Enhanced Gas sensing by Double-Shell V₂O₅ Hollow Nanospheres Functionalized with PdO Nanoparticles

Peng Sun, Sufang Zhang, Qi Yu, Tianshuang Wang, Xueli Yang, Geyu Lu*
State Key Laboratory on Integrated Optoelectronics, College of Electronic Science and Engineering,
Jilin University, Changchun 130012, People's Republic of China
pengsun@jlu.edu.cn, Lugy@jlu.edu.cn

Abstract:

Double-shell V_2O_5 hollow nanospheres decorated with PdO nanoparticles were synthesized via a template-free hydrothermal method combined with subsequent annealing process. The chemical composition and microstructure evolution were examined using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscope (SEM), and transmission electron microscope (TEM). The sensing properties of V_2O_5 hollow nanospheres before and after functionalization with PdO nanoparticles were investigated. The PdO-loaded Fe $_2O_3$ sensor exhibited obviously enhanced response to acetone compared with their unloaded counterparts. The improvement may arise from unique structure and catalytic effect of PdO in promoting the dissociation of gas molecules.

Key words: Hydrothermal method, V₂O₅ double-shell hollow nanospheres, Functionalization, PdO nanoparticles, Gas sensors.

Introduction

It is well known that the most important aspect of investigation of chemical sensors based on semiconductor oxide is its sensitivity, selectivity, and stability. Up to now, great efforts have been made to better resolve these problems^[1-3]. The synthesis of sensing materials with novel structure is one of the most promising solutions because they can be achieved easily. In this respect, Sensing materials with hollow structure exhibit a dramatic performance enhancement in gas sensor application owing to their unique structural features, such as well-defined interior voids, high specific surface area, low density, and good surface permeability. In this regard, materials with complicated hollow structures, have immediately intrigued many scientists all over the world because of their promising advantages compared with their single-shell counterparts. [4,5] Therefore, tremendous efforts have been dedicated to the design and preparation of complicated hollow structures. To date, a general strategy for the preparation of multiple-shell hollow structures is using sacrificial or removable templates. However, complicated hollow structures obtained from template routes are usually subjected to tedious synthetic procedures and high cost. Moreover, template residue mostly results in low activity of prepared materials. To avoid complex operations, many template-free methods have been developed to prepare complicated hollow microstructures and nanostructures. Despite many good results have been obtained, it is still very desirable to develop facile, template-free, and solution-based self-assembly strategies for the synthesis of complicated hollow structures. For that reason, we have successfully prepared amorphous unloaded and PdO-loaded V2O5 double-shell hollow nanospheres by combining template-free hydrothermal route subsequent thermal processes. A comparison with sensing properties shows that PdOfunctionalized double-shell hollow nanospheres exhibit a dramatic improvement in response toward acetone because of the unique structure and enhanced catalytic dissociation of the gas molecular.

Experimental section

In a typical synthesis, NH_4VO_3 (80 mg) was dissolved in 25 mL mixed solvent (glycerol and isopropanol) to form a clear solution, which was poured into a Teflon-sealed autoclave and maintained at 180 °C for 6 h. The product was collected by centrifugation, repeatedly washed with deionized water and absolute ethanol, and

dried at 80 °C for 12 h. Then, 30 mg of the asobtained powder and 3 mg of Pd(NO₃)₂ were added into deionized water. After that, the product was heat-treated at 350 °C for 1 h in air.

Results and disscusion

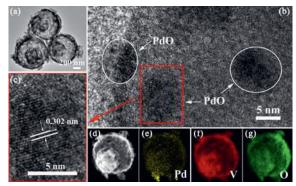


Fig. 1. TEM and elemental mapping images of PdO-loaded double-shell V_2O_5 hollow spheres.

and hollow interior architectural construction of V₂O₅ nanospheres were studied by transmission electron microscope (TEM). As can be seen from Figure 1a, it was found that there was clear gap between the outer and inner shell. Moreover, the obvious contrast between the dark solid edges and the pale hollow space indicated the existence of a double-shell structure in the resulting spheres. Figure 1b and c give the typical HRTEM image of PdO-loaded double-shell hollow sphere at low and high magnification. The fringe spacing was 0.302 nm, which corresponded to the (100) planes of PdO. The TEM elemental mapping taken from an signal PdO-loaded double-shell hollow sphere (Figure 1d) clearly identified the spatial distributions of Pd, V, and O in the nanosphere, as shown in Figure 1e-g. It was found that PdO nanoparticles were loaded uniformly on the shell of hollow nanosphere.

Figure 2a shows the responses of sensors based on single-, before and after PdO loading of double-shell V₂O₅ hollow spheres to different concentrations of acetone at 200 and 225°C. It is found that the responses of all the sensors increased with the increase concentrations. Obviously, the PdO-loaded V₂O₅ sensor was much more sensitive to test gases than the unloaded one. Moreover, compared with single-shell structure, the sensor based on the double-shell hollow exhibited high response. nanospheres Representative results of the response of sensors based on PdO-loaded during cyclic exposure to increasing acetone concentrations between 40 and 100 ppm are shown in Figure 2b. These almost square response shape observed indicates that the response and recovery characteristics of sensors were almost reproducible with the quick response and recovery. Gas responseS to 40, 60, 80, and 100 ppm acetone was 11, 14.1, 17.5, and 19.7.

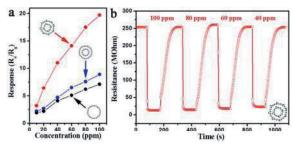


Fig. 2. (a) Responses of the sensors to different concentration acetone. (b) Transient responses of sensor using PdO-loaded hollow spheres.

Conclusion

We have described a facile strategy for controllable preparation amorphous PdO-loaded V_2O_5 hollow nanospheres with double-shell structure. When investigated as the sensing material for gas sensors, the V_2O_5 decorated with PdO double-shell hollow spheres exhibit the highest sensitivity. The enhancement in sensing properties can be explained by larger specific surface area and catalytic effect of PdO.

References

- [1] T. Hyodo, K. Sasahara, Y. Shimizu, M. Egashira, Preparation of Mmacroporous SnO₂ Films Using PMMA Microspheres and Their Sensing Properties to NO_x and H₂, Sensors and Actuators B:Chemical 106, 580-590 (2005); doi:10.1016/j.snb.2004.07.024M.
- [2] K.T.C. Chai, P.A. Hammond, D.R.S. Cumming, Modification of a CMOS Microelectrode Array for a Bioimpedance Imaging System, *Sensors and Actuators B:Chemical* 111-112, 305-309 (2005); doi: 10.1016/j.snb.2005.06.047
- [3] E. Chow, E.L.S. Wong, T. Böcking, Q.T. Nguyen, D.B. Hibbert, J.J.Gooding, Analytical Performance and Characterization of MPA-Gly-Gly-His Modified Sensors, *Sensors and Actuators B:Chemical* 111-112, 540-548 (2005); doi: 10.1016/j.snb.2010.03.046
- [4] L. Zhou, D.Y. Zhao, X.W. Lou, Double-Shelled CoMn₂O₄ Hollow Microcubes as High-Capacity Anodes for Lithium-Ion Batteries, Advanced Materials 24, 745-748 (2012); doi: 10.1002/adma.201104407
- [5] M. Yang, J. Ma, C. L. Zhang, Z. Z. Yang, Y. F. Lu, General Synthetic Route toward Functional Hollow Spheres with Double Shelled Structures, *Angew. Chem. Int. Ed.* 44, 6727-6730 (2005); doi: 10.1002/anie.200501556