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Flowerlike Agglomerates of Mn_3O_4 with Gas-sensing Properties Formed on Eggshell Membrane

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Abstract: Flowerlike agglomerates of Mn_3O_4 have been successfully synthesized under control of eggshell membrane. The flowerlike agglomerate was composed of nano-slices. Reaction temperature was found effective in the formation of the morphology. Gas sensing properties of the material were presented. It showed that Mn_3O_4 with flowerlike morphology is sensitive to reductive gas.

Keywords: Mn_3O_4; 3D structure; Gas-sensing

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Introduction

During the past few decades, manganese oxides have been widely exploited because of their potential applications in many fields, such as catalysis [1], supercapacitors [2], ion exchange [3], molecular adsorption [4], magnetic applications [5] and secondary batteries [6]. Among these manganese oxides, hausmannite Mn_3O_4 is most stable at high temperature relative to other oxides. Hausmannite Mn_3O_4 has high catalytic activity for many reactions, such as selective reduction of nitrobenzene [7], oxidation of methane and carbon monoxide [8], decomposition of waste gases [9] and combustion of organic compounds at temperature of the order of 373-773K [10].

It is reported that the relationship between shape of materials and their reactivity is of great importance [11]. In view of this, the most important challenge for material synthesis is to control the growth of a predefined crystal shape. Various approaches have been explored to pursue a simple and shape-controllable synthetic method for Mn_3O_4, including solvothermal method [12], sol-gel method [13], and hydrothermal method [14]. The reactivity of manganese oxides greatly depends on the preparation process, the exact composition, and the 3-demensional structure [15]. Therefore, much attention has been paid to obtain special shapes of Mn_3O_4 [16]. A variety of shapes have been reported, such as cubic [17], tetragonal [18], hexagonal [19], octahedral [20] and polyhedral [21] nanocrystals, nanoplates [22]. To the best of our knowledge, the 3D flowerlike Mn_3O_4 nanostructures have never been observed before.

In this paper, flowerlike agglomerates with 3D nanostructure were synthesized using eggshell membrane as template. Eggshell membranes, which are stable in aqueous and alcoholic media and undergo pyrolysis on heating, consist of the outer shell membrane, inner shell membrane and limiting membrane surrounding the egg white [23]. The inner shell membrane was used in this work. The influences of different reaction conditions on the morphology of final products have been discussed. The gas-sensing property to CO and CH_4 gases of such prepared Mn_3O_4 was also investigated.

Experimental

Synthesis of flowerlike Mn_3O_4

All the chemicals used in this experiment were of

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analytical grade and used without further purification. Eggshell membrane was separated from the $CaCO_3$ shell of commercial eggs and washed with distilled water. ESM spieces were cut into quadrilateral sheets of about 1 cm in side length and dried at room temperature in airflow. Subsequently, the above ESM sheets were immersed into 0.1 mol/L $MnCl_2$ water solution for 10 h at room temperature. After being fished out and rinsed with distilled water, the ESM was dried naturally and calcined at 500℃ for 2 h to remove organic ESM and achieve better crystallization of the products. The brown products were stored in vacuum for further characterizations.

Characterization

The phase purities of the obtained samples were measured on a Bruker D8-advance X-ray powder diffractometer with Cu Kα radiation (λ=1.5418 Å). Morphology analysis of the samples was conducted with Hitachi S-4800 scanning electron microscopy (SEM) operated at 5 kV.

Gas-sensing property

Gas sensors were fabricated as side-heated structure. The powder of as obtained Mn_3O_4 is mixed and ground with deionized water in an agate mortar to form a paste which is then coated on an alumina tube-like substrate on which a pair of Au electrodes had been printed. The tube was then dried at 100℃ for 2 h and subsequently calcinated at 500℃ for 2h. Finally, a Ni-Cr heating wire is inserted into the tube to get a gas sensor. The gas sensor is aged at 300℃ for 120 h to improve its stability. Measurements on gas-sensing property were performed with a static test system made by Zhengzhou Weisheng Electronics Co. Ltd., Henan Province, China. Detecting gas was injected into a test chamber and mixed with air. The gas response of the sensor to CO and CH_4 is defined as S=Ra/Rg, in which Ra and Rg are the resistance in air and in test gas respectively.

Results and discussion

Structure and morphology

The crystalline structure and purity were examined by X-ray diffraction analysis. As shown in Figure 1, all diffraction peaks can be indexed to body-centered tetragonal Hausmannite Mn_3O_4 phase (JCPDS 80-0382), with lattice constants of a=b= 5.765 Å, c=9.442 Å. No characteristic peaks ascribing to other phases were observed, which indicates high purity of the prepared flowerlike Mn_3O_4.

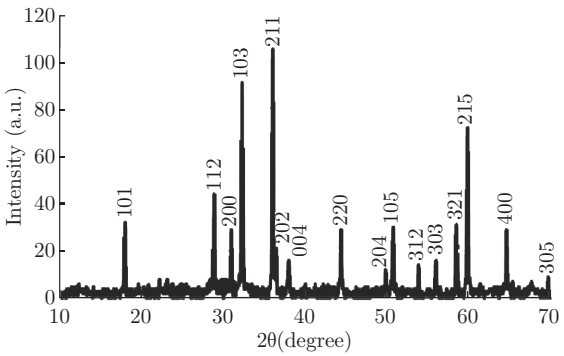

Fig. 1 XRD curve of flowerlike Mn_3O_4.

The morphology of the products was examined by SEM imaging. Figure 2 shows typical images of flowerlike Mn_3O_4 agglomerates. It can be seen from Fig. 2(a) that these agglomerates have diameter of about 250 nm. Figure 2(b) shows that these flowers are composed of nanoslices with thickness of about 5 nm.

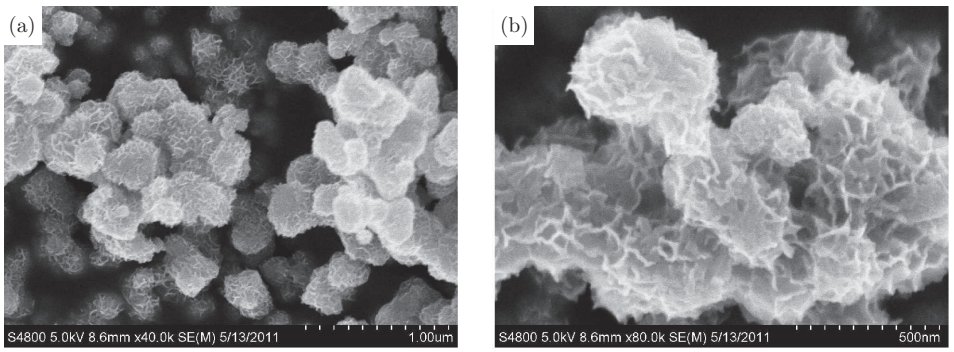

Fig. 2 SEM image of flowerlike Mn_3O_4.

It was found that calcination temperature played important role in the formation of flowerlike Mn_3O_4 agglomerates. Figure 3 shows the sample obtained at 600℃. The net structure of eggshell membrane was destroyed. So the morphology of Mn_3O_4 is irregular. This result indicates that eggshell membrane is the template controlling the formation of Mn_3O_4 crystal.

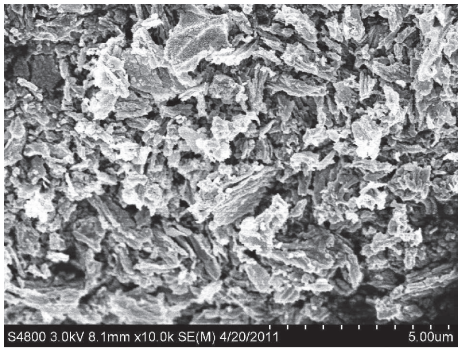

Fig. 3 Sample obtained at 600℃.

Gas response of the sample to CO

The sensitivity-concentration curves of Mn_3O_4 sensor are shown in Figure 4. The response to 5 ppm CO is 2.0, but the response to 50 ppm CO attains 5.8. It can be concluded that the sensor has higher sensitivity to CO than that to CH_4, which indicates that Mn_3O_4 sensor may have promising application to detect CO, and is worthy of further investigation.

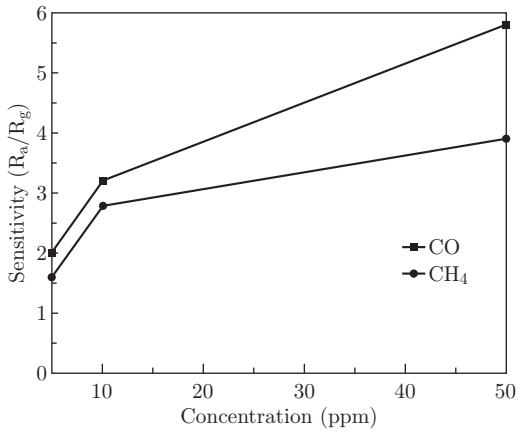

Fig. 4 Sensitivity of Mn_3O_4 sensor to concentration curve.

Conclusion

In conclusion, a facile method is developed to synthesize flowerlike Mn_3O_4 agglomerates in this paper and its gas-sensing properties to reductive gases such as CO and CH_4 are studied. The result indicates that the Mn_3O_4 sensor is sensitive to dilute CO gas. However, there is still more work need to do to detect CO.

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