterostructure was confirmed with characterizations. The possible grown mechanism was investigated. The hierarchical heterostructure was used to assemble gas sensor. The sensing performance of the assembled gas sensor was explored using different gas, and it is found that the hierarchical heterostructure sensor has excellent sensitivity and selectivity upon exposure to trimethylamine gas. The sensitivity was about 25 at the concentration as low as 5 ppm of trimethylamine. The best working temperature was determined to be 200 °C. The sensing mechanism was also discussed and proposed to be related to a surface-depletion model.

KEYWORDS: ZnO Nanorod, TiO2 Nanobelt, Hierarchical Heterostructure, Gas Sensor.

1. INTRODUCTION

Gas sensors based on semiconducting metal oxides have attracting much attention for a long period because of their small dimensions, low cost, high sensing performance and high compatibility with microelectronic manipulation. They are widely employed to detect the toxic and combustible gases, monitor emissions from vehicles, and quality control in chemicals, food and cosmetics. Trimethylamine is one of the toxic gases in biology and food industry. Trimethylamine is commonly used as target gas for the monitoring of the food quality through gas sensors. However, traditional gas sensors are based on metal oxide film consisted of nanoparticles, which has the disadvantages of low sensitivity and poor selectivity.

Recent years, one dimensional nanostructures such as nanowires[4,5] nanotubes[6,7] and nanobelts[8,10] are intensively used as the sensing materials for various detection applications due to the ultrahigh surface-to-volume ratio.[1,11] Among these metal oxides, ZnO in the form of nanorod, nanowire and nanobelt is one of the most promising sensing materials for gas sensor due to its high mobility of conduction electrons, good chemical and thermal stability, low cost and easy manipulation of various nanostructure.

TiO2 is also an important semiconductor used in various fields, such as photocatalysis[12] solar cell[13] biosensor[14,16] and gas sensor[17] because of its low cost, chemical stability and environmental-friendly. It has already been demonstrated that one dimensional TiO2 are the excellent material for gas sensor.[18,19] However, the sensing performance of these one dimensional nanostructures is limited to a very low level. Further improvement in the sensitivity of the gas sensor is urgently expected. To solve this problem, many methods have been developed and one of the most effective approach is to construct surface heterostructure. Several advantages can be introduced to the heterostructure such as increased effective surface area, improved charge transfer and synergistic effect of the different parts in the heterostructure. For example, the ethanol sensing performance of TiO2 nanobelts can be significantly enhanced by an acid corrosion method. With the aid of acid corrosion, the smooth surface of primary TiO2 nanobelts can be decorated with numerous TiO2 nanoparticles to form a surface heterostructure with dramatically increased surface area for the adsorption of more target gas molecules.[20] In addition, due to the excellent chemical stability and mechanical properties, TiO2 nanobelts can also be employed as the supporting material to assemble surface heterostructure by loading noble metal nanoparticles, such as Ag nanoparticles[9] and Pd nanoparticles[10] and metal oxide like SnO2.[21] Therefore, to assemble surface heterostructure on TiO2 nanobelt should be the potential strategy for gas sensing enhancement.

In this study, alkali-hydrothermal synthesized TiO2 nanobelts were used as the backbone to support ZnO nanorods for the construction of hierarchical surface.
heterostructure. The hierarchical structure was confirmed by several characterization methods. The results of the gas sensing experiments indicated that the hierarchical heterostructure showed improved sensing sensitivity to trimethylamine gas. It demonstrates that by assembling ZnO nanorods onto the surface of TiO2 nanobelts to form surface heterostructure is an effective way to improve the sensor performance.

2. EXPERIMENTAL DETAILS

2.1. Materials

Sodium hydroxide (NaOH, analytic grade), sulfuric acid (H2SO4), hexahydate zinc nitrate (Zn(NO3)2)·6H2O, zinc acetate Zn(CH3COOH)2 ethanol, hexamethylenetetramine (C6H12N4), Deionized water was used throughout the experiments. Titania P25 (TiO2, ca. 80 wt% anatase and 20 wt% rutile) was used as the Ti precursor to prepare TiO2 nanobelts.

2.2. Preparation of TiO2 Nanobelts

TiO2 nanobelts were synthesized through an alkali hydrothermal process.22 In a typical procedure, 60 mL of 10 M NaOH aqueous solution and 0.3 g titania P25 were homogeneously mixed together and then transferred into a 80 mL Teflon-lined autoclave. The autoclave was heated at 200 °C for 72 h. The products were collected and washed with copious deionized water through filtration. This step gave the formation of sodium titanate nanobelt, which was transferred into hydrogen titanate nanobelt through an ion exchange process with 0.1 M HCl aqueous solution for 48 h. The obtained hydrogen titanate nanobelts were then washed and dried in air at 70 °C. Finally, TiO2 nanobelts were prepared by thermally annealing hydrogen titanate nanobelts at 600 °C for 2 h.

2.3. Preparation of ZnO NDs@TiO2 NBs Hierarchical Surface Heterostructure

The ZnO NDs@TiO2 NBs hierarchical surface heterostructure was prepared by a hydrothermal process. Before the hydrothermal process, the TiO2 nanobelts were coated with ZnO seeds by a modified dip-coating method.23,24 In detail, 0.005 M zinc acetate was firstly dispersed into 40 mL ethanol followed by the addition of 0.1 g TiO2 nanobelts. The mixture was sonicated for 20 min and gently stirred for another 20 min. The homogeneous dispersion was then filtrated and dried at 70 °C. The dispersing-filtration-drying process was repeated for several times. By calcination at 350 °C for 20 min, ZnO seeds coated TiO2 nanobelts were obtained. Subsequently, ZnO seeds covered TiO2 nanobelts were added to an aqueous solution of 40 mL containing 0.005 M zinc nitrate and 0.005 M hexamethylenetetramine. The mixture was sealed into a 50 mL Teflon-lined autoclave and heated at 90 °C for 8 h. After reactions, the ZnO nanorods@TiO2 nanobelts hierarchical surface heterostructure (ZnO-NDs@TiO2-NBs HSH) was finally obtained by isolating the solution through filtration and washing with deionized water and ethanol. For comparison, ZnO nanorods were also prepared using the same hydrothermal procedure without the addition of TiO2 nanobelts.

2.4. Characterization Methods

The X-ray powder diffraction (XRD) patterns of the samples were recorded with a Bruker D8 Advance powder X-ray diffractionmeter with Cu Kα radiation with λ = 0.15406 nm over a 2θ scan range between 20° and 80°. The microstructure and morphology of the samples were observed using a HITACHI S-800 field-emission scanning electron microscope (FE-SEM). The fine structure and crystalline lattice were obtained using the high-resolution transmission electron microscope (HRTEM) on a JEOL JEM 2100F microscope. The Fast-Fourier-Transform (FFT) patterns acquired using the DigitalMicrograph software aligned to the HRTEM microscope.

2.5. Gas Sensing Experiments

The as-synthesized ZnO nanorods (ZnO-NDs), TiO2 nanobelts (TiO2-NBs), and ZnO-NDs@TiO2-NBs HSH were used as the sensing materials. To assembling the sensors, the as-prepared individual sample was uniformly mixed with a calculated amount of water to prepare the slurry, which was carefully coated onto the outer surface of a ceramic tube and dried in air. At the two ends of the ceramic tube two gold wires were inlaid as electrodes and connected to two Pt wires. The control over the temperature was achieved by inserting a resistive heating wire into the ceramic tube. Figure 1(a) shows the schematics of the sensor.

The gas sensing experiment was carried out with a WS-30A gas sensing system (Zhengzhou Winsen Electronics Co., Ltd., China). The gas sensing experiments were performed in a gas sensing system (Zhengzhou Winsen Electronics Co., Ltd., China) connected to two Pt wires. The control over the temperature was achieved by inserting a resistive heating wire into the ceramic tube. Figure 1(a) shows the schematics of the sensor. The microstructure and morphology of the samples were observed using a HITACHI S-800 field-emission scanning electron microscope (FE-SEM). The fine structure and crystalline lattice were obtained using the high-resolution transmission electron microscope (HRTEM) on a JEOL JEM 2100F microscope. The Fast-Fourier-Transform (FFT) patterns acquired using the DigitalMicrograph software aligned to the HRTEM microscope.

Fig. 1. Schematics of (a) the as-assembled gas sensor and (b) the corresponding equivalent circuit.
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Technology Co. Ltd., P. R. China). The ethanol with the desired amount was injected onto a beating platform in the test chamber to prepare ethanol-air mixed gas for ethanol sensing. Figure 1(b) shows the sensing electrical circuit. The electrical resistance of the sensors in air or in the target gas is calculated as $R = [R_s(V_{in} - V_{out})]/V_{out}$, where $R$ is the sensor resistance, $R_s$ is the load resistance, $V_{in}$ is the total loop voltage applied to the electrical circuit, and the $V_{out}$ is the output voltage across the load resistor. The sensor sensitivity $S$ is defined as $S = R_a/R_g$, where $R_a$ and $R_g$ is the sensor resistance measured in air and in the mixed air containing target gas at the same relative humidity of about 30%, respectively.9

3. RESULTS AND DISCUSSION

3.1. Structure and Morphology

To investigate the crystalline phase of the as-synthesized samples, X-ray diffraction analysis was performed. Figure 2 shows the XRD patterns of the as-prepared samples. Curve a and b are drawn from the PDF cards with the number of 79-2205 and 21-1272 of ZnO and TiO₂, respectively. The XRD patterns of the primary TiO₂ NBs (curve c), ZnO NDs (curve d), ZnO seeds@TiO₂-NBs (curve e) and ZnO-NDs@TiO₂-NBs hierarchical heterostructure were also illustrated for comparison. Obviously, the crystal phase of TiO₂ nanobelts backbone is mainly consist of anatase phase due to the existence of characteristic peaks located at 25.2°, 37.6°, 47.8°, 53.8°, 55° and 62.6° (curve c). The weak peak located at 28.2° indicates the existence of a little portion of TiO₂-B (JCPDF card no. 46–1237).25 Curve d shows the XRD pattern of ZnO-NDs. All the peaks can be indexed to hexagonal wurtzite ZnO with characteristic peaks at 31.7°, 34.3° and 36.1°, which is well consistent with the JCPDF card (curve b). The very sharp peaks with high intensity indicate the single crystalline feature of the as-prepared ZnO-NDs because no characteristic peaks can be observed for impurities. Curve e shows the XRD pattern of TiO₂ nanobelts coated with ZnO seeds. The peak located at 25.2° can be assigned to (101) crystalline plane of TiO₂-NBs, whereas the sharp peaks located at 31.7°, 34.3° and 36.1° can be indexed to the crystalline planes of (100), (002) and (101) of wurtzite ZnO. Curve f is the XRD pattern of ZnO-NDs@TiO₂-NBs hierarchical heterostructure. It is found that the XRD pattern of the hierarchical heterostructure shows the similar characteristic peaks with that of ZnO seeds coated TiO₂ nanobelts, meaning the success of growth of ZnO nanorods on TiO₂ nanobelt surface. The single crystalline feature of ZnO nanorods in the hierarchical heterostructure is expected to facilitate the charge transfer.

The micromorphology of ZnO-NSs@TiO₂-NBs hierarchical heterostructure was investigated by SEM. Figure 3 shows the SEM images of as-prepared hierarchical heterostructure, primary TiO₂ nanobelts and ZnO nanorods. The primary TiO₂ nanobelt with a width of 50–200 nm and length up to several micrometers has a typical smooth surface and rectangular cross section (Fig. 3(a)), which is consistent with our previously prepared TiO₂ nanobelts.20,22 By applying the hydrothermal growth process of ZnO-NDs, the initially smooth TiO₂ nanobelts branched out, forming a hierarchical heterostructure. The typical SEM images of such heterostructure are shown in Figures 3(c) and (d). It is interesting that ZnO nanorods were densely assembled onto the surface of TiO₂ nanobelts. The length of the secondary ZnO nanorods is up to 500 nm. The mace-like morphology of the hierarchical heterostructure has large exposed ZnO surface area. In addition, the dense ZnO nanorods on TiO₂ nanobelts formed numerous micro-channel between the nanorods. These advantages of the...
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Hierarchically assembled ZnO nanorods on TiO2 nanobelts for high performance gas sensor. The gas sensing performance is expected to improve the gas sensing performance.

To further examine the microstructure, transmission electron microscopy (TEM) was also used. Figure 4 shows the TEM images of the ZnO-NDs@TiO2-NBs hierarchical heterostructure. As shown in Figure 4(a), ZnO nanorods were vertically grown on the TiO2 nanobelt support. The clear crystalline lattice fringes of the ZnO nanorod branch and the TiO2 nanobelt support indicate the single crystalline feature of both the ZnO and TiO2. This conclusion can be well supported by the bright spots of the two dimensional FFT patterns shown in Figures 4(c) and (d). It should be pointed out that ZnO nanorods was grown on the ZnO seeds, which can be clearly seen from Figure 4(b). Both the nanorod and the seed part displayed similar crystalline lattice fringes. The measured lattice spacing is 0.35 nm for TiO2 and 0.27 nm for ZnO, corresponding to the (101) plane of TiO2 and (0002) plane of ZnO, respectively. Therefore, the growth direction of the TiO2 nanobelt support and the ZnO nanorod branch was determined to be along [010] and [0001], respectively.

Based on the above analysis, the growth process of the ZnO-NDs@TiO2-NBs hierarchical heterostructure is illustrated in Figure 5. Firstly, the primary TiO2 nanobelts were coated with a layer of ZnO seed nanoparticles. These ZnO nanoparticles acted as the specific nucleate sites which can be clearly seen from Figure 5(a). For the growth of ZnO nanorod, it is necessary to seed the TiO2 nanobelt with ZnO nanoparticles. In the initial stage, ZnO nanorods nucleated and crystallized along the [0001] direction on the ZnO seed sites. With the proceeding of the hydrothermal process, the initial nanorods absorbed Zn$^{2+}$ and OH$^{-}$ ions from the precursor solution to form Zn(OH)$_2$, which decomposed to form ZnO. Though the TiO2 has six different crystalline planes. The ZnO nanorods were still densely grown on the TiO2 nanobelt surface. This may be due to the high zinc salt concentration and extended hydrothermal reaction time.

3.2. Gas Sensing Performance

A good gas sensor should exhibit fast response once upon exposure to the target gas. Meanwhile, it also should have the ability to recognize the target gas at a concentration of target gas as low as possible. Summarily, the gas sensor should have good selectivity and sensitivity. Under the present experiments, we have investigated the gas sensing performance of the prepared ZnO-NDs@TiO2-NBs hierarchical heterostructure. For full comparison, the sensing behavior of TiO2 nanobelts and ZnO nanorods was also examined under the same condition.

Figure 6 shows the response/recovery curves at 200 °C of the TiO2 nanobelts sensor, ZnO nanorods sensor and the hierarchical heterostructure sensor. The gas concentration of trimethylamine was tuned from 5 ppm to 500 ppm. Obviously, once exposed to the trimethylamine gas, all the three sensors exhibited a remarkable response with different output voltage of $V_{out}$. However, there was still different response behavior for the three gas sensors. For example, at 500 ppm, the output voltage of $V_{out}$ was 1.14, 1.34 and as high as 4.0 for TiO2 nanobelts (Fig. 6(a)), ZnO nanorods (Fig. 6(b)) and ZnO-NDs@TiO2-NBs hierarchical heterostructure (Fig. 6(c)), respectively. Once the concentration decreased to 100 ppm, the $V_{out}$ value also decreased to 0.312, 0.434 and 2.47, respectively. This means that with decreasing the concentration of trimethylamine gas the output voltage of the three sensors decreased in a different rate, suggesting an increasing order of TiO2 nanobelts, ZnO nanorods, ZnO-NDs@TiO2-NBs hierarchical heterostructure of the sensing performance. Impressively, the sensor made from the hierarchical heterostructure even showed a high output value of about 0.956 at the very low concentration of trimethylamine gas.
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Fig. 6. Response/recovery curves gas sensors made from (a) TiO$_2$ nanobelts, (b) ZnO nanorods and (c) ZnO-NDs@TiO$_2$-NBs hierarchical heterostructure upon exposed to different concentrations of trimethylamine gas at 200 °C. (d) Calculated sensitivity $S$ as a function of gas concentration.

5 ppm, indicating the good sensing capability to trimethylamine gas.

The sensor performance can be directly illustrated in the sensitivity $S$. The corresponding sensitivity $S$ of the three sensors are shown in Figure 6(d). According to Figure 6(d), the sensitivity of the three sensors increases linearly with the concentration of trimethylamine gas. The sensitivity of the ZnO sensor is slightly higher than that of TiO$_2$ sensor, while notably the sensitivity of the hierarchical heterostructure sensor shows much higher values at all the gas concentrations. Even at the concentration as low as 5 ppm, the sensitivity of the hierarchical heterostructure sensor reaches to about 25, which is much higher than those listed in literatures. This means by assembling ZnO nanorods onto the surface of TiO$_2$ nanobelts can significantly improve the sensing capability.

Gas sensors also need to detect target gas at different working temperatures. Therefore, it is important to investigate the effect of temperature on the sensor performance. Figure 7 shows response/recovery curves of the ZnO-NDs@TiO$_2$-NBs hierarchical heterostructure sensor at different temperatures by exposure to trimethylamine gas at a constant concentration of 300 ppm. Clearly, as seen from Figure 7(a), the sensor shows good response/recovery gas at all the temperatures because the $V_{out}$ in trimethylamine gas recovered to similar value when fresh air was purged into the testing chamber. Notably, when the sensor was working at 100 °C, the increase of the output voltage $V_{out}$ of the sensor was the smallest. With the increase of the working temperature, the increase of the output voltage gradually increased and reached to the highest value of about 3.5 at 200 °C. While the temperature increased to 250 °C, the output voltage $V_{out}$ decreased to 1.8, much lower than 3.5 at 100 °C. This indicates that the hierarchical heterostructure sensor showed the best response/recovery behavior while working at 200 °C. The corresponding sensitivity at different temperatures as the function of gas concentration is shown in Figure 7(b). It is found that at all the concentrations the sensor hardly exhibited sensing capability at 100 °C and 150 °C. Similar increasing trend can be observed when the sensor was working at 200 °C and 250 °C. However, the sensitivity obtained at 200 °C was much higher than that at 250 °C. Therefore, it is concluded that the ZnO-NDs@TiO$_2$-NBs hierarchical heterostructure has the best sensing performance upon exposure to trimethylamine gas at 200 °C.

As stated previously, the selectivity of the gas sensor is another key parameter. Therefore, the sensing performance of the hierarchical heterostructure to different gas was also investigated at the same gas concentration and working temperature. Figure 8 shows the response/recovery curves of the ZnO-NDs@TiO$_2$-NBs hierarchical heterostructure upon exposure to trimethylamine gas, ammonia gas, and CO and ethanol vapor, respectively, at 200 °C and constant concentration of 300 ppm. It is found that though the sensor shows response to all the detecting gas, remarkably different response behavior can be seen from Figure 9. The value of the $V_{out}$ upon exposure to ethanol vapor,
CO, ammonia gas and trimethylamine gas was about 0.59, 0.97, 1.44 and 3.43, respectively, indicating the best detecting capability to trimethylamine gas. Actually, the present ZnO-NDs@TiO2-NBs hierarchical heterostructure sensor shows much better sensing performance to trimethylamine gas. The sensitivity of the hierarchical heterostructure sensor is much higher than those listed in literatures.3, 26, 27 Most impressively, the present hierarchical heterostructure sensor has excellent sensing performance at a very low gas concentration of 5 ppm. This gas concentration is much lower than 160 ppm of ZnO film sensor,28 400 ppm of ZnO and Al film,29 and 100 ppm of SnO2 and ZnO nanocomposite.30

3.3. Sensing Mechanism

Most semiconductor oxide based gas sensors operate on the basis of the variation of the electrical properties of the oxide materials.4 This variation of the electrical resistance is thought to be related to a surface depletion model. Actually, the sensing mechanism of the TiO2 nanobelts for detecting reductive gas has been discussed in literature.9 Trimethylamine gas belongs to the reductive gas type. Therefore, at the present sensor, TiO2 nanobelts for sensing trimethylamine gas should be based on the similar mechanism, i.e., the surface-depletion model.11 When TiO2 nanobelts are exposure to air, oxygen molecules are adsorbed onto the surface of TiO2 nanobelt and trap the electrons from the conduction band of TiO2 to form superoxo or perpxo-like species. This surface reaction brings about the formation of a surface depletion region within the nanobelt, resulting in the increase of the electrical resistance of the nanobelts. Once the reductive gas (the target gas) were introduced to contact with the surface of the nanobelts, effective electron transfer happens from the target gas to TiO2 nanobelt, leading to the decrease of the electrical resistance of the nanobelts.

Actually, ZnO should obey the similar surface depletion mechanism. The surface physical and chemical properties plays important roles in its gas sensing performance.11 Though the energy level of the conduction band of TiO2 and ZnO is similar with each other, the present hydrothermally synthesized TiO2 nanobelts dominantly belongs to anatase phase and are known to have many oxygen vacancies which will act as the electron trap. This will help to drain electrons from ZnO phase to TiO2 nanobelts through the interfacial heterostructure between ZnO and TiO2. The electron transfer will undoubtedly speed the electron transfer from the target reductive gas to the ZnO, and then to TiO2. In addition, the electron mobility of ZnO (1175 cm2/V·S) is much higher than that of TiO2 (0.2 cm2/V·S).32 Since the charge carriers diffusion from bulk to surface of the semiconductor is the rate-limiting step, once the hierarchical heterostructure sensor is exposed to air, the ZnO nanorod part should be more sensitive than the TiO2 nanobelt part to the oxygen molecule adsorption. In another word, ZnO nanorods should be more sensitive to the variation of the concentration of electrons induced by the oxygen adsorption and electron transfer between the reductive target gas and the semiconductor. The present hierarchical heterostructure displays several advantages which is beneficial for the gas sensing. The first one is the exposure of both the surface...
of ZnO nanorod and TiO₂ nanobelt. These two kinds of semiconductors are proved to be effective materials for gas sensor application. The second one is the exposure of more sensitive surface of ZnO nanorod. The third one is the specific hierarchical structure. The charge transport is faster in one dimensional ZnO nanorod and TiO₂ nanobelt, which both of them are highly crystallized. Meanwhile, the microchannel formed between the ZnO nanorods can facilitate the gas diffusion based on a capillary force. Therefore, based on the synergistic effect of ZnO and TiO₂, the hierarchical heterostructure sensor exhibits excellent sensing performance to the reductive trimethylamine gas.

4. CONCLUSION

In this study, ZnO nanorods were assembled onto the surface of TiO₂ nanobelts to form a hierarchical surface heterostructure through a hydrothermal process with the aid of seeds coating method. In the hierarchical heterostructure, the ZnO nanorods with single crystalline feature were perpendicularly grown on the surface of TiO₂. The grown mechanism has been investigated through XRD and HRTEM. The sensing performance of this hierarchical heterostructure was examined, and it was found that the hierarchical heterostructure sensor has excellent sensitivity and selectivity to trimethylamine gas. The potential sensing mechanism was also discussed and thought to be related to the surface-depletion model.

Acknowledgments: The authors are thankful for funds from National Natural Science Foundation of China (Grant No. 51372142), National Science Fund for Distinguished Young Scholars (NSFDYS: 50925205), Innovation Research Group (IRG: 51321091) and the ‘100 Talents Program’ of Chinese Academy of Sciences. Thanks for the support from the ‘thousands talents’ program for pioneer researcher and his innovation team, China.

References and Notes