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Highly Sensitive WO_3 Hollow-Sphere Gas Sensors

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In this paper, we describe how WO_3 hollow spheres have been synthesized in solution phase by the controlled hydrolysis of WCl_6 using novel carbon microspheres as the templates. All of the products were characterized by X-ray powder diffraction (XRD), scanning electronic microscopy (SEM), and transmission electron microscopy (TEM). The as-synthesized spheres had large diameters of about 400 nm and thin shells of about 30 nm composed of numerous small nanocrystals. Prompted by the porous structure and small crystal size of the shell wall, we constructed WO_3 hollow-sphere gas sensors and found that these sensors had good sensitivity to alcohol, acetone, CS_2, and other organic gases.

Introduction

As important wide band gap semiconductors, tungsten oxides have many outstanding properties, especially electrochromic, optochromic, and gaschromic properties. They have been used in vast areas including flat panel displays, photoelectrochromic "smart" windows, optical modulation devices, writing−reading−erasing optical devices, gas sensors, humidity and temperature sensors, and so forth.[1−4] WO_3 nanostructures,[5−9] including WO_3 nanoparticles, films,[5,6] nanowires, and nanotube arrays, have been widely synthesized.[7−9] However, in attempting to meet the needs of the development of display systems, catalysts, and sensors, the preparation of WO_3 nanostructures with small crystals and superior surface properties is still a primary challenge for scientists. Inorganic hollow spheres have tailored structures, low densities, high surface areas, and unique optical, electrical, and surface properties; materials with a hollow spherical structure might meet the needs of scientists and have promising applications in vast areas of miniature sensors, artificial cells, fillers, catalysts, acoustic insulation, microchip reactors, delivery vehicle systems, and photonic crystals.[10−13]

Herein, we report the synthesis of WO_3 hollow spheres by the controlled hydrolysis of WCl_6 by employing novel carbon microspheres as templates. The as-synthesized WO_3 spheres had large diameters of about 400 nm and a thin shells of about 30 nm composed of numerous small nanocrystals. According to the small crystal size and porous appearance, it was believed that WO_3 hollow spheres might be useful in fabricating fillers, catalysts, and sensors. In this paper, we

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mainly discuss their gas-sensing properties in detecting alcohol, acetone, and other organics.

Experimental Section

I. Materials. The templates were novel carbon microspheres, which were synthesized through the polycondensation reaction of glucose under hydrothermal conditions.[14] The carbon microspheres had many hydroxyl groups on the surface and were very suitable for use as templates in the synthesis of functional materials. Detailed information about carbon microspheres can be found in ref 14. All chemicals used in this work, including tungsten hexachloride (WCl_6) and dimethylfomamide (DMF), were analytical-grade reagents.

II. Synthesis of WO_3 Hollow Spheres. WO_3 hollow spheres were obtained by the controlled hydrolysis of WCl_6 in a coupling solvent and the subsequent removal of the template materials by calcination in air. The typical synthesis process was as follows. Analytical-grade tungsten hexachloride (WCl_6, 0.2 mmol) was dissolved in 10 mL of DMF, forming a 0.02 M solution. The core templates, carbon microspheres (about 0.25 g), were uniformly dispersed in 50 mL of DMF by ultrasonication, and then the WCl_6 solution was added slowly to the 50 mL of DMF at a speed of 20 s per drop while being ultrasonicated. After ultrasonicating for about 30 min, a small amount of distilled H_2O (e.g., 1 mL) was added to the solution dropwise to ensure hydrolyzation. After continuous ultrasonication for 1 h, the mixed solution was aged at room temperature for 1 day. The precipitate was filtered, washed with alcohol and distilled water, and dried in vacuum at 80 °C for 12 h. The carbon spheres were removed by a temperature programming treatment in a conventional muffle furnace. The as-prepared precursor was loaded into a quartz boat and put in the hot zone of the furnace. After calcination at 450 °C for 2 h in air, the product was cooled to room temperature, and tungsten oxide hollow spheres were finally obtained. The yield was calculated to be about 95% on the basis of W. The proportion of the spherical morphology was more than 95% on the basis of SEM.

III. Characterization. Powder X-ray diffraction (XRD) was performed on a Bruker D8-advance X-ray diffractometer with Cu Kα radiation (λ = 1.54178 Å). The 2θ range used in the measurement of tungsten oxides was from 10 to 70° in steps of 0.02° with a count time of 1 s. SEM images of as-synthesized WO_3 microspheres were taken on a JSM-6301F scanning electron microscope. The size and morphology of WO_3 hollow spheres were determined by using a Hitachi model H-800 transmission electron microscope with a tungsten filament at an accelerating voltage of 200 kV. The structure and composition of the spheres were measured by high-resolution transmission electron microscopy (HRTEM, JEM-200CX) and energy-dispersive X-ray spectroscopy (EDX).

Results and Discussion

The core−shell structure of WO_3-coated carbon microspheres showed no XRD peaks because the WO_3 coatings were amorphous. Thereby, the calcination treatment in air had two main effects: (1) carbon microspheres were removed during the treatment, and (2) the WO_3 coatings were well crystallized to form substantial shells.

The typical XRD pattern of the calcination products is shown in Figure 1. All of the reflection peaks could be indexed to the pure monoclinic WO_3 with lattice constants of a = 7.306 Å, b = 7.54 Å, c = 7.692 Å, and β = 90.88° (JCPDS card no. 72-0677).

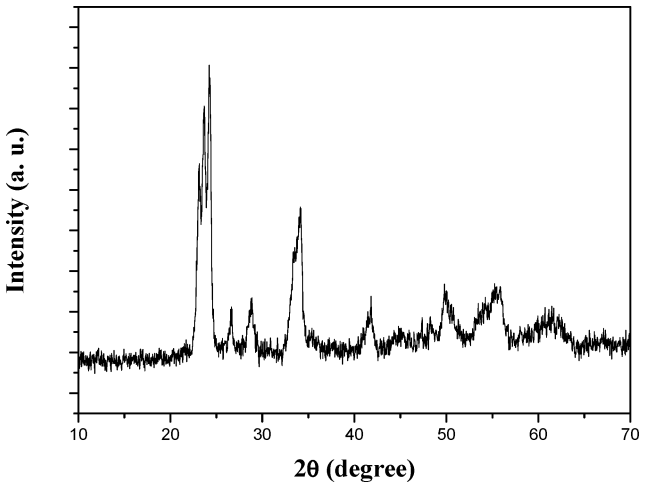

Figure 1. Typical XRD pattern of the WO_3 hollow spheres.

A series of SEM images of WO_3 hollow spheres is shown in Figure 2(a and b). Figure 2a is the low-magnification image, showing that more than 95% of the samples were hollow spheres. In the image, some dumbbells and aggregated spheres were also found. Because the amorphous WO_3 was coated on the surface of some dumbbell-like or aggregated carbon spheres, resulting in the replica of the templates' contour. Thus, hollow dumbbells and aggregated spheres were formed after the templates were removed. The enlarged SEM pattern of WO_3 spheres is shown in Figure 2b, in which all of the spheres had uniform morphology and almost the same dimension of about 400 nm. As marked in the image, most spheres had a partial cave-in or a small opening in their shell wall. We believe that the cave-in occurred because the shell wall was very thin, whereas the opening might be the imprint from the template removal. Although some spheres remained closed during the removal of the templates, we are not yet sure of the exact reason. It might be ascribed to something that made the formed CO_2 escape effectively without breaking the shell wall.

TEM images of the microspheres are shown in Figure 3a−d. Electron microscopy studies have indicated that the walls of the spheres are porous and structurally robust. From Figure 3a and b, the diameter of the spheres and the thickness of their shell wall could be estimated. Generally, the spheres were about 400 nm thick, in accord with the SEM results. The spheres had uniform thin shells of about 30 nm. Because the walls of the spheres were very thin, we could sometimes see holes and wrinkles on the spheres. HRTEM provided further insight into the structure of the shell wall, indicating that the walls of the hollow spheres were composed of numerous small nanocrystals. Figure 3c showed a typical HRTEM image in which the lattice structures of the nanoparticles could be seen clearly. The lattice fringes were about 0.38 nm. Statistical results of many HRTEM images have shown that the spheres were constructed by numerous nanoparticles with an average diameter of about 12 nm. Figure 3d was the selected area electron diffraction (SAED)

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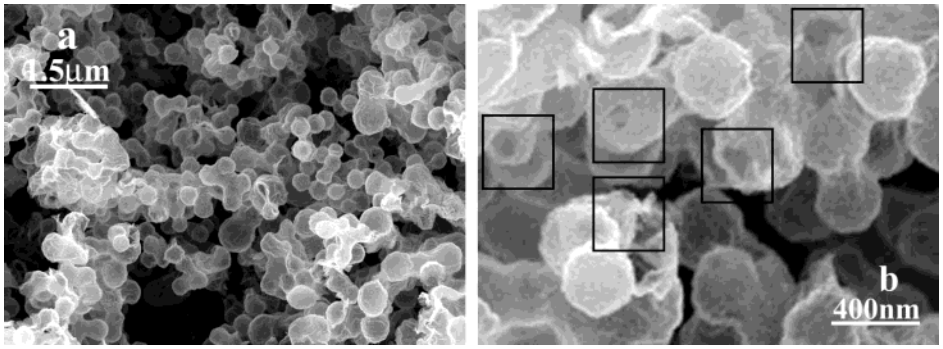

Figure 2. SEM images showing the spherical morphology of WO_3. (a) Low-magnification images. (b) High-magnification images. A small opening in the shell wall of some spheres has been indicated clearly in part b.

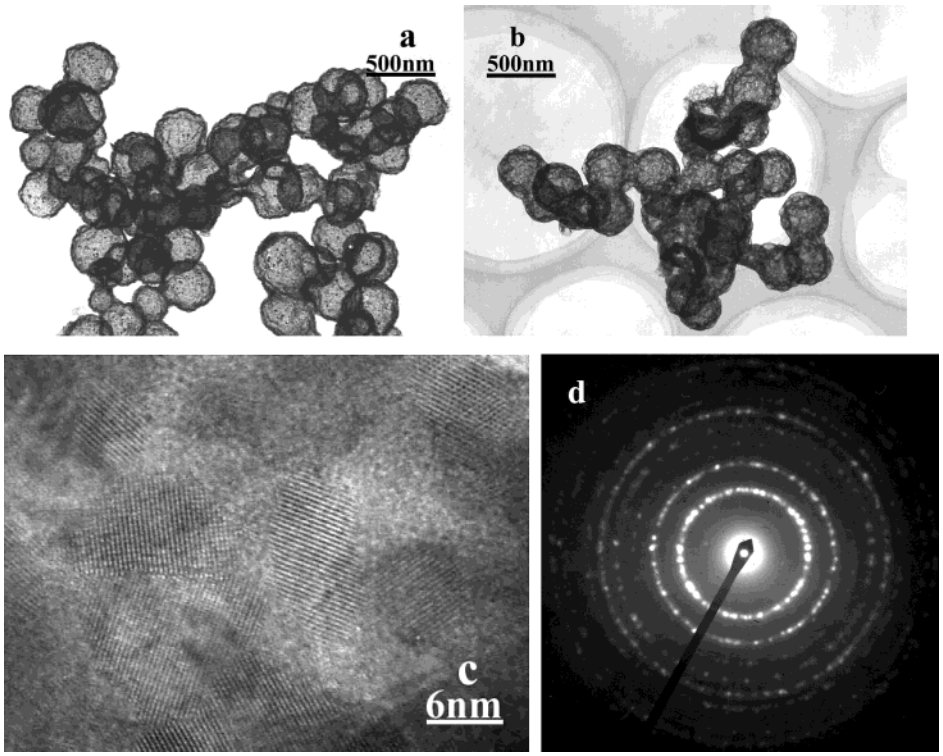

Figure 3. TEM and HRTEM images of WO_3 hollow spheres. (a, b) TEM images of different magnifications. (c) HRTEM image showing the structure of the shell wall. The lattice fringes were 0.38 nm. (d) SAED pattern.

pattern of the hollow spheres. As shown in the image, the WO_3 hollow spheres were well crystallized.

The EDX spectrum was used to determine the composition of the WO_3 hollow spheres. It confirmed that the hollow spheres were composed of W and O, and the quantitative analysis results indicated that the molar ratio of tungsten and oxygen was about 1:2.98, coincident with XRD and other analyses (figure not shown). The BET surface area was about 129 m^2/g, measured on a Micromeritics ASAP 2010 instrument.

To develope a comprehensive understanding of the synthesis of WO_3 hollow spheres, it was essential to investigate the influences of some reaction factors. Hence, a variety of reaction parameters such as the solvents, WCl_6 concentrations, ultrasonic mixing conditions, aging time, and template concentrations have been investigated.

Effect of the Tungsten Source. The investigation of the tungsten source provided useful information about the formation of WO_3 hollow spheres. Usually the WO_3 hollow spheres are synthesized by the deposition reaction of Na_2WO_4 and acids. In our system, experimental facts showed that WCl_6 was in favor of the formation of core−shell structures and that Na_2WO_4 was not suitable. Using WO_4^{2-} as the starting material, we could not obtain hollow spheres, and most of the products were aggregated large particles. The reason might be found in the different forms of tungsten ions: WCl_6 provided W^{6+} cations, whereas Na_2WO_4 provided WO_4^{2-} anions in solution phase. Because the carbon microspheres had many surface hydroxyl groups, W^{6+} cations were absorbed into the surface layer of carbon microspheres, and WO_3 was formed directly on the surface of the carbon microspheres, resulting in the core−shell structure.[14] Na_2WO_4 resulted only in the formation of large aggregating WO_3 particles.

Influence of the Solvents. WO_3-coated core−shell structures are generally exceptionally difficult to synthesize

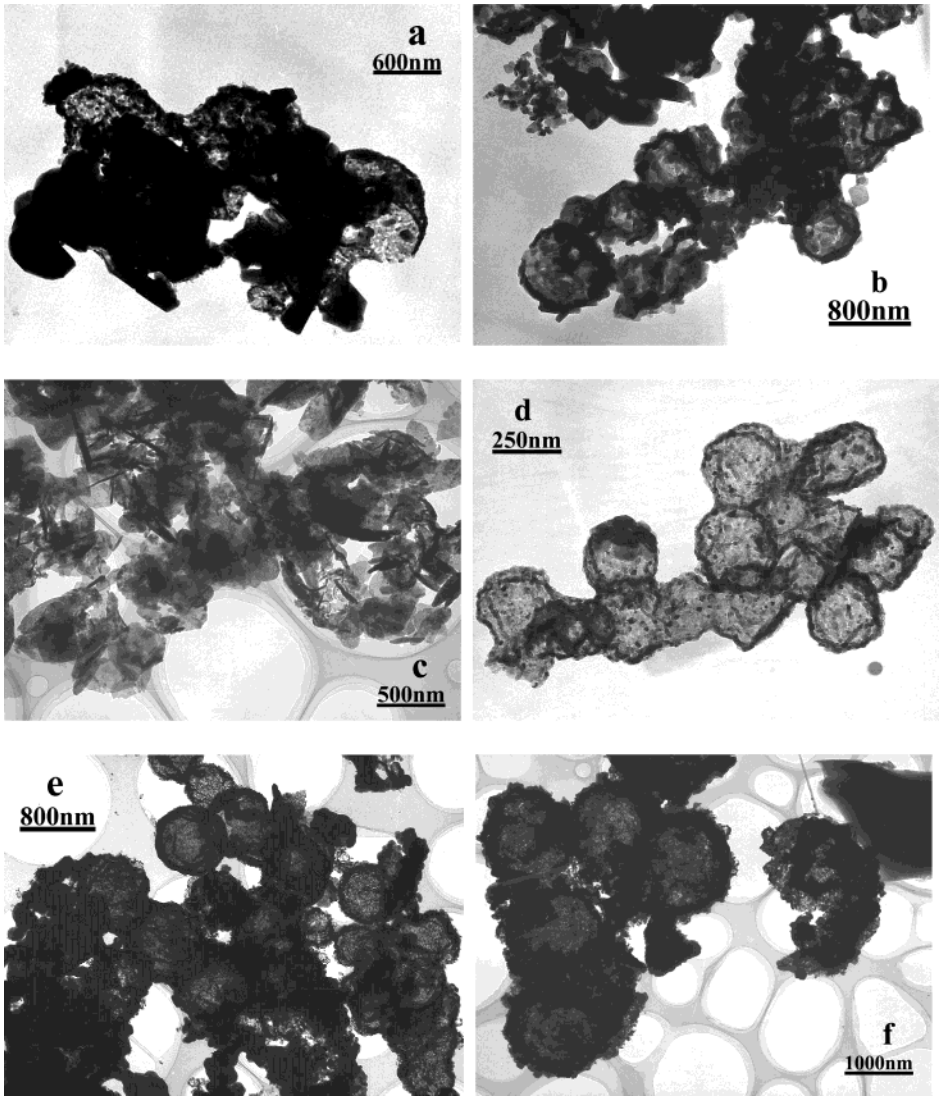

Figure 4. WO_3 obtained using different solvents: (a) alcohol, (b) acetone, (c) CCl_4, (d) acetylacetone, (e) acetonitrile, and (f) dimethylaniline.

because the WO_3 precursors are highly reactive, making it difficult to control their precipitation. This easily allowed WO_3 to form aggregating particles.

The hydrolysis of WCl_6 was very fast. To ensure the formation of a smooth coating and to prevent the formation of secondary WO_3 particles, the hydrolyzation reaction must be well controlled. Thus, the solvent was very important in building a favorable environment for the reaction. DMF was an important aprotic solvent and had many advantages in spatial geometry, polarity, alkalinity, and coordination ability. We have found that DMF is a very suitable solvent for controlling the hydrolysis reaction of WCl_6. As shown in Figures 2 and 3, more than 95% of the products were hollow spheres when DMF was used as the solvent. We have done control experiments with many other organic solvents, such as alcohol, acetone, acetylacetone, carbon tetrachloride, acetonitrile, and dimethylaniline, and so forth. In alcohol, acetone, and CCl_4 systems, almost all of the products were aggregated WO_3 particles, and no spheres were found (Figure 4a−c). When using acetylacetone as the solvent, we could obtain large portions of WO_3 spheres, although the shells of the spheres might have many defects (Figure 4d). Using acetonitrile and dimethylaniline as solvents, the coexistence of hollow spheres and large-scale irregular particles was found (Figure 4e and f).

In the investigation of the relationship between the product morphology (shown in Figure 4) and the solvent's characteristics,[15] we found that the intrinsic characteristics of the solvents such as the spatial geometry, polarity, alkalinity, and coordination ability had an integrative effect on the morphology of the products. CCl_4 had neither polarity nor coordination atoms, thus the product obtained had the worst morphology. Alcohol was a protic solvent, thus the product morphology was also poor, although its hydroxyl group had good polarity and coordination ability. Because the coordination ability of the nitrogen atom was weaker than that of the oxygen atom, the products obtained in dimethylaniline and acetonitrile had poorer results than those obtained in acetyl-

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acetone. Acetylacetone was an aprotic solvent with good polarity and coordination ability, hence the products obtained had good morphology. DMF was an aprotic solvent and had excellent spatial geometry, polarity, alkalinity, and coordination ability, thus excellent WO_3-coated carbon spheres and excellent WO_3 hollow spheres were easily obtained. Further investigation of the solvent effects is still needed.

Other factors, including the concentration of WCl_6 and the templates, the ultrasonic mixing condition, and the aging time, were also investigated. Long-time and high-power ultrasonic treatment was favorable for the coating of WO_3. Adequate aging time was also very necessary to form complete, stable amorphous coating layers to avoid breaking the spheres' walls during the template removal process. Thus, integrated hollow spheres were obtained after the carbon spheres were removed. We were unsure of the exact quantitative relationship between WCl_6 and the template concentrations at this stage. However, we could ensure that the products were all hollow spheres by adding enough templates. The removal of the templates also influenced the hollow sphere formation. An intermediate temperature (for example, 450 °C) and a slow heating rate were favorable for the formation of WO_3 hollow spheres.

Gas-Sensing Properties. Many studies on the fabrication of WO_3 sensors for many inorganic gases, including NO_x, H_2S, H_2, SO_2, and so forth, have been reported in the literature.[4,16−18] However, most of the studies focused on WO_3 solid polycrystalline films made of large particles.[16−18] Because they were limited by surface structures and particle size, the sensitivity and selectivity of those sensors were poor. High sensitivity and reversibility could be achieved only at elevated temperatures by exposure to UV light or by doping the sensors with other materials.[17,18] Here, it was found that only with porous morphologies and small nanocrystals in the shell wall did the WO_3 hollow spheres exhibit high sensitivity to organic gases at intermediate temperature.

The sensors were fabricated using thin films prepared from a powder suspension of as-synthesized WO_3 hollow spheres. The materials were dispersed in tetraethyl orthosilicate, formed into a slurry, and slightly grinded before fabricating the sensors. No conductive binder was added. The schematic diagram of a typical gas sensor is shown in Figure 5a and b.

We have investigated the response of various gases, including alcohol, acetone, CS_2, NH_3, H_2S, benzene, petroleum ether, acetonitrile, and so forth, using the commercial gas-sensing measurement system of HW-30. The measurement was carried out at various concentrations at 400 °C. Figure 6a−e shows the typical isothermal response curves when the thin-film sensor is exposed to alcohol, acetone, CS_2, NH_3, and H_2S. As shown in the images, the WO_3 hollow-sphere sensors had good response to the gases at low concentrations. Figure 7 shows the typical response curves of benzene, petroleum ether, and acetonitrile at higher concentrations. Table 1 summarizes all of the response results.

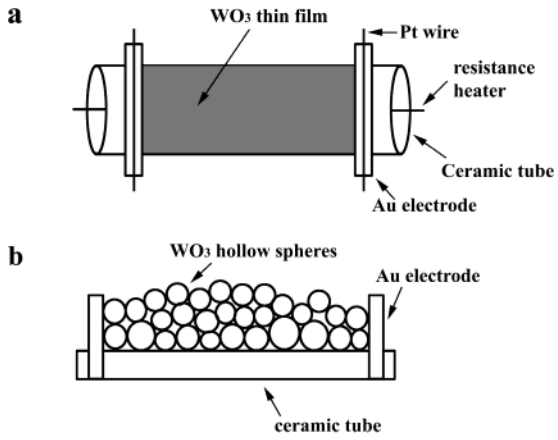

Figure 5. Schematic diagram showing the structure of a typical WO_3 hollow-sphere gas sensor. (a) Topic view. (b) Sectional view.

Table 1. Response Results (ppm) to Various Gases

sensor	10	50	100	200	500	1000	2000	5000
H_2S	21.8	52.9	67.2					
NH_3		1.5	1.7	2.14	2.89	3.15	3.57	4.38
alcohol		2.09	2.46	3.16	6.14	7.79	9.35	12.4
acetone		3.53	4.56	6.04	13.5	16	18.6	23.1
CS_2		1.56	1.83	2.54	5.06	7.2	11.2	14.3
benzene					2.56	3.06	3.43	4.06
CH_3CN					3.18	4.07	4.85	5.73
petroleum ether					2.72	2.92	3.67	4.91

As shown in Table 1, WO_3 hollow-sphere gas sensors had satisfactory sensitivity. With increasing concentration of the gases, the sensitivity of the sensors sharply increased. The sensors were more sensitive to alcohol and acetone than to other organics. We did control experiments with traditional sensors made of WO_3 particles, keeping other conditions the same. The results showed that the sensors made of WO_3 particles had poor responses to the organic gases. Figure 8a shows their response curve to alcohol, which gave a glimpse of the poor sensitivity of traditional sensors made of WO_3 particles. The morphology of the WO_3 particles used in the control experiments is shown in Figure 8b. Compared to the traditional sensors, WO_3 hollow spheres showed much higher sensitivity to the standard inorganic species of H_2S.[16−19] On the basis of the experimental facts and the literature,[16−19] we believe that the WO_3 hollow-sphere gas sensors have high sensitivity to inorganic species.

The hollow-sphere sensors showed great differences in response intensities for different gas species. As indicated in Table 1, the sensor showed much higher responses to H_2S and acetone than to alcohol, CS_2, and NH_3. At low concentrations, the sensor sensitivities to H_2S, acetone, alcohol, CS_2, and NH_3 were in descending sequence. The sensors had no response to benzene, petroleum ether, and

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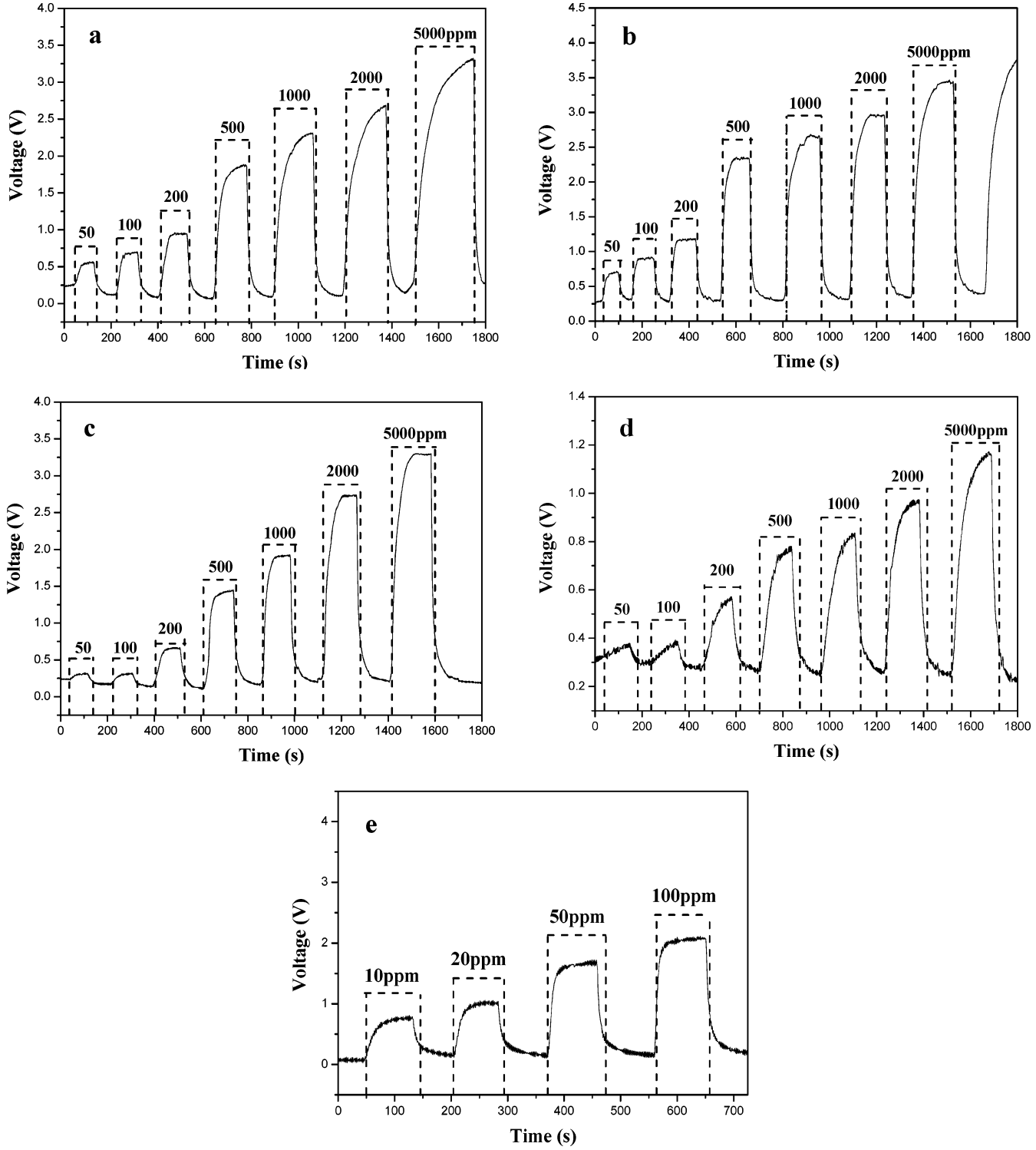


Figure 6. Response curves to (a) alcohol, (b) acetone, (c) CS_2, (d) NH_3, and (e) H_2S at 400 °C.

acetonitrile when the gas species were at low concentrations. Only when the concentration of those gases was quite high (up to 500 ppm) did the sensors give a small response. We have also tested the sensors with hexane and dichloromethane at concentrations up to 5000 ppm, and no response was obtained. On the basis of all of the experimental facts, we could say that WO_3 hollow-sphere sensors showed some selectivity to organic gases, although it was very far from the specificity response extent.

The sensing mechanism of semiconducting oxide sensors usually is believed to be the surface conduction modulation by the absorbed gas molecules. That is, (1) the electrical properties of the semiconducting oxides showed dramatic changes with or without the adsorption of gas molecules (mechanism of sensitivity). (2) With different kinds of adsorbing gas molecules, the electrical properties would show different changes (mechanism of selectivity). Recently, Yang et al. developed the sensing mechanism for SnO_2-based

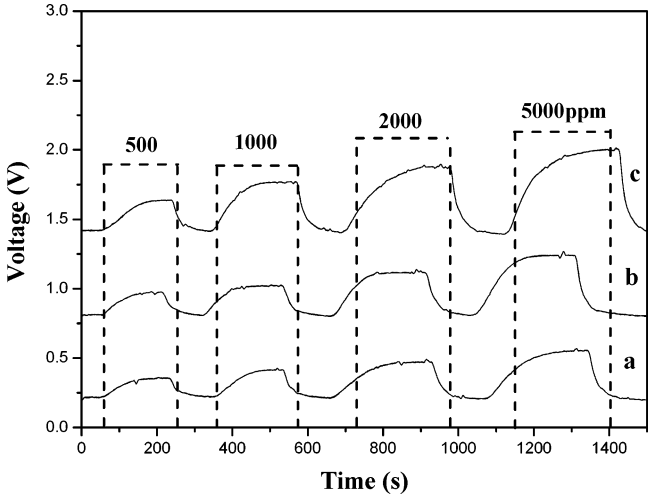
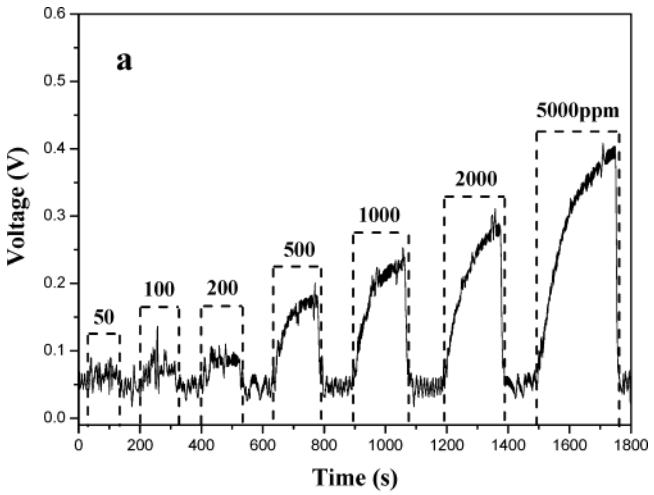


Figure 7. Response curves to (a) benzene, (b) petroleum ether, and (c) acetonitrile at 400 °C.



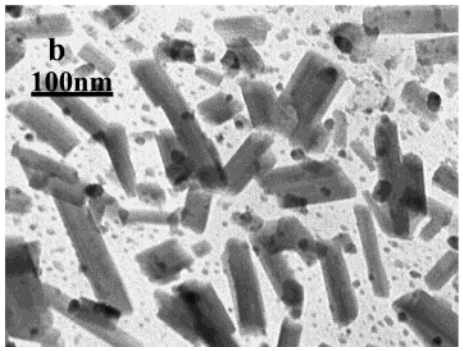


Figure 8. (a) Response curve of the sensors made of WO_3 particles to alcohol at 400 °C. (b) TEM image showing the WO_3 particles.

sensors.[20] Because of the analogies among the semiconducting oxides, we believe that the sensing mechanism of WO_3 sensors follows the surface conduction modulation theory. The porous structure of WO_3 hollow spheres had large fractions of atoms that were presented at the surface of the sensors; hence, with the adsorption of gas molecules, the electrical properties of WO_3 might change more dramatically

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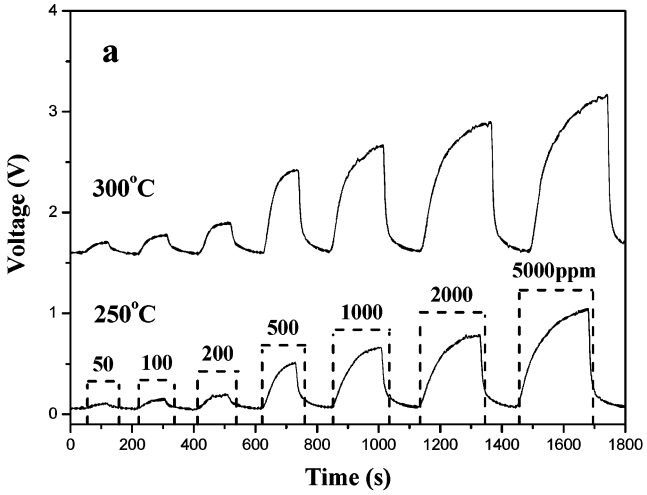

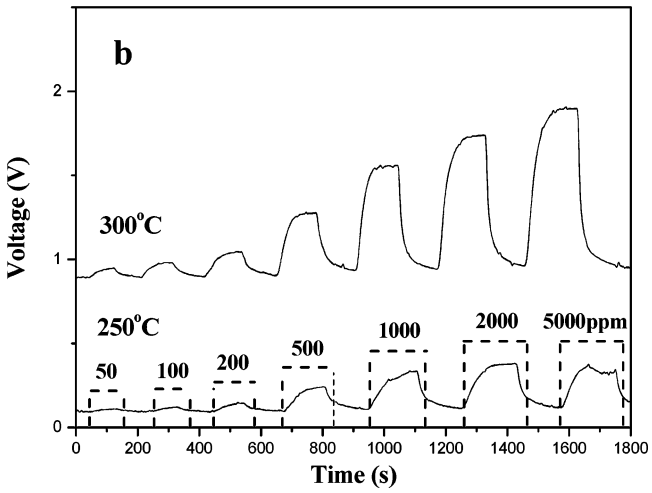

Figure 9. Temperature-dependent response curves to (a) alcohol and (b) acetone.

than those of traditional sensors. WO_3 hollow-sphere sensors had high sensitivity to gas molecules. WO_3 might have different adsorption and interaction behaviors with different gas species. Hence, WO_3-based sensors should have different responses to different gases. However, because of the poor surface structure of traditional WO_3 particle films, the sensors had a poor ability to reveal the different adsorption behaviors of different gases. In our case, with the porous structure, WO_3 hollow spheres had enough sensitivity to distinguish those gases. Therefore, WO_3 hollow-sphere gas sensors showed obviously different responses to different gases.

The sensitivity of the sensors changed with the working temperature. We have investigated the temperature-dependence behavior of the sensors and found that they might have responded to some gases even at 250 °C. We investigated the response curves of several gases from 200 to 450 °C. At low working temperatures, the sensors had poor sensitivity. At 250 °C they have a satisfactory response to acetone and alcohol but only when the concentration was higher than 10 ppm. The sensitivity to other organic gases was poorer. Figure 9a shows the response curves to alcohol at 250 and 300 °C. Figure 9b shows the curves that were obtained at 250 and 300 °C when the sensor was exposed in acetone.

The stability of the sensors was also investigated. The sensors still had good response even after several months. The reversibility of the sensors was good; they recovered quickly and showed good sensitivity to low concentrations of gases, even after exposure in 5000 ppm organics.

We think that the WO_3-based hollow-sphere gas sensors have high sensitivity and stability. After further investigation, they might be used in industry in the future.

Conclusions

In summary, we have synthesized WO_3 hollow spheres in the solution phase by the controlled hydrolysis of WCl_6 using novel carbon microspheres as templates. The as-synthesized spheres had large diameters and thin shells. With the porous structure, it was found that WO_3 hollow spheres had good sensitivity to alcohol, acetone, CS_2, and other organic gases. We believe that WO_3 hollow-sphere gas sensors might have promising applications in the future and stimulate research for other kinds of nanostructured gas sensors.

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