Synthesis of TiO2 decorated Co3O4 acicular nanowire arrays and their application as an ethanol sensor†

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A novel heterostructure of TiO2 modified Co3O4 (TiO2/Co3O4) acicular nanowire (NW) arrays has been fabricated in this study, which demonstrates a good performance for ethanol detection at working temperatures as low as 160 °C. Co3O4 NW arrays were first grown on an Al2O3 substrate patterned with an Ag/Pd electrode by a hydrothermal method, and then TiO2 nanoparticles were decorated on the surface of Co3O4 NW arrays by using pulsed laser deposition (PLD). It is found that after decoration of TiO2, the TiO2/Co3O4 NW array sensor exhibits a much higher response to ethanol (Ra/Rs = 65, Ra is the sensor resistance measured in a mixture of target gases and Rs is the resistance measured in air) compared with the pristine Co3O4 NW sensor (Ra/Rs = 25). Importantly, the TiO2/Co3O4 sensor has shown a detection limit as low as 10 ppm, and a good reproducibility. The reason for the enhanced sensing properties of TiO2/Co3O4 is considered to be due to the formation of a p–n junction between the p-type Co3O4 and n-type TiO2.

1. Introduction

Co3O4 is an important semiconductor with a normal spinel structure, which has been widely studied as a promising material applied in lithium-ion batteries, supercapacitors, catalysis, etc.1–6 Among its numerous applications, Co3O4 based gas sensors have attracted much attention recently, which exhibit good gas-sensing characteristics.7–14 To optimize the gas performance of Co3O4, a large amount of effort has been made to control the morphology and size of Co3O4 in the previous studies.5,13,17,18 The synthesis of various nanostructures of Co3O4 such as nanoparticles,7 nanorods,6,7 nanowires,10,18,19 nanosheets10 and hollow nanospheres9 has been carried out by using various techniques including electrospinning,18 hydrothermal methods,12 solid state thermal decomposition, etc.17,19 Among these Co3O4 based nanomaterials, a one-dimensional nanowire array is considered to be a promising architecture with a high chemical response.20 Yoon et al. have prepared Co3O4 nanowires with one-dimensional morphologies by electrospinning, which exhibited a high response to 100 ppm C2H5OH at 300 °C.21 Wen et al. have synthesized one-dimensional rhombohedral-shaped Co3O4 nanorod arrays via a hydrothermal route, which showed a high sensitivity to ethanol up to ~70.12 As we know, designing a heterojunction structure between different band gap and energy level semiconducting materials is an effective way to enhance the photocatalytic and catalytic activity, and gas sensing performance of the nanocomposite material.2,22–24 Recently, it has been found that designing a p–n junction by combining Co3O4 with other n-type semiconductors would be a significant route to enhance its gas response.12,25–26 In the heterogeneous region, the p-type semiconductor Co3O4 and the n-type semiconductor TiO2 can form a self-built electric field, and establish a depletion layer. When exposed to air, the hole density on the surface of the Co3O4 increase while the electrons on the surface of the TiO2 decrease due to the ionization of absorbed oxygen species, which leads to a lower resistance of the Co3O4. When ethanol was introduced into the chamber, the electrochemical reaction between oxygen and gas molecules will be quickly neutralized with more holes.

† Electronic supplementary information (ESI) available: The optical micrographs of the Al2O3 substrates, the as-synthesized precursor, pristine Co3O4 and TiO2/Co3O4 NW arrays; the image of the gas sensing analysis system; the sensing properties of TiO2/Co3O4 is considered to be due to the formation of a p–n junction between the p-type Co3O4 and n-type TiO2.

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But at this moment, the electron transfer from n-type TiO₂ to p-type Co₃O₄ is impeded because of energy band bending, which makes the resistance of the TiO₂/Co₃O₄ demonstrate a more obvious change than the pristine Co₃O₄. As a consequence, it demonstrates a higher gas sensitivity than the pristine Co₃O₄. Based on the above discussion, controlling the morphology and building a p–n junction at the same time is expected to be an effective way to enhance its gas response. However, such a kind of important and interesting topic has not yet been fully investigated.

In this study, we report the synthesis of Co₃O₄ acicular NW arrays with acicular morphology via a facile hydrothermal route. TiO₂ nanoparticles were subsequently deposited on the Co₃O₄ NW by using pulsed laser deposition (PLD) and formed a p–n junction with it. The gas sensing performance was systematically investigated and compared with the pristine Co₃O₄ acicular NW arrays. It is found that the TiO₂ decorated Co₃O₄ nanocomposite shows a much better sensing performance than the pristine Co₃O₄ NW arrays.

2. Experimental details

The synthesis of TiO₂/Co₃O₄ NW arrays includes two steps, one is preparing Co₃O₄ acicular NW arrays on an Al₂O₃ substrate by using the hydrothermal route, and the other is decorating TiO₂ nanoparticles on the surface of Co₃O₄ by using PLD. In a typical procedure for fabricating the Co₃O₄ acicular NW arrays, 4 mmol (1.16 g) of cobalt nitrate (Co(NO₃)₂·6H₂O), 8 mmol (0.29 g) ammonium fluoride (NH₄F) and 8 mmol (1.12 g) of urea (CO(NH₂)₂) as sources were dissolved in 40 ml deionized (DI) water under stirring at room temperature. In the synthesis of acicular Co₃O₄ NWS, the roles of NH₄F and (CO(NH₂)₂) have already been discussed in detail in a previous study. After stirring for 20 min, the homogeneous solution was transferred into a 100 ml Teflon lined stainless steel autoclave. A piece of polycrystalline Al₂O₃ ceramic plate substrate (13.4 mm × 7 mm, 0.5 mm in thick) that had been plated with an Ag/Pd electrode substrates was immersed in the reaction solution against the bottom of the autoclave. The polycrystalline alumina ceramic substrates were bought from Beijing Elite Tech Co., Ltd, China. As the amount of Co₃O₄ NW arrays deposited on the Pd–Ag electrode substrates is not enough for the BET detection, we also took another piece of cleaned titanium (Ti) foil (80 mm × 20 mm) with a much larger surface area and immersed it in the autoclave, which could collect much more Co₃O₄ powders for the BET detection. The autoclave was sealed and maintained in an electric oven at 95 °C for 24 h. After cooling down to room temperature, the substrate was removed, rinsed with distilled water several times in order to remove the free standing nanoparticles or residual reactant, and dried at 60 °C under vacuum for 2 h. After that, the as-prepared pink precursors of Co(CO₃)₁₀·5(OH)·0.11H₂O were converted to Co₃O₄ via thermal decomposition at 500 °C in air for another 4 h. After the fabrication of Co₃O₄ NWS, TiO₂ nanoparticles were modified on the surface of Co₃O₄ by using PLD. The TiO₂ ceramic target applied in PLD was sintered at 1300 °C using the TiO₂ (5 N) powder directly. The target was placed at a distance of 4.5 cm from the substrate during deposition and a KrF excimer laser (Compex 102, 248 nm, 5 Hz) was used as the ablation source. Prior to the deposition, the chamber was evacuated to a low pressure of ~10⁻⁶ Pa. Then pure O₂ (99.999%) was introduced as the working gas with a pressure of 10 Pa. The TiO₂ nanoparticles were fabricated at 500 °C with a typical radius of about 5–20 nm.

The structure of the sample was characterized by using a Bede D1 X-ray diffraction (XRD) system with Cu Kα radiation (λ = 0.15406 nm). Surface morphology of the sample and its element contents were studied by using an FEI Quanta 200F scanning electron microscope (SEM) operated at a voltage of 20 kV equipped with an energy-dispersive X-ray spectrometer (EDX). An X-ray photoelectron spectrometer (XPS, Thermo Fisher K-Alpha American with an Al Kα X-ray source) was also used to measure the elemental composition of samples. Specific surface areas of the samples were obtained from the results of N₂ adsorption–desorption isotherms at 77 K (Micromeritics ASAP 3020) by using the Brunauer–Emmet–Teller (BET) method. The structure of the sample was identified by using an FEI Tecnai G2 F20 transmission electron microscope (TEM) equipped with a selected area electron diffractometer (SAED) and a scanning transmission electron microscope (STEM), which was operated at 200 kV. Microscopic Raman spectroscopy was carried out by using a micro-Raman spectrometer (InVia Reflex, Renishaw, UK) with an excitation wavelength of 532 nm, and the laser power was kept below 0.85 mW to avoid the laser induced heating effect on the sample. All peaks in the Raman spectra were fitted with Lorentzians. A 100× objective lens with a numerical aperture (NA) of 0.95 was used in the Raman experiments, and the spot size was estimated to be about 500 nm. Thermogravimetric analysis (TGA, SDT Q600) was carried out under an air atmosphere at 10 °C min⁻¹ with a temperature range of 10–900 °C.

The gas sensing experiment of the samples was performed on an intelligent gas sensing analysis system (CGS-1TP, Beijing Elite Tech Co., Ltd, China), which provided an external and precious temperature control from room temperature to 500 °C with a minimum step of 1 °C. Prior to the experiment, the sensors were pre-heated at different temperatures for about 30 min. When the resistance of the sensor was stable, the target gas was injected into the chamber using a micro-injector through a rubber plug. The gas response was designated as Rg/Ra, where Rg is the sensor resistance measured in a mixture of target gases and Ra is the resistance of the sample measured in air. The detailed gas-sensing experiment process can be found in the previous report by Wen et al.\textsuperscript{12}

3. Results and discussion

The fabrication process of TiO₂/Co₃O₄ acicular NW arrays is schematically illustrated in Fig. 1. First, Co related precursor arrays were obtained by a hydrothermal method using the Co(NO₃)₂·4H₂O, NH₄F, and CO(NH₂)₂ as sources at 95 °C for 12 h. And then, the precursor was converted to uniform porous acicular Co₃O₄ NW arrays via calcination at 500 °C for 4 h. The detailed formation process of the TiO₂/Co₃O₄ acicular NW
arrays is illustrated in the ESI.† Finally, uniform TiO2/Co3O4 NW acicular arrays could be obtained after decorating TiO2 nanoparticles on its surface by using PLD.

Fig. 2 shows the XRD patterns of the as-synthesized precursor (a), Co3O4 NW arrays (b) and TiO2/Co3O4 NW arrays (c), respectively. In the XRD pattern of the as-synthesized precursor, excluding those peaks arising from the substrate, all of the peaks are in good agreement with the Co(CO3)0.5(OH)0.11H2O (JCPDS PDF#48-0083). In the XRD pattern of the annealed precursor, all the diffraction peaks can be indexed to the face-centered cubic Co3O4 (JCPDS PDF#43-1003), which confirms the complete conversion from cobalt carbonate hydroxide to Co3O4. According to the XRD pattern of TiO2/Co3O4, all of the observed diffraction peaks correspond to the Co3O4 and Al2O3 substrates. No obvious TiO2 related peaks were found in the XRD pattern of the TiO2/Co3O4, probably owing to the small content of TiO2 in the nanocomposites.

The morphology of the TiO2/Co3O4 NW arrays was characterized by SEM, as shown in Fig. 3. In Fig. 3(a), large scale, high density and acicular like TiO2/Co3O4 arrays are found to deposit uniformly on the substrate. In the cross-sectional SEM image of TiO2/Co3O4 in Fig. 3(b), the TiO2/Co3O4 acicular NW arrays are homogeneously aligned on the substrate, and the length of Co3O4 NW arrays was about 1–3 μm. Fig. 3(c) demonstrates a typical SEM image of the TiO2 decorated Co3O4 acicular NW arrays in a high magnification, in which obvious acicular like Co3O4 NWs are observed. In this study, it is found that the growth temperature plays a significant role in affecting the morphologies of the as-prepared precursor, which is discussed in detail in Fig. S1.† Fig. 3(d) shows the EDX information of the TiO2/Co3O4, confirming the coexistence of Ti, Co and O. Fig. S2† demonstrates a top view of the pristine Al2O3 substrate, the precursors of Co(CO3)0.5(OH)0.11H2O, the as-prepared Co3O4 acicular NW arrays and the TiO2/Co3O4. The surface of the substrate would be covered with pink precursors after the hydrothermal reaction, which can be fully converted to the black Co3O4 via the thermal decomposition process. There are no obvious colour differences between the as-prepared Co3O4 acicular NW arrays and the TiO2/Co3O4.

The TEM images of the as-prepared Co(CO3)0.5(OH)0.11H2O precursor, Co3O4 NW, and TiO2/Co3O4 NW are compared in Fig. 4(a)–(c), respectively. All of them display an obvious acicular like structure. No obvious macroscopic defects were found in the as-prepared Co(CO3)0.5(OH)0.11H2O, as shown in Fig. 4(a). While after annealing, plenty of nanopores were formed in the Co3O4 NW, which may be generated due to the dehydration and lattice contraction occurring during the thermal treatment (Fig. 4(b)). After the deposition of TiO2, the acicular morphology of the Co3O4 does not demonstrate obvious changes, as shown
in Fig. 4(c). Because of so many nanopores existing in the Co₃O₄ NW, leading to a large surface area, it is supposed to be a good structure for gas sensing. N₂ sorption was used for characterizing the porous structure of acicular Co₃O₄ NW arrays (Fig. S3†). Its isotherm has a typical character of IV type loop, indicating the mesoporous structure. The BET surface areas of Co₃O₄ NW arrays are calculated to be 22 m² g⁻¹, and the pore size distribution shows a peak located at 18.5 nm, while that of the as-prepared precursor is only 3 m² g⁻¹. Although the substrate also plays a significant role in controlling the kinetics of the growth, we succeeded in producing the Co₃O₄ NW arrays with an acicular structure on the Ti foil (Fig. S4†). Thus in this study, we can select Ti foil as the substrate for collecting more powders for BET characterization, which has been applied in our previous studies. The TEM images of the as-prepared Co₃O₄ NW, and TiO₂/Co₃O₄ NW are compared in (a)–(c) respectively. (d) SAED pattern of the TiO₂/Co₃O₄ NW collected from the yellow circle. (e) A STEM image and the element distribution of the TiO₂/Co₃O₄. (f) A HRTEM image of the TiO₂/Co₃O₄ NW.

Fig. 4 The TEM images of the as-prepared Co(CO₃)₀.₅(OH)·0.11H₂O precursor, Co₃O₄ NW, and TiO₂/Co₃O₄ NW are compared in (a)–(c) respectively. (d) SAED pattern of the TiO₂/Co₃O₄ NW collected from the yellow circle. (e) A STEM image and the element distribution of the TiO₂/Co₃O₄. (f) A HRTEM image of the TiO₂/Co₃O₄ NW.

Fig. 5 shows the thermodecomposition behavior of Co(CO₃)₀.₅(OH)·0.11H₂O, which was characterized by using TGA. It is found that there exist three apparent decomposition steps: the first one appears when the temperature is below 80 °C, during which the weight loss is mainly due to the evaporation of adsorbed water. The second turning point appears at 350 °C, which may be due to the decomposition of the residual reactant Co(NO₃)₂. The third turning point appears at 500 °C, corresponding to conversion from Co(CO₃)₀.₅(OH)·0.11H₂O to Co₃O₄. During the oxidation process of the precursor, a weight loss of ~11.6% was found. Thus, in order to improve the stabilization of the gas sensor in a long term application, all of the samples were annealed at 500 °C.

In order to investigate the chemical composition of the prepared TiO₂/Co₃O₄, XPS measurement was carried out (Fig. 6). During the XPS analysis, the C 1s peak located at 284.5 eV was selected as the reference. Fig. 6(a) shows a full survey scan spectrum of the TiO₂/Co₃O₄ NW arrays, and two peaks located at 780.2 and 795.6 eV are related to the Co 2p₃/₂ and Co 2p₁/₂, which corresponds to the standard Co₃O₄ spectra, as seen in Fig. 6(b). Similarly, the peaks appearing at 457.5 eV and 463.4 eV in Fig. 6(c) are ascribed to the Ti 2p₃/₂ and Ti 2p₁/₂ for a typical TiO₂. And subsequently, the O 1s core-level spectra of the as-prepared series of samples were studied, as shown in Fig. 6(d). On comparison of the data on the spectra of other related studies, the lowest BE component located at 530 eV (referred to as O intr) is attributed to O₂⁻ ions in the structure of Co₃O₄.

Fig. 5 The thermodecomposition behavior of the Co(CO₃)₀.₅(OH)·0.11H₂O, which was characterized by using TGA in air.

Fig. 6 (a) XPS spectra of the TiO₂/Co₃O₄. (b) An enlarged spectra of Co 2p, (c) Ti 2p, and (d) O.
the Co$_3$O$_4$ and TiO$_2$ array. While the middle one located at 531 eV (referred to as O$_{\text{def}}$) is attributed to O$^-$ ions that are in oxygen deficient regions. And the higher BE peak located at 532 eV (referred to as O$_{\text{surf}}$) is due to the presence of other adsorption states such as H–O bonds or loosely bound oxygen on the surface. From the XPS pattern of the TiO$_2$/Co$_3$O$_4$, it further confirms that the as-prepared sample is composites with Co$_3$O$_4$ and TiO$_2$. 

The Raman spectra of the Co$_3$O$_4$ and TiO$_2$/Co$_3$O$_4$ NW arrays are shown in Fig. 7. The vibration bands located at 475, 516, 615, and 680 cm$^{-1}$ in the Raman spectrum are attributed to the Co$_3$O$_4$, while the vibration bands appeared at 396, 516, and 639 cm$^{-1}$ are attributed to the TiO$_2$. After decorating with TiO$_2$, the Raman vibration bands of Co$_3$O$_4$ are broadened, which may be due to the interaction between the TiO$_2$ and Co$_3$O$_4$ and the disorder in the sublattice.

During the gas sensing measurement, 100 ppm of ethanol was introduced into a sealed chamber and the sample was heated up to an optimal temperature. The gas-sensing measurements were performed on an intelligent gas sensing analysis system, which is shown in Fig. S5. The current–voltage ($I$–$V$) characteristics of the sample verified the ohmic contacts between the Co$_3$O$_4$ nanowire arrays and the electrodes (Fig. S6†). In order to find the optimal working temperature of the sample, the maximum responses to ethanol for the Co$_3$O$_4$ and TiO$_2$/Co$_3$O$_4$ at a series of working temperatures are studied. In Fig. 8(a), all of the samples demonstrate an enhanced gas response with increasing working temperature, and then they decrease when the temperature is higher than the optimal one. The optimal working temperatures of the Co$_3$O$_4$ and TiO$_2$/Co$_3$O$_4$ are 170 °C and 160 °C, respectively. The gas sensing behaviour can be explained according to the kinetics and mechanics of gas adsorption and desorption on the surface of Co$_3$O$_4$. When the operating temperature is too low, not enough chemical activations (such as OH$^-$, CO$_3^{2-}$, COO$^-$, etc.) of gas-sensing materials are generated, leading to a small response. By increasing the temperature, the driving force for desorption of O$_2$ is increased, contributing to an increase of the response. When the operating temperature is too high (higher than the optimal working temperature), O$_2$ adsorbed on the surface may quickly escape before their reaction, thus the response will decrease correspondingly. A sensor can demonstrate its maximum gas sensing performance only at the optimal working temperature. Fig. 8(b) compares the response characteristic curves of these two sensors at the optimal temperatures. It shows that the gas response of the TiO$_2$/Co$_3$O$_4$ ($R_g/R_a = 65$) sensor to 100 ppm ethanol is much higher than that of the pristine Co$_3$O$_4$ ($R_g/R_a = 25$), which indicates that the interaction between the TiO$_2$ and Co$_3$O$_4$ can effectively improve its gas sensing ability. The superiority of the p–n junction sensor to the conventional chemi-resistive sensor is illustrated in the ESI (Fig. S7†). As reported previously, TiO$_2$ is not a good gas sensing material, so an optimal content of TiO$_2$ deposited on Co$_3$O$_4$ may play a significant role in affecting its response. The gas responses of the TiO$_2$/Co$_3$O$_4$ sensor to a series of TiO$_2$ contents are shown in Fig. S8†. It is found that the TiO$_2$...
deposited by PLD for 20 s contributes to the maximum gas response for 100 ppm of ethanol.

Not only enhancing the maximum value of gas response, the TiO$_2$/Co$_3$O$_4$ sensor also displays a good response to a series of concentrations of ethanol. As shown in Fig. 9(a), the responses of the TiO$_2$/Co$_3$O$_4$ sensor follow an almost linear increase with the increase of ethanol concentration from 10 ppm to 500 ppm, indicating its good response to ethanol over a wide range. In order to confirm that the TiO$_2$/Co$_3$O$_4$ sensor displays an obviously enhanced sensing ability compared to the pristine Co$_3$O$_4$, the gas responses of the Co$_3$O$_4$ and TiO$_2$/Co$_3$O$_4$ to a series of concentrations of ethanol are compared in Fig. S9.† It is found that the TiO$_2$/Co$_3$O$_4$ sensor always displays a higher response than the pristine Co$_3$O$_4$ to the same concentration of ethanol.

Moreover, the reproducibility performance of the sensor is also measured. Fig. 9(b) shows that the on and off responses of Co$_3$O$_4$ could be repeated after continuous measurement without obvious changes, showing that the sensor based on TiO$_2$/Co$_3$O$_4$ has good reversibility and stability. In order to confirm the selectivity behavior of the sensor, we select some other gases such as NH$_3$, benzene, acetone and methanol to characterize its sensing activities (Fig. S10†). The responses of the sensor to these gases with a concentration of 100 ppm were determined at 160 °C. The gas response to 100 ppm ethanol is 65, which is significantly higher than acetone and methanol. Meanwhile, it shows a pretty low response to NH$_3$ and benzene. The significant gas response difference indicates the selectivity of the TiO$_2$/Co$_3$O$_4$ sensor.

The on and off gas response process can be explained by gas adsorption, surface chemical reaction and desorption, which lead to significant electrical conductivity changes resulting from the chemical interaction of gas molecules with the oxygen species on its surface. At the optimal operating temperature, the adsorption of negatively charged oxygen can generate plenty of holes for the conduction, which leads to the formation of a charge accumulation layer on the surface of Co$_3$O$_4$. When the sensor is exposed to ethanol, the oxygen species on Co$_3$O$_4$ could promote the oxidation of ethanol gas molecules to CO$_2$ and H$_2$O. Meanwhile, it also releases plenty of extra electrons, which would neutralize the holes existing in the Co$_3$O$_4$, as a result, its resistance demonstrates a dynamic increase.

Herein, a typical p–n heterojunction is formed when n-type TiO$_2$ is decorated on p-type Co$_3$O$_4$, which greatly improves its gas sensing response. Based on the calculation and experiment reported previously, the energy band structure diagram for the p-type Co$_3$O$_4$/n-type TiO$_2$ heterojunction is described in Fig. 10. In the heterogeneous region, the holes in p-type semiconductor Co$_3$O$_4$ and the electrons in the n-type semiconductor TiO$_2$ form a self-built electric field, which could establish a depletion layer until they get an equalization of the Fermi level. The heterojunction region of TiO$_2$/Co$_3$O$_4$ is believed to easily attract reductive and oxidative gases. When exposed to air (1), the hole density on the surface of Co$_3$O$_4$ increases while the number of electrons on the surface of TiO$_2$ decreases due to the ionization of absorbed oxygen species, during which the holes can easily transfer to the p-type Co$_3$O$_4$ semiconductor, leading to a lower resistance of the sensor.

![Fig. 9](image-url) (a) Response of the TiO$_2$/Co$_3$O$_4$ sensor to a series of concentrations of ethanol at 160 °C. (b) The typical response and recovery curve of the TiO$_2$/Co$_3$O$_4$ sensor between 100 ppm ethanol and ambient air.

![Fig. 10](image-url) The energy band structure diagram for the p-type Co$_3$O$_4$/n-type TiO$_2$ heterojunction.
1/2O2 (g) → O− (ads) + h+  (1)

When ethanol was introduced into the chamber, the charge carrier accumulation layer near the surface is thinned by the electrochemical interaction between O− (ads) and C2H5OH molecules (2), which releases free electrons and neutralizes the holes in the Co3O4. But at this moment, the electron transfer from the n-type semiconductor to the p-type semiconductor is impeded, which makes the resistance of the device increase rapidly. As a consequence, the TiO2/Co3O4 demonstrates a higher gas sensitivity than the pristine Co3O4. The reaction process can be described as follows:

C2H5OH (g) + 6O− (ads) → 2CO2 (g) + 3H2O (g) + 6e−  (2)

When the ethanol flow stopped, oxygen molecules in air could be adsorbed onto the surface of the Co3O4 again. Consequently, its resistance returns to its initial value.

4. Conclusion

In summary, TiO2/Co3O4 arrays have been synthesized on the Ag/Pd electrode substrate by combining hydrothermal and PLD methods. The structure and morphology of TiO2/Co3O4 were characterized by XRD, TEM, STEM, XPS, and Raman spectroscopy, which confirm that TiO2 nanoparticles were uniformly decorated on the surface of Co3O4. The heterojunction structure of TiO2/Co3O4 displayed enhanced sensing ability to ethanol by almost three times compared with pristine Co3O4, which is due to the formation of the p−n junction between the p-type Co3O4 and the n-type TiO2. The self-built electric field originating from the p−n junction effect can enhance the thickness of the depletion layer, which improves its gas sensitivity. Our study has evidently confirmed that the surface modification is an effective approach to enhance the sensing performance of the ethanol sensor.

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