Articles Chinese Science Bulletin

Electronics Physics

January 2010 Vol.55 No.3: 228–232
doi: 10.1007/s11434-009-0727-9

Improved and excellent CO sensing properties of Cu-doped TiO_2 nanofibers

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Received July 28, 2009; accepted September 20, 2009

Cu-doped TiO_2 nanofibers with an average diameter of about 80 nm are synthesized through an electrospinning method. Both anatase and rutile crystallographic structures are found in the fibers based on XRD results. Compared with pure TiO_2 nanofibers, the Cu-doped TiO_2 nanofibers exhibit improved CO sensing properties at 300°C. The sensitivity of Cu-doped TiO_2 nanofibers is up to 3 when the sensor is exposed to 5 ppm CO, and the response and recovery times are about 4 and 8 s, respectively. Good selectivity is also observed in our investigations. These results indicate that the Cu-doped TiO_2 nanofibers can be used to fabricate high performance CO sensors in practice.

CO, nanomaterials, metal oxide semiconductors, gas sensors, chemical sensors

Citation: Wang B, Zhao Y D , Hu L M, et al. Improved and excellent CO sensing properties of Cu-doped TiO_2 nanofibers. Chinese Sci Bull, 2010, 55: 228–232, doi: 10.1007/s11434-009-0727-9

The gas sensor, as an important field in chemical sensors, gains considerable attention driven by its practical applications in monitoring and control of air quality, detection of flammable or toxic gases, medical diagnosis, and optimization of combustion efficiency [1–6]. Based on their high response value, fast response, quick recovery, excellent stability and simplicity in fabrication, metal-oxide semiconductors (MOS) have been widely chosen as the sensing materials for gas sensors over the last forty years [7–10]. MOS nanoparticles with small sizes exhibit high sensitivity to the detected gases, but their sensing properties often suffer from degradation because of the aggregation growth among MOS nanoparticles. In recent years, one-dimensional (1D) MOS nanostructures have received considerable attention because they avoid such degradation. On the other hand, the large surface-to-volume ratio of 1D MOS nanostructures and the congruence of the carrier screening length with their lateral dimensions make them highly sensitive and efficient transducers of surface chemical processes into electrical signals. Hitherto, impressive and promising results regarding the synthesis, fabrication, chemical and physical properties of these 1D nanostructures have been achieved [11–13].

TiO_2 is an important MOS with a variety of applications in environmental cleaning and protection, photocatalysis, solar cells, and chemical/physical sensors [14–18]. For gas sensors, TiO_2 is proven to be a highly sensitive material for the detection of both reducing and oxidizing gases. Many scientific and technological efforts have been put on improving the sensing performance based on the TiO_2 gas sensors, such as adding catalysts, doping metals and metal oxides, decreasing grain size, controlling pore and surface defects, etc. Among these methods, doping metals or metal oxides (such as Al, La, Nb, Cu, ZnO and SnO_2) on TiO_2 have been proved to be a simple and efficient route to enhance the sensing properties [19,20]. However, to the best of our knowledge, few papers on the doped 1D TiO_2 gas sensors have been reported. On the other hand, the fabrication of sensitive gas sensors with rapid response/recovery

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and good selectivity is still in great demand.

Herein, we report a simple and effective route for the synthesis of a highly efficient CO sensing material of Cu-doped TiO_2 nanofibers. CO is a kind of colorless, tasteless, widespread and toxic gas, which can be generated during the burning of fossil fuels and be produced by malfunctioning domestic appliances. Even at low concentrations, well below immediately dangerous to life and health (IDLH) levels, it can have negative effects on human health. The National Air Quality Standards for CO adopted by the UK Government in January 2000 is currently a concentration of 10 ppm for a running mean of 8 h [21]. At the same time, the addition of Cu is widely used to improve the gas sensor performances [22]. The sensor fabricated from Cu-doped TiO_2 nanofibers exhibits excellent CO sensing properties with low detection limit (the sensitivity is 3 when the sensor is exposed to 5 ppm CO), indicating the potential application of Cu-doped TiO_2 nanofibers for fabricating high performance CO sensors.

1 Experimental

All chemicals (analytical grade reagents) were purchased from Beijing Chemicals Co. Ltd. and used as received without further purification. To prepare the Cu-doped TiO_2 nanofibers, 1.5 g of tetrabutyl titanate was mixed with 3 mL of acetic acid and 3 mL of ethanol in glovebox under vigorous stirring for 10 min. Subsequently, this solution was added to 7.5 mL of ethanol containing 0.45 g of poly(vinyl pyrrolidone) (PVP, M_w=1,300,000) and 0.05 g of $CuCl_2 \cdot 2H_2O$ under vigorous stirring for 30 min. Then, the mixture was loaded into a glass syringe and connected to high-voltage power supply. 12 kV was provided between the cathode (a flat aluminum foil) and anode (syringe) at a distance of 20 cm. The conversion of tetrabutyl titanate to TiO_2 and the complete removal of PVP in the as-spun nanofibers were achieved by calcining at 500°C for 3 h in the air. Pure TiO_2 nanofibers were prepared through the same method without the $CuCl_2 \cdot 2H_2O$ adding process [23].

The as-synthesized sample was mixed with deionized water in a weight ratio of 100∶25 to form a paste. Then the paste was coated on a ceramic tube, on which a pair of Au electrodes was previously printed. Pt lead wires attaching to these electrodes were used as electrical contacts. After the ceramic tube was sintered at 300°C for 2 h, a small Ni-Cr alloy wire was placed through the tube as a heater, which provided the operating temperature.

Gas sensing properties were measured using a static test system [24]. Saturated target vapor was injected into a test chamber (20 L in volume) by a microinjector through a rubber plug. After fully mixed with air (relative humidity was about 25%), the sensor was put into the test chamber. When the sensitivity reached a constant value, the sensor was taken out to recover in the air. The electrical properties of the sensor were examined by the CGS-1 intelligent test system (Beijing Elite Tech Co. Ltd., China). The sensitivity value (S) was defined as $S = R_a/R_g$, where R_a and R_g denoted the sensor's resistance in the presence and in the absence of the target gases. The time taken by the sensor to achieve 90% of the total resistance change was defined as the response time in the case of adsorption or the recovery time in the case of desorption.

The crystal structure of the samples was characterized by Shimadzu XD-3AX X-ray diffractometer (XRD). The component of the sample was determined by an energy dispersion X-ray spectroscopy (EDX) equipped in scanning electron microscopy system (HITACHI S-4700). Field emission scanning electron microscopy (FE-SEM) was performed on a JEOL JSM-6700F microscope at 3 kV. Transmission electron microscopy (TEM) images were obtained on a HITACHI H-8100 microscope by using an acceleration voltage of 200 keV.

2 Results and discussion

TiO_2 mainly exists in three crystallographic structures, anatase, rutile and brookite. The XRD peaks at 2θ = 25.28° (101) and 2θ = 27.4° (110) are often taken as the characteristic peaks of anatase and rutile crystallographic structures, respectively [25]. Figure 1 shows the XRD patterns of pure and Cu-doped TiO_2 nanofibers. Both anatase and rutile crystallographic structures can be found in these two samples. No peak corresponding to the dopant is observed, but the relative intensity of the peaks is found to decrease by Cu doping. The crystallite sizes of anatase and rutile TiO_2 are about 22.4 nm and 21.9 nm for pure TiO_2 nanofibers respectively, and are about 17.5 nm and 16.3 nm for those of Cu-doped TiO_2 nanofibers (which are estimated by Scherrer formula [26]). The crystallographic compositions are calculated with the following equation [27]:

$$\text{Content of anatase (\%)} = \text{IA}/(\text{IA}+1.265\text{IR})\times 100\%, \quad (1)$$

where I_A and I_R are the main peak intensities of anatase and rutile, respectively. For pure TiO_2 nanofibers, the composition of anatase TiO_2 is calculated to be about 26%, and that of rutile TiO_2 is about 74%. The corresponding compositions are about 20% (anatase) and 80% (rutile) for Cu-doped TiO_2 nanofibers. The Cu content in the Cu-doped TiO_2 nanofibers is about 4 wt%, as determined by EDX.

Figure 2(a) and (b) show the FE-SEM images of pure and Cu-doped TiO_2 nanofibers, respectively. The products are highly dominated by the nanofibers with an average diameter of about 80 nm. Features of pure and Cu-doped TiO_2 nanofibers were also examined by TEM (Figure 2(c) and (d)), which shows typical characteristics of the nanofibers. No obvious difference can be found in the FE-SEM and

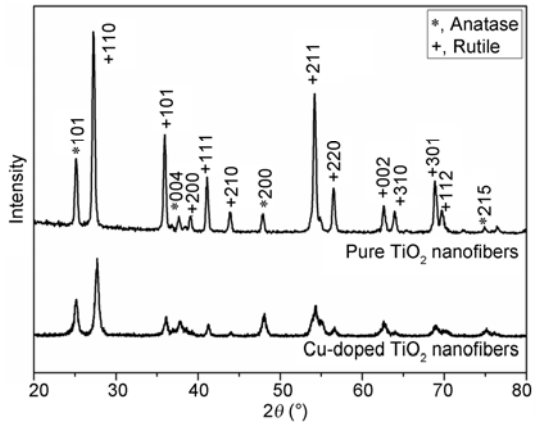

Figure 1 XRD patterns of pure and Cu-doped TiO_2 nanofibers.

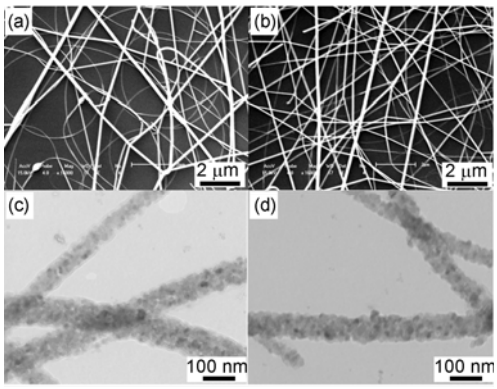

Figure 2 FE-SEM images of pure (a) and Cu-doped TiO_2 (b) nanofibers, TEM images of pure (c) and Cu-doped TiO_2 (d) nanofibers.

TEM images, indicating that doping Cu does not change the morphology of TiO_2 nanofibers evidently.

In order to find the optimum condition of our products, the sensors were exposed to 100 ppm CO at different operating temperatures (Figure 3). For each curve, the sensitivity is found to increase with the increase of the operating temperature, which attains the maximum at 300°C, and then decreases with a further rise of the operating temperature. Thus 300°C can be defined as the optimum operating temperature and applied in all the investigations hereinafter. Compared with pure TiO_2 nanofibers, the Cu-doped TiO_2 nanofibers exhibit much higher sensitivity to CO at 300°C, and the sensitivity is about 21 for Cu-doped TiO_2 nanofibers to 100 ppm CO. which is 17 times larger than that of pure TiO_2 (the corresponding sensitivity is about 1.8), indicating that the addition of Cu is beneficial to the CO sensing of TiO_2 nanofibers.

The sensitivity versus time cure at different CO concentrations is shown in Figure 4. When exposed to 5 ppm CO, the response of the sensor is ~ 3. With the increase of CO concentration, the sensitivity increases significantly. For CO at the level of 20, 50, 100 and 200 ppm, the sensitivity is about 6, 10, 21 and 42, respectively. The response time and

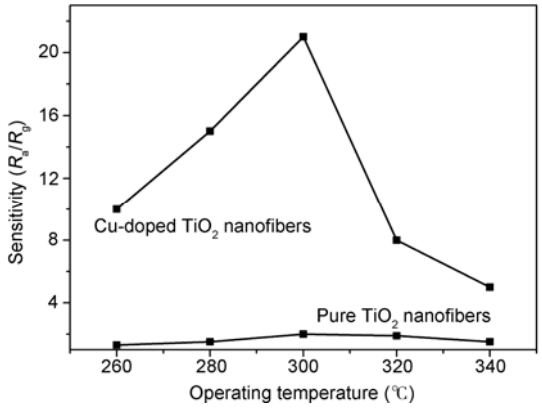

Figure 3 Dependence of sensitivity on the operating temperature of pure and Cu-doped TiO_2 nanofibers.

recovery time are about 4 and 8 s, respectively. Such a rapid response is based on the structures of as-prepared fibers. The large surface of the TiO_2 nanofibers makes the absorption of CO molecules on the surface of the material easy. The 1D structures of the fibers can facilitate fast mass transfer of the CO molecules to and from the interaction region as well as improve the rate for charge carriers to transverse the barriers induced by molecular recognition along the fibers. Those advantages lead to significant gain in the fast response/recovery of the as-prepared sensors [11–13].

The dependence of sensitivity on CO concentration was measured and shown in Figure 5. In the low concentration range (from 5 to 500 ppm), the increase in the sensitivity depends near linearly on the concentration (insert in Figure 5), while the sensitivity increases slowly and is gradually saturated at higher concentrations (above 1000 ppm). In fact, the response of the semiconducting oxide gas sensitive sensor can usually be empirically represented as $R=A[C]^N+B$, where A and B are constants and $[C]$ is the concentration of the target gas. N usually has a value between 0.5 and 1.0, depending on the charge of the surface species and the stoichiometry of the elementary reactions on the surface [28]. For the Cu-doped TiO_2 nanofibers, N is around 1 for CO in the range of 5—500 ppm at 300°C. Such a linear dependence further shows that Cu-doped TiO_2 nanofibers are very suitable for the detection of CO at low levels.

To further understand the performance of our fibers, the sensor was exposed to 100 ppm different gases at 300°C. The selectivity shown in Figure 6 indicates that the Cu-doped TiO_2 nanofibers are less sensitive to C_2H_5OH, CH_3OH, H_2, CH_4, C_2H_2 and NO. Thus the obtained nanofibers exhibit prominently and highly selective, and can be put into various practical applications.

The sensing mechanism can be explained as follows [29–31]. When TiO_2 nanofibers are exposed to the air, the O_2 molecules adsorbed on the surface will generate active oxygen species and result in the formation of the surface

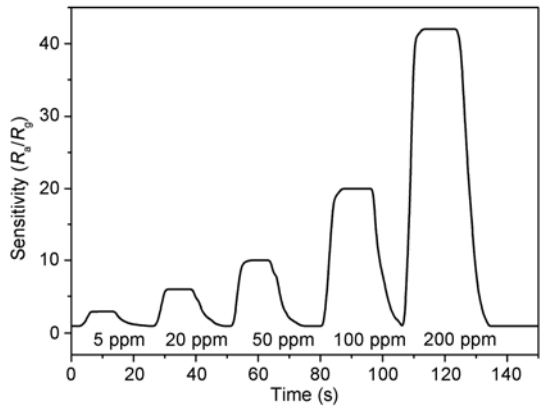

Figure 4 Response and recovery characteristics of Cu-doped TiO_2 nanofibers to CO at 300°C.

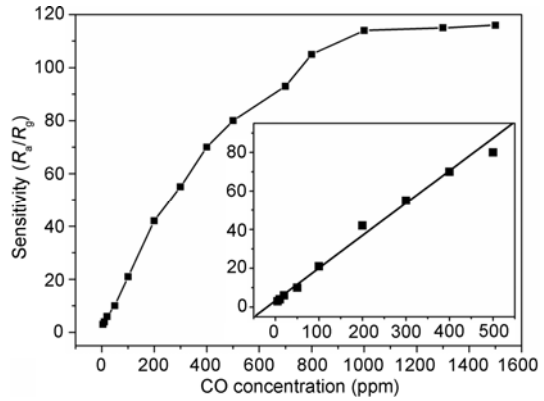

Figure 5 Dependence of sensitivity on the CO concentration of Cu-doped TiO_2 nanofibers at 300°C. The insert shows the relationship in the range of 5—500 ppm.

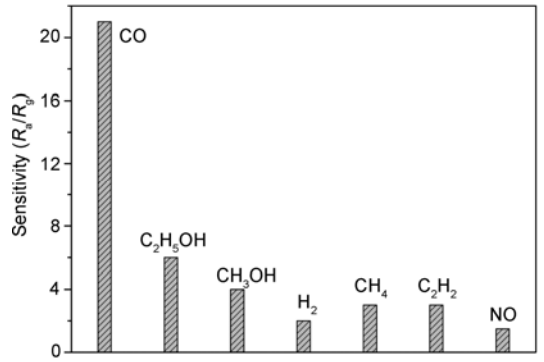

Figure 6 Selectivity of Cu-doped TiO_2 nanofibers at 300°C.

depletion region. When the TiO_2 nanofibers are exposed to a reducing gas at moderate temperature, the gas reacts with the surface oxygen species, decreasing the depletion width and resulting in the increase of the carrier concentration and electron mobility of the TiO_2 nanofibers, which eventually increases the conductivity of the fibers. To explain the influence of electron-depleted space-charge layer near the inter face. By reacting with CO, CuO is reduced releasing the electrons back to the semiconductor, which eventually improves the sensing performance of TiO_2 nanofibers.

3 Conclusion

In summary, Cu-doped TiO_2 nanofibers are synthesized through an electrospinning method and investigated as the CO sensing materials. High sensitivity, rapid response/recovery and good selectivity are observed in our investigations. The results demonstrate that Cu-doped TiO_2 nanofibers have excellent potential applications for fabrication high performance CO sensors.

This work was supported by the special research project in preparation period of Suzhou Institute of Biomedical Engineering and Technology (*Grant No. O91901L090*) *and open topics of State Key Laboratory on Integrated Electronics, Jilin University* (*Grant No. IOSKL–KF200908*).

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