

The enhanced ethanol sensing properties of multi-walled carbon nanotubes/SnO₂ core/shell nanostructures

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Abstract

Multi-walled carbon nanotubes/SnO₂ (CNT/SnO₂) core/shell nanostructures were synthesized by a simple wet-chemical method. The thickness of the SnO₂ shell was about 10 nm and the diameters of the SnO₂ particles were 2–8 nm. Sensors based on the core/shell heterostructures exhibited enhanced ethanol sensing properties. The sensitivity to 50 ppm ethanol was up to 24.5, and the response time and recovery time were about 1 and 10 s, respectively. In addition, the fluctuation of the sensitivity was less than $\pm 3\%$ on remeasurement after 3 months. These results indicate that the core/shell nanostructures are potentially new sensing materials for fabricating gas sensors.

1. Introduction

SnO₂ nanostructured materials with unique optical and electrical properties [1–4] have been applied in many areas [5–16]. Due to their small grain size, very high surface-to-volume ratio and very great surface activities, SnO₂ nanoparticles have been investigated for fabricating gas sensors. When their size is comparable to the space-charge layer (L_d), the electron transport properties of the nanoparticles can be strongly modulated by absorption and desorption phenomena, and in this case they will exhibit very high gas sensitivity to ambient gases. For example, ~ 2 nm SnO₂ nanoparticles showed very high sensitivity to CO at room temperature [8]. However, their sensing properties often suffered a degradation resulting from the growth of aggregations among the nanoparticles. Up until now, several technologies have been developed to inhibit this degradation. Pang *et al* reported that 3.5 nm SnO₂ nanoparticles could be obtained even after calcination at 600 °C due to the addition of

SrCO₃ during the synthesis process [17]. Pinna *et al* developed a non-aqueous synthesis approach to prepare 2–2.5 nm SnO₂ nanoparticles [18]. Recently one-dimensional (1D) SnO₂ nanostructures such as nanobelts, nanowires and nanorods for gas sensors have attracted great interest due to their low degradation as a result of their special morphologies [19–25]. However, there are still many challenges in reducing their diameters down to L_d [24, 25].

Core/shell heterostructures exhibit improved physical and chemical properties over their single-component counterparts, and thus have applications in many areas [26–30]. One typical example of a core/shell nanostructure is type I core/shell nanoparticles for enhanced photoluminescence quantum efficiency of the nanoparticles. In these an electron and a hole are predominantly located in the same part of the core or the shell [27–30]. Recently we reported synthesis of CNT/SnO₂ and SnO₂/CdS core/shell heterostructures [31, 32]. They exhibited enhanced gas sensing properties involving reduction of the resistance of the sensors or improvement of gas sensitivities, and may possibly be potential new gas sensing materials for gas sensors.

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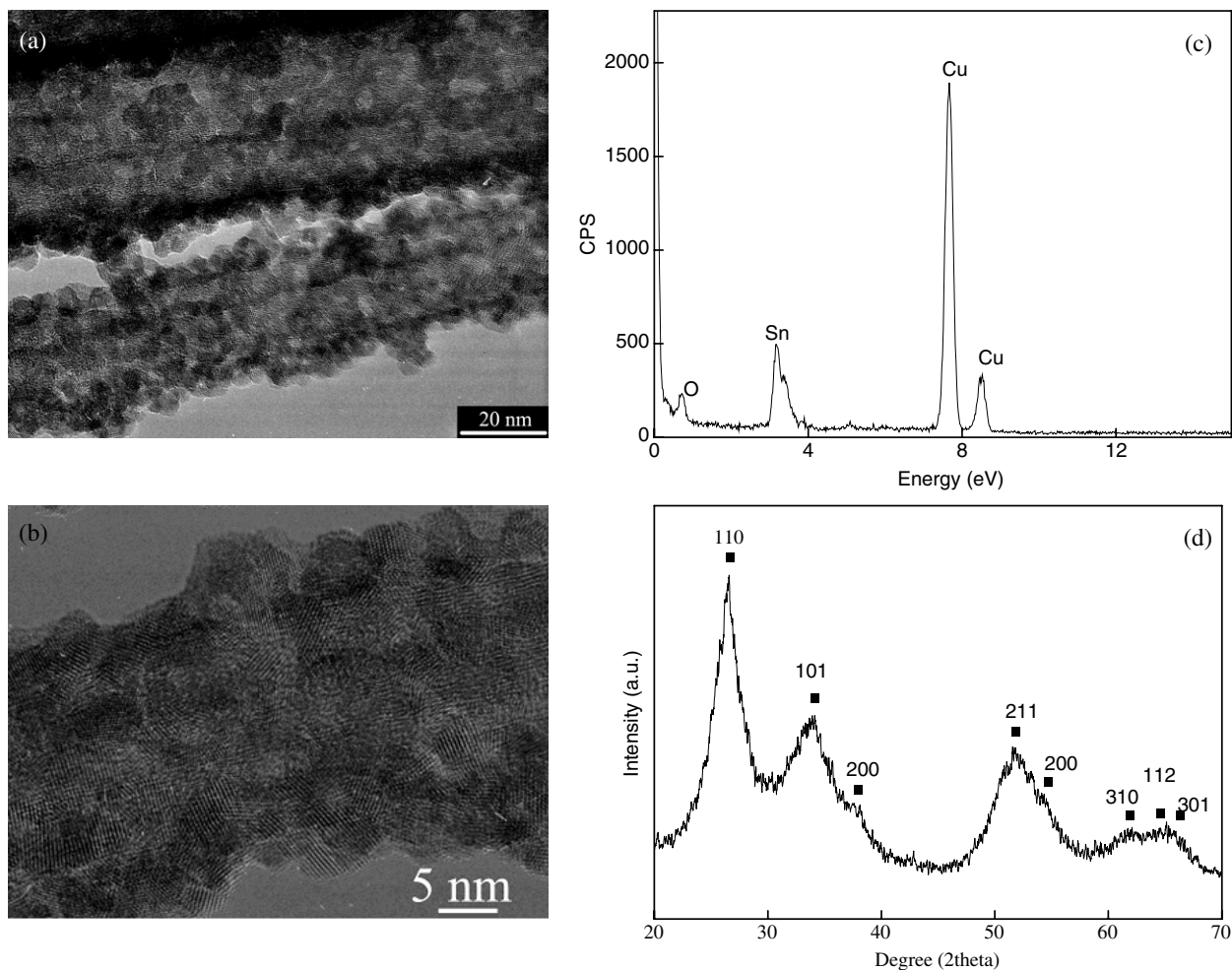


Figure 1. (a) A low-resolution TEM image and a (b) HRTEM image of the CNT/SnO₂ core/shell nanostructures. A typical EDS spectrum (c) and XRD spectra (d) of the core/shell structures.

The sensing properties of CNT/SnO₂ structures prepared by a wet-chemical method were reported in our previous work [31]. The resistance of the sensors based on the core/shell was reduced; however, their sensitivities were still low. For example, the sensitivity was only 2.8–50 ppm ethanol. In this paper, we develop this method to enhance the sensing properties of the core/shell heterostructures by increasing the reaction time in the synthesis process. This allowed a thicker SnO₂ shell to form on the outer surface of the carbon nanotube. The sensitivity of the core/shells obtained in this work was up to 24.5–50 ppm ethanol, and the stability of the core/shell structures was also very good.

2. Experimental details

The carbon nanotubes used in this work are multi-walled carbon nanotubes prepared by a conventional arc discharge method. Their diameters range from 10 to 30 nm. The CNT/SnO₂ core/shell nanostructures were synthesized by a similar method reported in our previous work [31], but the reaction time was increased to 4 h in order to obtain a thicker SnO₂ shell. The core/shell structures were collected through filtering, and characterized using powder x-ray diffraction

(XRD: Cu K α radiation), scanning electron microscopy (SEM: JEOL JEM 2010) and transmission electron microscopy (TEM: JEM-2010F TEM). The sensor fabrication process was depicted in our previous publication [24, 25, 31].

3. Results and discussion

Figure 1(a) is a typical low-resolution TEM image of the core/shell structures. It shows that the carbon nanotubes are covered with a dense layer of SnO₂ nanoparticles, resulting in the formation of CNT/SnO₂ core/shell heterostructures. The high-resolution TEM (HRTEM) image reveals that the thickness of the SnO₂ shell is about 10 nm and the diameters of the particles are in the range from 2 to 8 nm, as shown in figure 1(b). The clear lattice fringes of the nanoparticles are also observed in the image, suggesting their crystalline nature. An energy-dispersive x-ray spectrometer (EDS) reveals the presence of Sn and O in the core/shell structures, as shown in figure 1(c). The Cu peaks in the figure come from the copper grid used in the measurement. Other element peaks such as Cl are not found in the EDS, which indicates that the shell is only composed of the elements Sn and O. Figure 1(d) is the XRD spectrum of the core/shell structures. The main

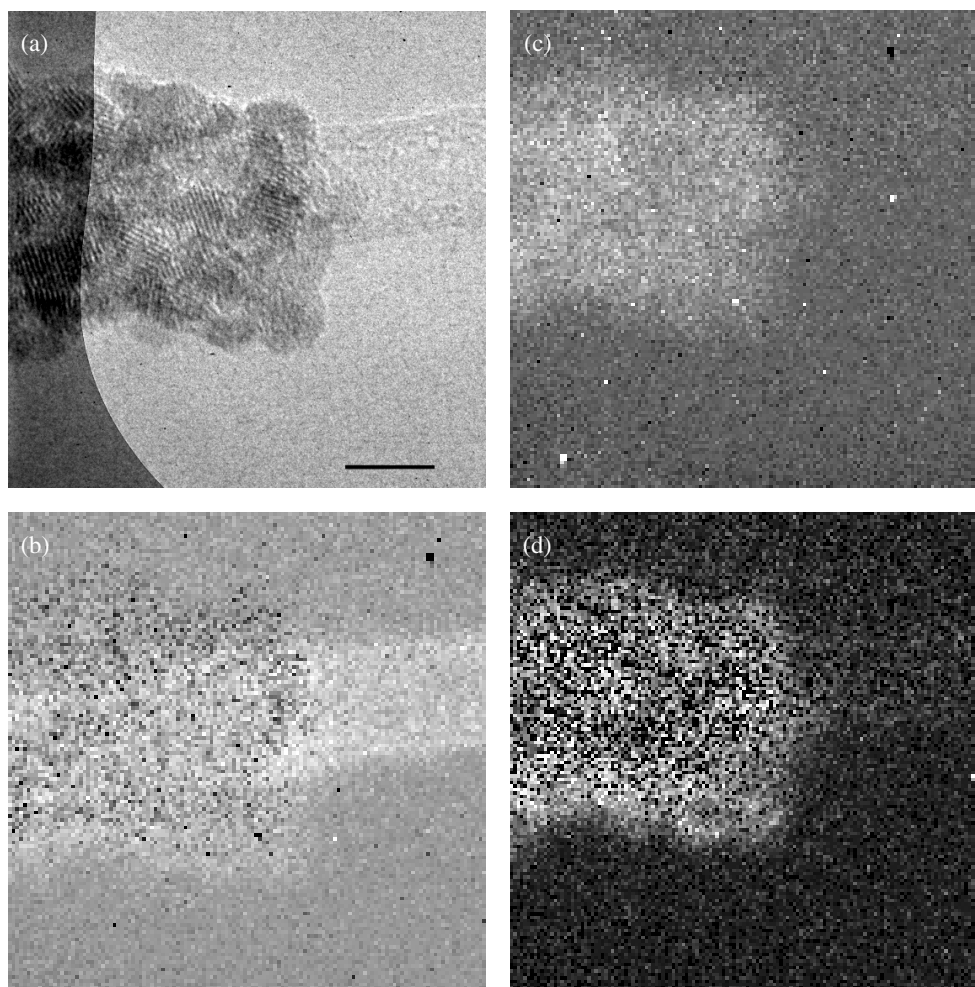


Figure 2. (a) A low-resolution TEM image of the core/shell structure with an end of a carbon nanotube not covered with a SnO_2 shell, the scale bar is 10 nm. (b), (c) and (d) show C, Sn and O mapping images, respectively.

peaks can be indexed to the tetragonal rutile structure of SnO_2 , with lattice constants of $a = 0.4748$ nm and $c = 0.3190$ nm. These parameters agree well with the reported values from the JCPDS card (41-1445). The broad SnO_2 peaks indicate that the particle size is very fine, which is consistent with the HRTEM observation.

In order to determine the elemental distribution in the core/shell structures, the elemental mappings were taken along one core/shell structure, as shown in figure 2. Figure 2(a) shows a TEM image of the core/shell structure, in which the end of the carbon nanotube is not covered with a SnO_2 shell. Figures 2(b)–(d) are C, Sn and O mapping, respectively. By comparing the different shades in these mappings, it can be clearly seen in the spectra that Sn and O elements are distributed uniformly over the outer surface of the carbon nanotubes.

All the results above demonstrate that the crystalline SnO_2 nanoparticles with diameters of 2–8 nm coat the outer surface of the carbon nanotubes, and they form core/shell heterostructures. Due to their small sizes and their special structures, the CNT/ SnO_2 core/shells are expected to have excellent gas sensing properties [5, 6, 24]. Here their sensing properties were investigated by using ethanol with various

concentrations as the target gas at a working temperature of 300 °C and an ambient relative humidity of 25%. The sensitivity (S) is defined as $S = R_a/R_g$, where, R_a is the sensor resistance in air and R_g is the resistance in a mixture of ethanol and air.

Figure 3(a) shows the variation of the voltage as the sensor is exposed to ethanol at various concentrations (10, 50, 200 and 500 ppm). The sensitivities are 11.1, 24.5, 32.2 and 41.2 to 10, 50, 200 and 500 ppm of ethanol, respectively, as shown in the left inset in figure 3(a). The results are comparable to those of small-sized 1D SnO_2 nanostructures [21, 24], which reveals that the core/shell heterostructures exhibit a very high sensitivity to ethanol gas. As well as the natural properties of the gas, the high sensitivity can be ascribed to the small sizes of the SnO_2 grains. Generally, when the grain size is reduced down to $2L_d$, the sensitivity can be exponentially increased [5, 33]. For SnO_2 , $2L_d$ is about 6 nm. The diameters of SnO_2 grains in the shells are 2–8 nm, which are very close to $2L_d$. Thus the core/shell heterostructures exhibit a very high sensitivity to ethanol gas.

Comparing the sensing properties of the core/shell heterostructures with those in previous work [31], it was found that the sensitivity of the heterostructures obtained in this

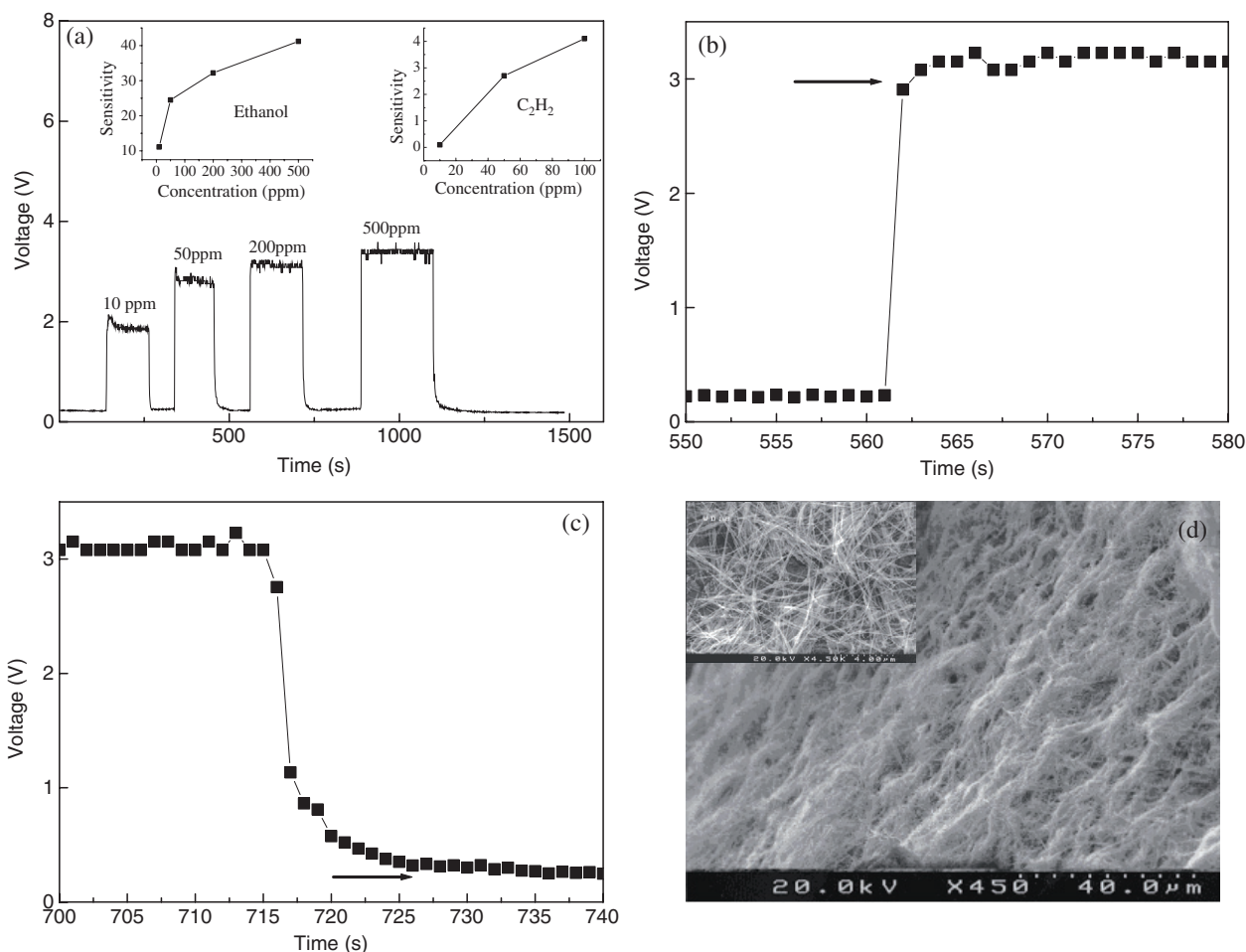


Figure 3. (a) The ethanol sensing characteristics of the core/shell nanostructures. The left inset shows the sensitivity of the structures to various ethanol concentrations, and the right inset shows the response to C₂H₂ gas. (b) The response time of the core/shell structures. (c) The recovery time of the core/shell structures. (d) The morphology of the core/shell nanostructures in the sensors. The inset shows a magnified image of the structures.

work was greatly enhanced. The sensitivity was only 2.8 to 50 ppm ethanol for the core/shell prepared for the case with a reaction time of 30 min [31]; however, it sharply increased to 24.5 for the core/shell obtained when the reaction time was increased to 4 h. We think that the enhanced sensing property is related to the sensing mechanism of the core/shell structures. In the heterostructures, the carbon nanotube plays a role in reducing the resistance of the sensing materials [31], while the SnO₂ shell mainly controls the sensing properties. In order to clarify this, sensors based on naked carbon nanotubes were also fabricated. However, the experimental results demonstrated that those sensors had a little response even to 1000 ppm ethanol vapour. Hence an appropriate proportion of SnO₂ among the core/shell structures is necessary to obtain a high gas sensitivity. The TEM and HRTEM observations indicated that the longer reaction time was advantageous for obtaining a thicker SnO₂ shell, as shown in figures 1(a) and (b). Therefore the core/shell structures obtained in this work exhibited enhanced ethanol sensing properties.

The selectivity of the core/shell structures was tested for C₂H₂ gas in air, as shown in the right inset of figure 3(a). The sensitivity of the structures to 100 ppm C₂H₂ is 4.1.

This relatively low response may be related to the low reducing properties of C₂H₂. In addition ethanol decreases the resistance while NO₂ increases the resistance of the core/shell structures [21, 31]. These results demonstrated that the core/shell structures had good selectivity.

The response time defines the time taken for the sensor to reach the saturation value after the core/shell structures are exposed to ethanol vapour, and the recovery time is the time for recovery of the resistance to 97% of the initial level after removal of ethanol vapour. It is found that the response time and the recovery time of the core/shell structures are about 1 and 10 s, respectively, as indicated with an arrow in figures 3(b) and (c). Such a fast response has also been observed in other 1D nanostructure sensors, but the recovery time was very long. In order to decrease the recovery time, some additional methods were used, such as ultraviolet illumination and high-temperature treatment [34, 35]. However, those methods often caused a lot of inconvenience for sensor fabrication or when the sensors were required to continuously detect the target gases. Therefore, core/shell sensors with a very short recovery time are more promising for further applications. Figure 3(d) shows a SEM image of the core/shell heterostructures in the

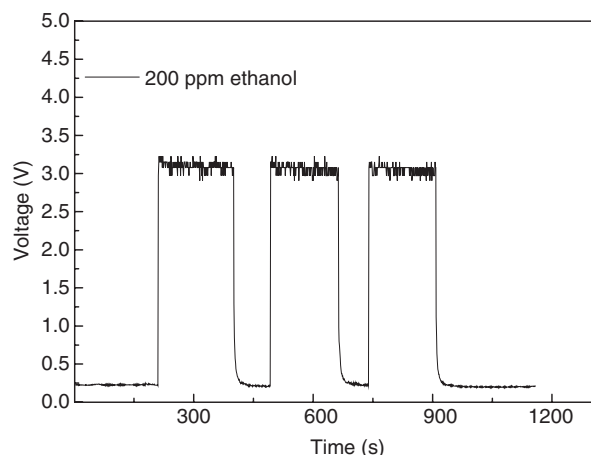


Figure 4. The response of the sensors to 200 ppm of ethanol after 3 months.

sensor. The morphology of the porous network structures is clearly observed. The pores are disordered and irregular, and their sizes range from several nanometres to micrometres. These pores play a crucial role in reaction efficiencies during gas diffusion, and may play a part in their short recovery time [36]. According to the Knudsen diffusion model the diffusion constant (D_K) can be represented as:

$$D_K = \frac{4r}{3} \sqrt{\frac{2RT}{\pi M}},$$

where r is the pore radius, R the gas constant, T the temperature and M the molecular weight of the diffusing gas. According to this equation, gas molecules diffuse more easily in porous structures due to the larger D_K in porous structures than in other denser structures. Thus both the response time and the recovery time are very short for the core/shell heterostructures with a porous structure. Recently, such fast response and recovery times were also observed in the porous structure of SnO₂ nanosized [37] and dendritic SnO₂ nanorod films [24, 25], which supports our explanations above.

It should be noted that the working temperature of the core/shell structures is relatively high (300°C). In this case, the sensing stability of the core/shell structures is very important for their further application. Therefore we tested the stability and repeatability of the sensors. Figure 4 shows the measured results for the sensor exposed to 200 ppm ethanol 3 months after the previous measurement. Compared to the results of 3 months before, the fluctuation of the sensitivity is less than $\pm 3\%$. This indicates that the sensing properties of the core/shell structures are stable. The carbon nanotubes and the network structures in the sensors can avoid contacts among SnO₂ nanoparticles and further limit the growth of aggregations among the nanoparticles. Therefore, the core/shell structures show stable sensing properties.

4. Conclusions

In summary, sensors based on the core/shell structures exhibit high sensitivity, fast recovery and good stability to ethanol gas. The enhanced ethanol sensing properties are attributed to the

small sizes of SnO₂ nanoparticles and the special morphology of the core/shell heterostructures. These results demonstrate that the core/shell nanostructures can be used as gas sensing materials for fabricating high-performance gas sensors.

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