

Synthesis of Highly Ordered Macroporous Titania Using TiCl_4 Hydrolysis

Chong Wang, Cancan Yang, Mei Yu*, Zhe Yu.

Biomedical Microdevices Research Laboratory, Shenzhen Institutes of Advanced Technology, Chinese Academy of Sciences, 1068 Xueyuan Avenue, Shenzhen 518055, China

* Corresponding Author E-mail: mei.yu@siat.ac.cn

Abstract: The high quality ordered macroporous titania has been successfully synthesized with the hydrolysis of titanium tetrachloride (TiCl_4) by heating the hydrochloric acid solution of TiCl_4 which filled in polystyrene templates. In this method, there is no need of filling the interspaces of polystyrene template repeatedly and no introduction of organic impurities either. The best conditions of synthesizing ordered macroporous titania are found that the pH value is 2.0~2.5, the filling time is 3h and the calcination temperature for the filled templates is 500°C. The macroporous titania synthesized show highly ordered structure and obvious photonic bandgap.

1. Introduction

The ordered macroporous titania has attracted considerable interest due to their large specific surface area, high porosity and high order degree. It is widely used as absorption materials [1], battery materials, macromolecular catalysts and especially a kind of high-quality photonic crystals[2, 3]. Because of the periodical distribution of the dielectric constant, the ordered macroporous titania is extensively used in the fields of optical wave-guide[4], low-threshold lasers, photonic chip polystyrene, optical communications and so on.

At present, the template method[5-7], regarded as an economical and well size-controlled way, is commonly used to synthesize the ordered macroporous titania. However, to fill the template interspaces with the titania effectively is always arduous. Mostly, the Sol-gel [8-12] method is used to fill the template interspaces. In the Sol-gel method, the collosol is prepared with butyl titanate first, then the template is immersed in the collosol to fill the interspaces, at last the template substance is removed by pyrolysis. The collosol has formidable access to the template interspaces, thus the filling of the collosol must be repeated several times, which affects the structural integrity of the ordered macroporous titania. Moreover, a mass of organic impurities is introduced in the process, which might affect the structural uniform of the macroporous titania. In addition, there are some other methods of filling the template interspaces, such as chemical vapor deposition and electrochemical deposition method [13]: the former with even filling and good controlled filling-rate but high experimental conditions and complex operation while the latter inapplicable to the titania materials.

For the purpose of filling the template interspaces more effectively, we have adopted a novel approach. First we prepared the polystyrene template, and then put the template into the hydrochloric acid solution of titanium tetrachloride. Adjusting the pH value of titanium tetrachloride solution by heating



to make hydrochloride volatilize, the titanium tetrachloride in the template interspaces began to hydrolyze slowly at a certain pH value, until to fill the template interspaces uniformly by the hydrated titania. At last, the polystyrene template was removed by pyrolysis and the hydrated titania turned to titania at one time. This method is a simple and effective way to synthesize the ordered macroporous titania. There is no organic impurities introduced or no need of repeated filling process. With the uniform structure and high order rate, the macroporous titania synthesized has an obvious photonic bandgap in the infrared area.

2. Experimental

Firstly, the polystyrene microspheres were synthesized by non-soap emulsion polymerization method, and then the polystyrene templates were assembled by the vertical deposition method [14]. The vertical deposition was carried on with a temperature at 65 °C and a humidity at 90%. At last, the polystyrene templates were heated for 5 hours at 85 °C.

The synthesis steps of the ordered macroporous titania are as follows: 1) the hydrochloric acid solution of titanium tetrachloride was prepared: the concentration of titanium tetrachloride was 0.8mol/L and the concentration of hydrochloric acid was 2mol/L; 2) the prepared polystyrene templates were immersed in the hydrochloric acid solution of titanium tetrachloride and heated at 80 °C, in the entire process to maintain the hydrochloric acid solution of titanium tetrachloride in the constant temperature and simultaneously using the hydrochloric acid solution (1mol/L) to adjust the pH value between 2.0 ~ 2.5, until to fill the template interspaces uniformly by the hydrated titania after 3 hours; 3) the polystyrene templates were removed out and drying at room temperature; 4) the filled templates were calcined at 500 °C for 30 minutes in high-temperature furnace. Finally, the ordered macroporous titania was prepared.

Figure 1. shows the process of the ordered macroporous titania. The interspaces of polystyrene templates could be filled with the hydrochloric acid solution of titanium tetrachloride at first. Then by heating, hydrogen chloride in the solution was gradually volatilized, making the pH value of the solution rising. As a higher pH value, titanium tetrachloride began the process of hydrolysis and generated hydrated titania. Finally, after calcining at 500 °C, polystyrene was completely decomposed meanwhile titania was generated by dehydration of hydrated titania.

SEM images were taken with scanning electron microscope S440 produced by Leica Cambridge LTD. (voltage=25Kv and current=200pA). Raman spectra were characterized with laser Raman spectrometer InVia produced by Renishaw corporation. Optical absorption spectrum were recorded on a UV-Vis-NIR spectrometer UV-3150 produced by Shimadzu corporation.

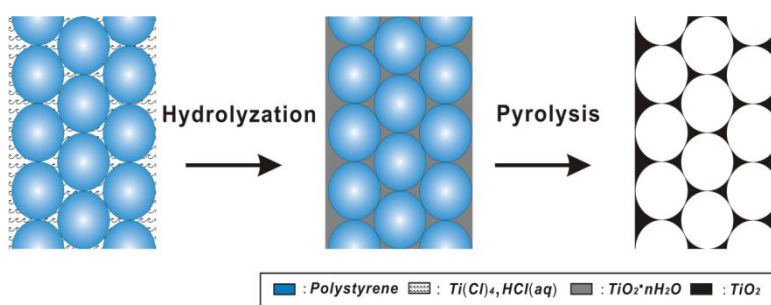


Figure 1. The process schematic diagram of synthesis of ordered macroporous titania

3. Results and discussion

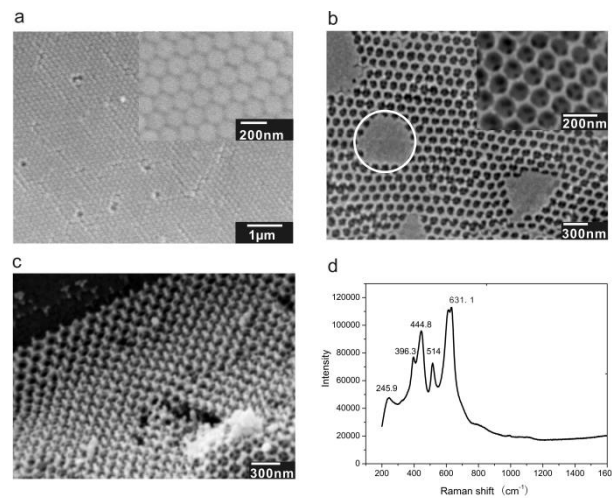


Figure 2. SEM image of (a) PS template, (b) the surface of ordered macroporous titania, (c) the section of ordered macroporous titania; (d) Raman spectrum of ordered macroporous titania.

The structure of ordered macroporous titania is determined by the polystyrene templates, so the quality of the template is indispensable. Figure 2(a) shows that the polystyrene microspheres in the templates, which has the size of $155\text{nm} \pm$, were packed close and arranged in order.

Figure 2(b) shows that the average pore size of the macroporous titania is $130\text{nm} \pm$, relatively contractive compared with the templates ($155\text{nm} \pm$), which resulted from the dehydration of hydrated titania in the process of calcination. Due to the defects in polystyrene template, there are also a few defects in the ordered macroporous titania. It is also show that the pores in the sample are distributed symmetrically in a highly ordered structure. In the circular marked area there are no pores, it is because the process of filling inside the templates has been finished already, nevertheless, the hydrated titania generated by titanium tetrachloride is still hydrolyzing and depositing on the surface and thus make the pores on the surface disappear. On the other hand, the ordered macroporous structure is still demonstrated inside the templates, as shown in Figure 2(c). SEM images imply that the structure of the macroporous titania is symmetrical and orderly from the surface to the bottom. Therefore, by the use of TiCl_4 hydrolysis, the interfaces of templates can be filled with titania adequately and efficiently. Figure 2 (d) shows that the sample is the coexistence of anatase and rutile. In the vibration mode of anatase phase, the peak at 396.3cm^{-1} is B1g vibration mode; the peak at 514cm^{-1} is B2g vibration mode and the peak at 631.1cm^{-1} is Eg vibration mode. In the vibration mode of rutile phase, the peak at 245.9cm^{-1} is vibration mode of multi-phonon processes; the peak at 444.8cm^{-1} is Eg vibration mode and the peak at 613.5cm^{-1} is A1g vibration mode.

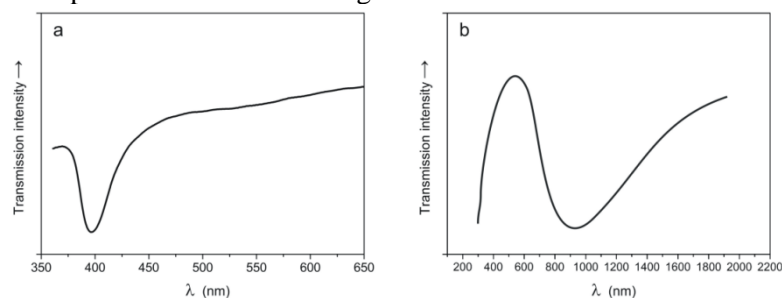


Figure 3. Optical absorption spectrum: (a) Polystyrene template and (b) Ordered macroporous titania.

The pore structure of the macroporous titania prepared is highly ordered and periodically arranged in space, thus the titania and pore with different refractive indexes are also arranged alternately and periodically in space. Figure 3(b) shows that the bandwidth of the photonic bandgap of the macroporous titania sample is 200nm and the central wavelength is 925nm and the bandgap bandwidth of the template of polystyrene microspheres is 26nm and the central wavelength is 395nm in Figure 3(a). It reveals the bandgap position of the macroporous titania sample showing red shift and the

bandgap width is widened obviously. Therefore, the highly ordered macroporous titania can be widely applied to the photonic bandgap materials.

4. Conclusion

In order to fill the polystyrene template interspaces more effectively with titania, a novel method is adopted for filling the interspaces of templates by the titanium tetrachloride hydrolysis. In this method, there is no need of filling the interspaces repeatedly and no introduction of organic impurities either. The best conditions for the synthesis are found: the pH value is 2.0~2.5; the filling time is 3h and the temperature of calcinations is 500°C. The Raman spectra show that the samples are the coexistence of anatase and rutile and the SEM images show that the samples are filled uniformly and the structure is orderly. Moreover, the optical absorption spectra illustrate that the samples, highly ordered, have an obvious photonic bandgap.

Acknowledgments

This work was supported by National Natural Science Foundation of China (61374013), National Program on Key Basic Research Project (973 Program, 2015CB755500), Shenzhen "Layout of Disciplines" Program on Basic Research Project (JCYJ20160331174854880), and China Postdoctoral Science Foundation 59th (162438).

References

- [1] Schroden RC, Al-Daous M, Sokolov S. *Hybrid macroporous materials for heavy metal ion adsorption*. Mater Chem 2002;12: 3261–7.
- [2] Yablonovitch E. *Inhibited spontaneous emission in solid-state physics and electronics*. Phys Rev Lett 1987, 58 : 2059–62.
- [3] John S. *Strong localization of photons in certain disordered dielectric superlattices*. Phys Rev Lett 1987;58: 2486–9.
- [4] Mekis A, Chen JC, Kurland I. *High transmission through sharp bends in photonic crystal waveguides*. Phys Rev Lett 1996; 77: 3787–90
- [5] Zhou Z, Zhao XS. *Opal and inverse opal fabricated with a flow-controlled vertical deposition method*. Langmuir 2005; 21: 4717–23.
- [6] Jiu J, Wang F, Sakamoto M, Takao J, Adachi M. *Performance of dye-sensitized solar cell based on nanocrystals TiO₂ film prepared with mixed template method*. Sol Energy Mater Sol Cells 2005;87:77–86.
- [7] Al-Daous MA, Stein A. *Preparation and Catalytic Evaluation of Macroporous Crystalline Sulfated Zirconium Dioxide Templated with Colloidal Crystals*. Chemistry of Materials 2003; 15: 2638–45.
- [8] Yan HW, Smyrl WH, Blandford CF, Holland BT. *General synthesis of periodic macroporous solids by templated salt precipitation and chemical conversion*. ChemMater 2000; 12: 1134–8.
- [9] Abdelsalam ME, Bartlett PN, Baumberg JJ. *Preparation of arrays of isolated spherical cavities by self assembly of polystyrene spheres on self assembled prepatterned macroporous films*. Coyle S Adv Mater 2004; 16:90–3.
- [10] Zukalová M, Zukal A, Kavan L, Nazeeruddin MK, Liska P, Gratzel M. *Organized mesoporous TiO₂ films exhibiting greatly enhanced performance in dye-sensitized solar cells*. Nano Lett 2005; 5: 1789–92.
- [11] Zhong Z, Yin Y, Gates B, Xia Y. *Opal and inverse opal fabricated with a flow-controlled vertical deposition method*. Adv Mater 2000; 12: 206–9.
- [12] Wijnhoven JE, Vos WL. *Preparation of photonic crystals made of air spheres in titania*. Science 1998; 281: 802–4.
- [13] Bartlett PN, Duinford T, Ghanem MA. *Templated electrochemical deposition of nanostructured macroporous PbO₂*. Mater Chem 2002; 12: 3130–5.
- [14] Dimitro AS, Nagayama K, Langmuir. *Continuous convective assembling of fine particles into two-dimensional arrays on solid surfaces* 1996; 12:1303–11.