研究简报

聚苯乙烯球模板法制备二氧化钛纳米环

叶 琳 段月琴 袁志好*
(天津理工大学纳米材料与技术研究中心,天津市材料物理与化学重点学科,天津 300191)

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Preparation of TiO_2 Nano-ring Based on Polystyrene Nanosphere Template

YE Lin DUAN Yue-Qin YUAN Zhi-Hao*
(*Nanomaterials and Nanotechnology Research Center, Tianjin University of Technology,Tianjin Key Subject for Materials Physics and Chemistry, Tianjin*, 300191)

Abstract: TiO_2 nanorings were synthesized using the polystyrene nanospheres of 85 nm prepared by micro-emulsion polymerization as template. The result TiO_2 nanorings were characterized by FE-SEM and XRD. Results showed that the inner diameter of the TiO_2 nanorings matched size of the polystyrene nanospheres used, and the thickness with nanometer size depended on that of the TiO_2 gel coated on the PS surface.

Key words: TiO_2 nanoring; polystyrene template; sol-gel

In recent years, various nanoring-structures have aroused great excitement due to their novel physical and chemical properties as well as potential applications in future nanodevices[1-4]. Several techniques have been employed to fabricate the nanorings including metal [5], and inorganic [6] and organic [7] compounds. Torres et al. [8] investigated the magnetic states and switching processes of Co nanorings with lateral dimensi ons of 200 nm using micromagnetic simulations. Duan et al. [9] prepared hexangular crystal AlN nanorings structure by evaporating of aluminum alloy in ammonia/nitrogen atmosphere at 1 100 ℃. Brands et al.[7] synthesized polymer nanorings on GaAs and Si by means of an electron-beam lithography process based on dose-dependent negative PMMA. However, the established techniques seem to have technologic and economic limits[10].

Until now, there has been interesting in a so-called template-synthesis of micro-and nano-structures (i.e. composite nanoparticles, core-shell nanostructure) by using polystyrene (PS) as template because the procedure can be performed under a milder chemical condition. The PS spheres, usually prepared by micro-emulsion polymerization [11] or dispersion polymerization [12], with a broad size range from 50 to 500 nm, and a good monodispersivity are promising templates for micro- and nano-structures. Using the PS nanospheres as template, a wide variety of core-shell nanostructures and composite nanoparticles including ZnO、TiO_2、SiO_2、SnO_2 were prepared[1,13-15]. Here, we demonstrate

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*通讯联系人。E-mail:zhyuan@tsinghua.edu.cn, zhyuan@tjut.edu.cn
第一作者:叶 琳,女,26 岁,硕士研究生;研究方向:纳米材料与纳米结构。

a simple route to synthesize TiO_2 nanorings based on the template method using the PS nanospheres. The sizes of the obtained TiO_2 nanorings are matched to those of the PS nanospheres.

1 Experimental

The preparation of TiO_2 nanorings mainly involves three steps: fabricating PS nanospheres and TiO_2 sol, coating TiO_2 gel on PS surface, firing PS to form TiO_2 nanorings. The procedure is illustrated in Fig.1.

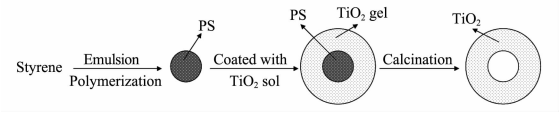


Fig.1 Schematic diagram for fabricating TiO_2 nanorings

The PS nanospheres were prepared by micro-emulsion polymerization as described elsewhere [16]. Briefly, sodium dodecylsulfate (0.24 g) as emulsifier and sodium hydrogen carbonate (0.125 g) as buffer were mixed in a reactor with distilled water (225 g) under stirring at 80 ℃ for 10 min, and then styrene monomer (25 g) was also added to the reactor to form emulsion. After approximately 1 h, potassium persulfate (0.125 g) as initiator was introduced into the emulsion to make styrene monomer polymerizing. When polymerization was performed under atmosphere for 18 h, a stable micro-emulsion with PS colloidals was achieved. The diameter of the PS nanospheres is regulated to the quality of the emulsifier. In the preparation of TiO_2 sol, tetrabutyl titanate, $Ti(OBu)_4$, anhydrous ethanol, nitric acid and distilled water with a molar ratio for $Ti:C_2H_5OH:H^+:H_2O$ being 1:15:0.3:4 were mixed under vigorous stirring until a transparent sol was formed[17].

The resultant PS emulsion and TiO_2 sol were mixed at a ratio of $V_{PS}:V_{TiO_2}=1:1\sim1:3$ under magnetic stirring at room temperature for 2 h. During stirring, PS spheres were caped with TiO_2 sol. The PS spheres with TiO_2 sol were coated on glass substrate by dipping technique, and then dried for 30 min at 60 ℃. During drying, the TiO_2 sol on PS surface was transformed into TiO_2 gel. Finally, the PS spheres coated with TiO_2 gel were calcined at 500 ℃ in air for 3 h to fire PS spheres. The PS spheres and as-prepared TiO_2 nanorings on glass were observed by field-emission scanning electron microscopy (FE-SEM; JEOL JSM-6700F) with 10 kV accelerating voltage. The corresponding XRD measurement was performed using a Rigaku D/MAX-2500 X-ray diffractometer with Cu $K\alpha$ incident radiation at a scanning rate of 0.02° per second in 2θ range from 10° to 80°.

2 Results and discussion

Fig.2 shows a typical FE-SEM image of the as-prepared PS spheres prepared by the above-described micro-emulsion polymerization. It can be seen from the figure that the PS spheres on glass are well-aligned with almost uniform size, and have an average diameter of 85 nm.

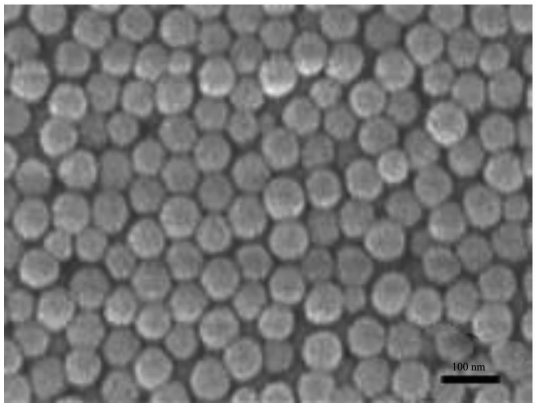


Fig.2 FE-SEM image of the PS nanospheres on glass substrate

Fig.3 and 4 show representative FE-SEM images of the PS nanospheres coated with TiO_2 gel before and after calcination at 500 ℃, respectively. When the TiO_2 sol was dropped into the PS micro-emulsion under stirring, the TiO_2 colloidal particles with much larger size than molecules and ions can not penetrate into the PS nanospheres, but they can form a coating layer on PS nanosphere surface. A further dipping PS nanosphere capped with TiO_2 sol to glass substrate and subsequent drying makes the TiO_2 sol coating on PS surface gradually transform into TiO_2 gel, as shown in Fig.3. The TiO_2 gel on the PS surface has a thickness of approximately 60 nm. The TiO_2 nanorings can be achieved by firing the PS nanospheres as template. It can be seen from Fig.4 (a) that the

resultant TiO_2 nanorings have an inner diameter of approximately 85 nm, and a thickness of approximately 60 nm. The former is consistent with the diameter of the PS nanosphere template, while the latter is the same as the thickness of the TiO_2 gel on the PS surface.

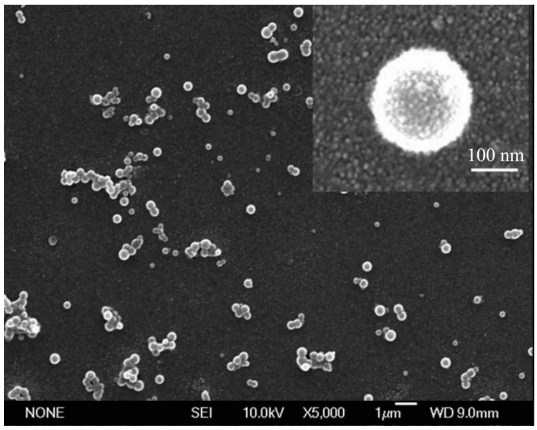
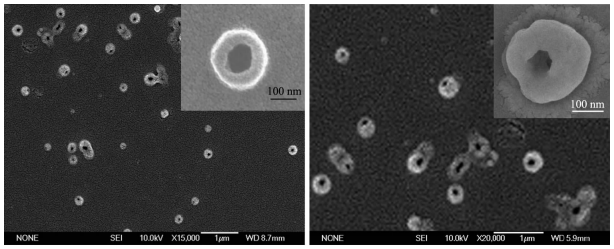


Fig.3　FE-SEM image of the PS nanospheres coated by TiO_2 gel with a ratio of V_{PS}:V_{TiO_2}=1:2 on glass (the inset is the corresponding high-magnification image)



(a)　(b)

Fig.4　FE-SEM image of the TiO_2 nanorings on glass achieved by firing PS nanospheres at 500 ℃ in air for 3 h (the inset is the corresponding high-magnification image): (a) V_{PS}:V_{TiO_2}=1:2; (b) V_{PS}:V_{TiO_2}=1:3

Formation of the TiO_2 nanorings mainly depends on ratio of PS to TiO_2. In our experiment, the optimum condition is a volume ratio of PS:TiO_2=1:2. According to the ratio, the TiO_2 sol partly covers on the PS nanospheres (see Fig.3), and then generates ring contacts between the PS nanospheres and the substrate when coated by dipping technique [10]. A suitable annealing treatment results in the formation of the TiO_2 nanorings. However, the PS nanospheres can be mostly or fully covered with the TiO_2 sol when the ratio is less than 1/2, which leads to forming hollow TiO_2 nanospheres with a breaking end, as shown in Fig.4 (b), and even porous TiO_2 nanocrystalline film. And when the ratio is more than 1/2, the PS nanospheres cannot be ring-covered with the TiO_2 sol, which usually forms ringent TiO_2 nanorings.

Fig.5 gives XRD pattern of the TiO_2 nanorings achieved by firing PS nanospheres at 500 ℃. The broad bulging diffraction peak in the XRD pattern is caused by glass substrate. The weak peaks at 2θ = 25.2°,37.2°,48.1° are attributed to the diffractions of anatase-TiO_2, showing that the TiO_2 nanorings is in polycrystalline anatase structure.

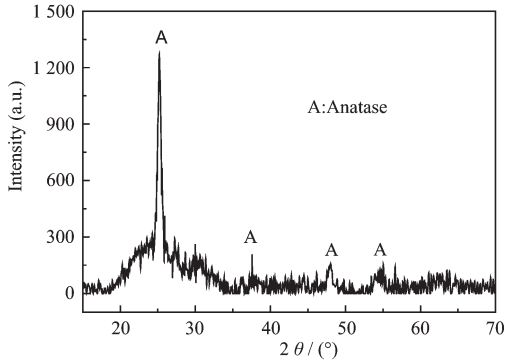


Fig.5　XRD pattern of the TiO_2 nanorings on glass shown in Figure 4(a)

3　Summary

We have developed a template method for fabricating TiO_2 nanorings by using PS nanosphere as template. The inner diameter of the nanorings depends on the size of the PS nanosphere, while the thickness is consistent with that of the TiO_2 gel on the PS surface.

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