Porous WO_3 beads fabricated by microfludic device

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Abstract. In this study, we have fabricated porous WO_3 beads by microfluidic device. The polystyrene(PS) nanosphere arrays were filled by WO_3 to prepare porous beads by using a template method. At the same time, in this paper, the raw materials used in this experiment is tungsten oxide which has the photoelectrochromic characteristics. In addition, tungsten oxide has the catalytic, magnetic, photosensitive performance.

Introduction

Inverse opal photonic crystal with a large internal surface area have been used for catalyst supports and gas-sensing devices, such as [1-3], through which the color change can be detected that the change amount of the catalyst and the gas. WO_3 is a very excellent performance inorganic metal oxides with catalytic, magnetic, photochromic, electrochromic, high-sensitivity gas sensing and other characteristics, showing broad application prospects in terms of materials. WO_3 gas sensing with high sensitivity in terms of so many high gas selectivity, such as: hydrogen, ammonia, hydrogen sulfide, nitrogen oxides (NOX) and the like. Ghimbe et al[4] had prepared deposited WO_3 films for detecting H_2S, SO_2, NO_2 and other toxic gases, and showed a higher sensitivity. As WO_3 hollow ball made of a structure which can increase the internal surface area, thereby increasing the sensitivity of the gas [5]. More concerns are WO_3 formed nanostructures have large surface area to get a higher catalytic efficiency. In addition, there are many structures have also been concerned about, such as core-shell structure, layered and other structures. Our purpose is to prepare macroporous beads use polystyrene(PS) nanosphere array filled with WO_3, namely using a template to prepare prepare PS/WO_3 beads, and then burned the template, the inverse opal structure of WO_3 were got. This kind materials can be used for optoelectronic devices, catalysis and other carriers.

Experimental

Chemicals and materials. Different size of polystyrene nanospheres were sythesized according to a literature[6]. Anhydrous ethanol, 200mesh tungsten powder, hydrogen peroxide(30%), acetic acid and normal hexane were purchased from Sinopharm Chemical Reagent co.,Ltd.

Preparation of peracetic acid derivatives. 10ml of deionized water was added into a 500ml three-necked flask with stirring in an ice-salt bath, and added 100ml hydrogen peroxide solution of (30%) and 100ml glacial acetic acid. After the mixture is formed a homogeneous solution, the solution was cooled for until it's temperature is the same with the ice-salt bath's. In addition, 16.25g of tungsten powder was added into the three-necked flask and stirred for 24h. What's more, the solution was dried at 40^{o}C in an oven to obtain the powder while the solution had refluxed for 18h at 55 ^{o}C. Then, the obtained powder was dissolved in the ethanol as the ratio between the powder and the ethanol was 1:5(w:w) after which the solution was dried at 50 ^{o}C so as to obtain yellow powdery peroxy tungstic acid derivative. Finally, peracetic acid derivatives was redissolved in the ethanol by the ratio of 31:70 (w:w)[7].

Treatments of polystyrene colloidal particles. Firstly, Polystyrene colloidal nanoparticles was centrifuged several times meanwhile removed the upper layer solution after which added deionized water, ultrasonic dispersion. To select appropriate polystyrene colloidal particles, it's necessary to change the centrifugal speed, the typically centrifugal speed various from 7000rpm to 12000rpm.

Preparation of polystyrene/WO_3 beads. First of all, to prepare the sol, the polystyrene colloidal nanoparticles and peroxy tungstic acid derivative was mixed by the volume ratio of 74:26. Meanwhile, adjusting the viscosity of the sol by adding ethanol. Preparation of a suitable viscosity sol to be the next step to use. Use homemade microfluidic devices and set up the experimental apparatus. 2ml sol was drawed with 10ml syringe and 50ml syringewith a needle to draw a viscosity of 500cst silicone oil 50ml. Start syringe pump, adjusting the flow rate of the solution and the silicone oil to obtain a suitable particle size and uniform microbeads. 1cm thick silicone oil was added in Polypropylene boxes as a receiving device of beads. It is time to stop push the ball once get enough beads. The box was then placed in an oven for 8h at 50^{o}C after which raised the temperature to 60^{o}C for 12h, after then cooled to room temperature. The silicone oil was completely washed off by n-hexane while the upper layer of silicone oil had been drained. Finally the beads was saved in n-hexane for the next step.

Preparation of WO_3 beads. To remove the polystyrene and obtain an porous structure of the beads, the solvent should be wiped off from WO_3/polystyrene beads, and then burn the WO_3/polystyrene beads with a crucible in the muffle furnace at 500^{o}C for 1h. Finally, they were cooling to room temperature.

Results and discussion

Fig.1 shows that the self-made PS nanoparticles has the feature of uniform particle size, which is suitable for the preparation of colloidal crystals.

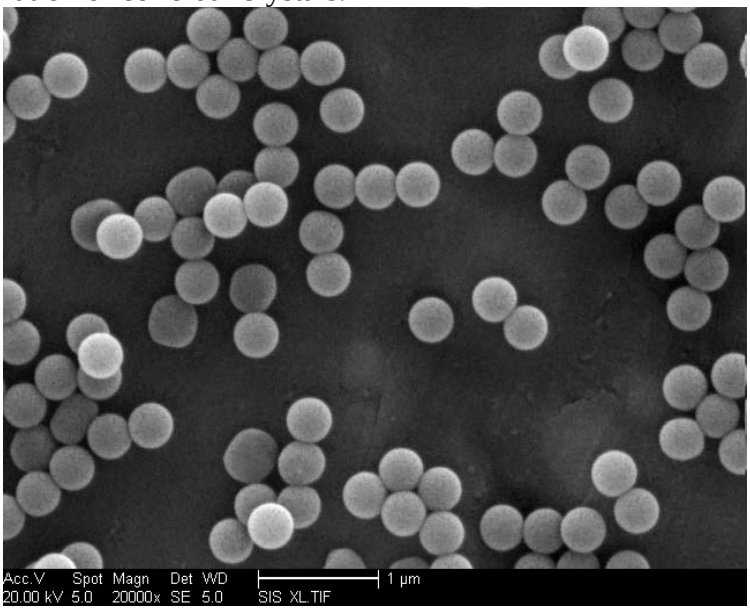

Fig.1 SEM image of self-made PS nanospheres

Fig.2 is the SEM image of WO_3/PS beads after burning off the PS, which indicate the uniform particle size, smooth surface beads can be obtained by this method.

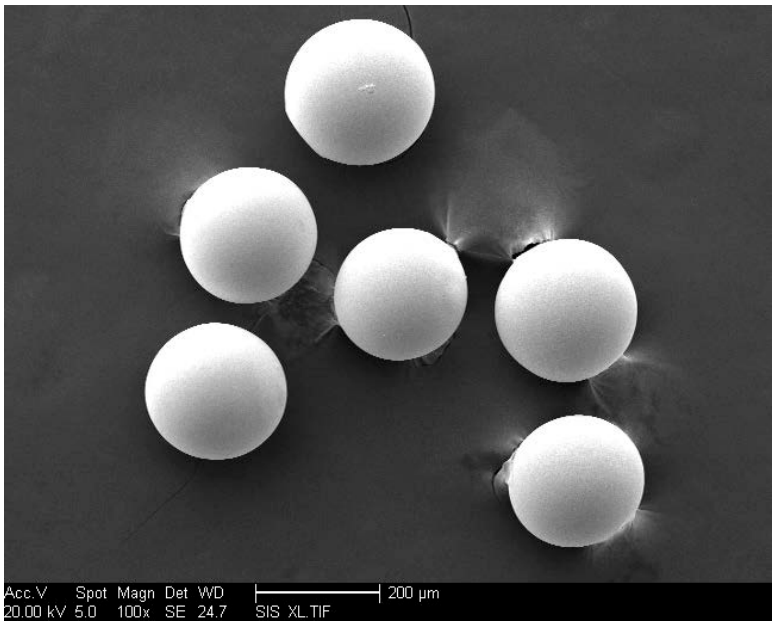

Fig.2 SEM image of WO_3 beads

Fig.3 exhibits that WO_3 beads have a little bit yellow fluorescence, nevertheless the WO_3 beads has a strong fluorescence under bright field.

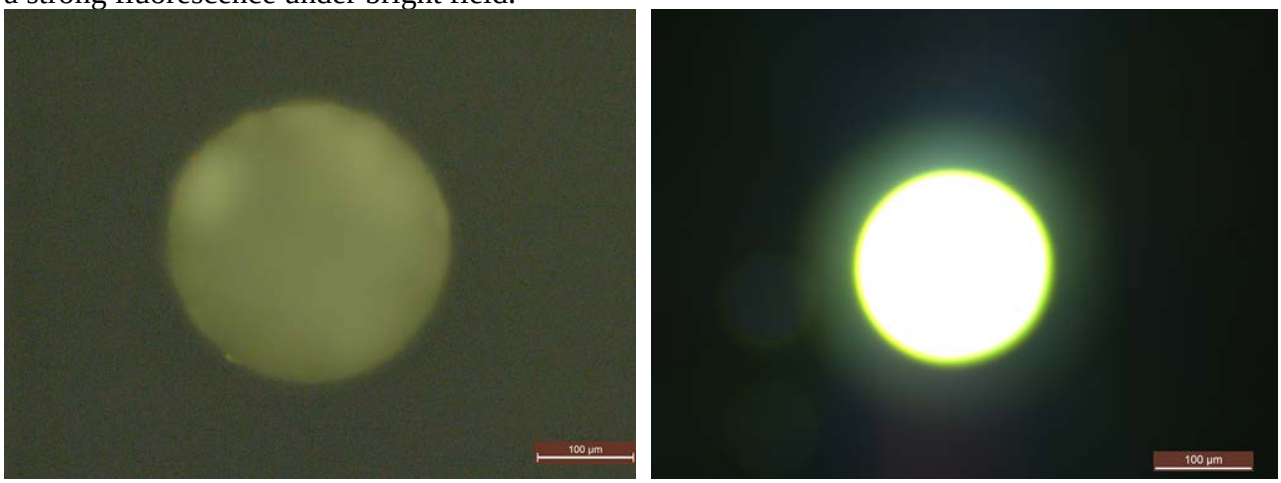

Fig.3 Microscope images of WO_3 beads under dark filed(left) and bright field(right)

Fig.4 shows the surface structure and the internal structure of the WO_3 beads after burning off the PS. As a kind of structure that has a variety of applications and potential value can act as catalyst carrier and so on.

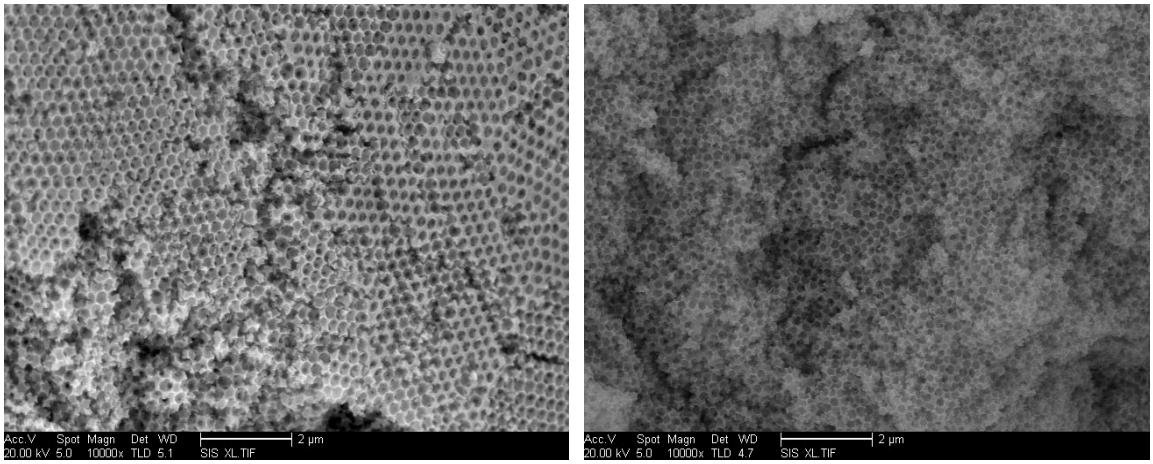

Fig.4 SEM images of the surface structure(left) and the internal structure(right) of WO_3 beads

Conclusion

In this paper, the WO_3 porous beads were succsessfully pepared by microfludic device. This kind WO_3 material has potential applications in carrier field.

Acknowledgments

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Reference

[1] R. Qasem, S. Victor and P. P. Daniel: Biosensors and Bioelectronics Vol. 21(2006), p.1693

[2] N. Kengo, T. Takasumi and S. Akihiko: Nature Photonics Vol. 4(2010), p. 477

[3] Y. J. Zhao, X. W. Zhao and J. Hu: Adv. Mater. Vol. 21(2009), p. 569

[4] X. L. Li, T. J. Lou and X. M. Sun: Inorg. Chem. Vol. 43(2004), p. 5442

[5] M. A. Gondal, M. A. Dastageer and A. Khalil: Cat. Comm. Vol. 3(2009), p. 214