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结晶二氧化钛多孔球的常压液相制备

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摘要：利用沸水处理有机钛前驱体球较为便捷地制备出结晶二氧化钛多孔球，采用 XRD、SEM 和 TEM 对二氧化钛球进行表征，并探讨了二氧化钛球锐钛矿纳米晶形成以及形貌变化的机理。结果表明：延长沸水处理时间有利于多孔结构的形成和纳米粒子的晶化，随处理时间的增加，前驱体球表面变得越来越粗糙，二氧化钛结晶度也逐渐增强。其形成机理主要归因于沸水处理过程中有机钛前驱体球原位发生的完全水解和聚合。

关键词：二氧化钛球；多孔性；结晶；常压；液相
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Preparation of Porous Crystalline Spherical Titania under Atmospheric Liquid Phase Conditions

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Abstract: Porous crystalline spherical titania was facilely prepared by treating the organic titanium precursor spheres with boiling water. The spherical titania was characterized by X-ray diffraction, scanning electron microscopy and transmission electron microscopy. The probable mechanism for formation of anatase nanocrystal and the morphology change of precursor spheres was also discussed. The results demonstrate that extending the treating time in boiling water is helpful for the formation of porous structure as well as the crystallization of nanoparticles. With increasing in treating time, the surface of the procursor spheres become rougher and rougher, and the crystallinity of anatase titania improves gradually. The forming mechanism of porous structure and anatase nanocrystal is attributed to the complete in-situ hydrolysis and condensation of the organic titanium precursor spheres in boiling water.

Key words: spherical titania; porosity; crystallization; atmospheric pressure; liquid phase

Porous titania materials have been drawn more and more attention, because a highly porous surface structure can absorb organic molecules effectively and offer a much larger number of catalytic sites than a dense surface [1~3]. Moreover, porous titania can effectively make the photogenerated electrons and holes diffused to the surface before they recombine, exhibits higher quantum yields and photocatalytic activity[4].

The most common approach to synthesis porous titania materials is using template-assisted method. The organic templates are eliminated from titania materials via an annealing step in a typical procedure, and titania

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is transformed from amorphous to crystalline state at the same time[5~8]. Certainly, the templates can also be eliminated by organic solvent or alkali solution treatment[2,9,10]. However, only a few studies involve in the synthesis of porous titania without templates. Yu et al[11] reported that the sponge-like macro-/mesoporous titania was prepared without template by hydrothermal treatment of tetrabutyl titanate ($Ti(OC_4H_9)_4$) precipitates in pure water. Raveendran et al.[12] demonstrated a template-free method based on the microphase separation phenomenon for the preparation of meso-structured spherical anatase titania with high surface area and thermal stability(400 ℃) by hydrolytic condensation of Ti(IV) *n*-butoxide dispersed in ethyl acetate followed by mild heating.

Here we report a facile template-free route for fabrication of porous anatase spherical titania at low temperature under atmospheric pressure. The changes in crystal structure and morphology of spherical titania with different treating time are compared. The probable mechanism for the simultaneous formation of porous structure and anatase nanocrystal are also discussed.

1 Experimental

1.1 Preparation

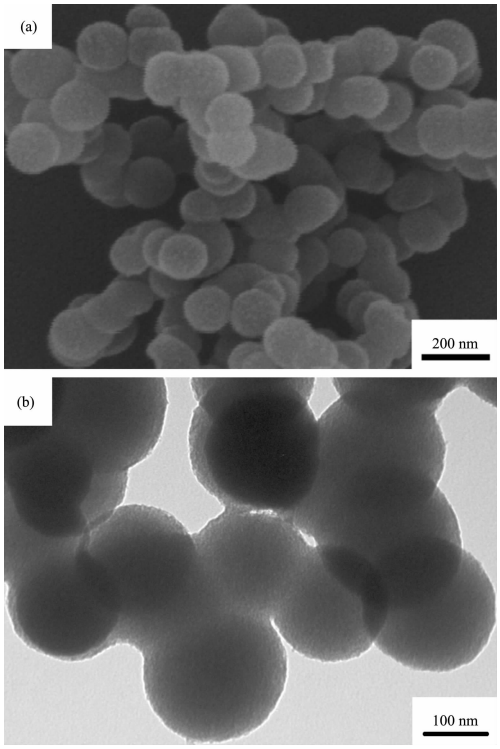
All reagents were of analytical grade and were used as received. In a typical synthesis, 2.0 g tetrabutoxytitanium was added to 55.5 g ethylene glycol in a sealed conical flask and was magnetically stirred for 8 h at room temperature, then the product was immediately poured into acetone containing ~2% water. After vigorous stirring for 30 min, the mixture was aged for 30 min. The white precipitate was harvested by centrifugation, followed by washing with ethanol and deionized water several times to remove ethylene glycol from the surfaces of the organic titanium precursor sphere and was dried at 50 ℃. Then, 0.5 g above precursor sphere was dissolved in 100 g deionized water and ultrasonic vibrated for 15 min to attain a better dispersion, and the solution was stirred at boiling temperature for different periods of time. The white precipitate was recovered by centrifugation, then washed with deionized water and ethanol several times, and dried at 50 ℃.

1.2 Characterization

Crystallinity of the spherical titania was examined from the X-ray diffraction(XRD) patterns using a PAN alytical X Pert Pro diffractometer (Cu $K\alpha$, λ=0.154 18 nm, 40 kV, 40 mA) for 2θ in the range from 10° to 80°. The morphology and microstructure changes of the spherical titania was examined using eld-emission type transmission electron microscope (TEM, JEOL JEM-1200EX), high-resolution transmission electron microscope(HRTEM, PHILIPS CM200) and scanning electron microscope(FE-SEM, FEI SIRION-100).

2 Results and discussion

Fig.1a shows the SEM image of the organic titanium precursor spheres with a size of ~200 nm. TEM image of the spherical particles(Fig.1b) indicates that the sphere surface is very smooth. When mixed with tetrabutoxytitanium, ethylene glycol is sufficiently reactive to form glycolates or mixed alkoxide/glycolate derivatives (see the reactions below)[13]. Once the derivatives is poured into an acetone bath with a little water (~2%), the organic titanium precursor spheres are obtained due



(a) SEM image; (b) TEM image

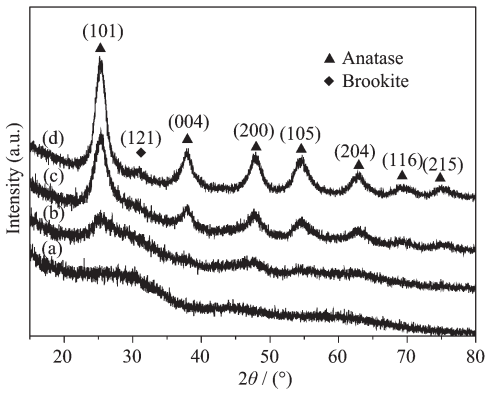
Fig.1　Electron microscope images of the organic titanium precursor sphere

to the partial hydrolysis and fast growth.

$$Ti(OBu)_4 + HOCH_2CH_2OH \rightarrow Ti(OCH_2CH_2O)(OBu)_2 + 2HOBu \quad (1)$$

$$Ti(OBu)_4 + 2\,HOCH_2CH_2OH \rightarrow Ti(OCH_2CH_2O)_2 + 4HOBu \quad (2)$$

Fig.2 presents the XRD patterns of the organic titanium precursor sphere with boiling water treatment for various times. It is apparent that the spheres do not show any diffraction peak, suggesting its amorphous nature. When the precursor is treated for 30 min, several diffraction peaks appear and all of them could be clearly attribute to the anatase phase of titania. With the increase of treating time, the diffraction peak of the



(a) 0, organic titanium precursor sphere; (b) 30 min; (c) 60 min; (d) 90 min

Fig.2 XRD patterns of samples with various treating time in boiling water

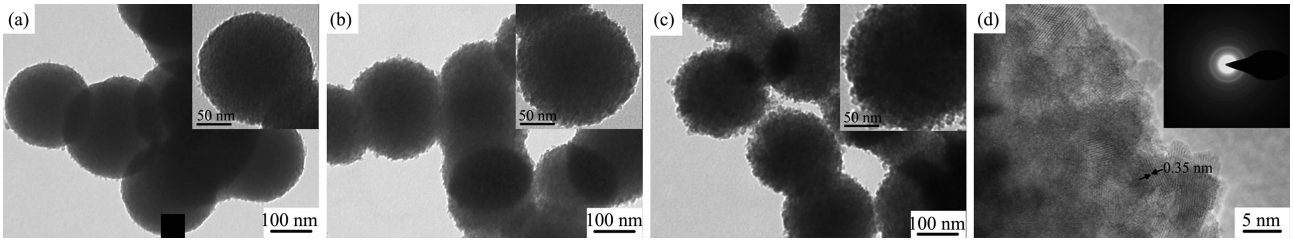
anatase phase becomes sharper and the intensity of the peaks gets stonger. The weak peak belonging to the brookite was also detected. The crystallization of titania nanoparticle below the traditional crystallization temperature(350~500 ℃) is considered as the complete hydrolysis of titanium glycolate precursor in a water-excessive reaction system (see the reactions below). The hgrowth unit could form in the complete hydrolysis process. According to the "growth unit" model, while the surface hydroxylizing percentages are the same, the double-cone anatase growth unit has the highest stable energy, so it is much easier to form anatase phase of titania crystallites[14,15]. Based on that, the condensation of the precursor proceeds somewhat faster at the boiling temperature, and makes the Ti-O_6 octahedron arrange in the way of the most probability, according to the thermodynamics metastable state. Thus, the product is mainly anatase with some brookite as the impurity.

$$Ti(OCH_2CH_2O)(OBu)_2 + 4H_2O \rightarrow Ti(OH)_4 + 2HOBu + HOCH_2CH_2OH \quad (3)$$

$$Ti(OCH_2CH_2O)_2 + 4H_2O \rightarrow Ti(OH)_4 + 2HOCH_2CH_2OH \quad (4)$$

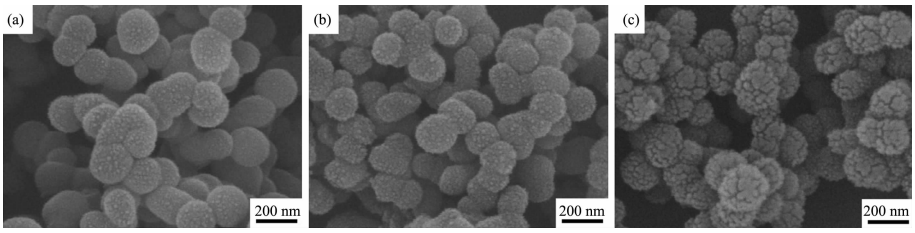
TEM images of samples with various boiling water treating time are shown in Fig.3. After treating the sample in boiling water for 30 min (Fig.3a), the surface of spheres becomes a little rough, this is due to the hydrolysis and crystallization of nanoparticles in the surface. When the treating time increases to 60 min, the sphere surface gets much rougher and the porous structure begins to form (Fig.3b). The loose porous structure immerses deeply into the interior of the sphere and wonderful anatase crystals are observed after treating for 90 min (Fig.3c). In particular, the spherical morphology of these particles is essentially preserved, and the spheres are consisted of interconnected nanocrystal and pores. The corresponding HRTEM image with the selected-area electron difraction (SAED) pattern in the inset is shown in Fig.3d. The nanocrystal with a lattice fringe of 0.35 nm is attributed to the spacing of(101) in anatase titania, and also reveals that the crystalline anatase phase is formed below the traditional crystallization temperature.

Fig.4 shows SEM images of samples with various



(a) 30 min; (b) 60 min; (c) 90 min. Inset is the enlarged image; (d) 90 min, HRTEM image with the electron diffraction pattern in the inset

Fig.3 TEM images of samples with various treating time in boiling water



(a) 30 min; (b) 60 min; (c) 90 min

Fig.4　SEM images of samples with various treating time in boiling water

boiling water treating time. It can be seen that the particle surface morphology changes from smooth to rough with increase in the treating time. This is in good agreement with TEM results. When the organic titanium precursor spheres are added to the boiling water, the precursor spheres incompletely hydrolyzed undergo a further in situ hydrolysis and condensation on the surface shell and begin to nucleate preferentially in certain region. The surface of the sphere becomes rough, and even forms the cracks with the increase in treating time, so the water could penetrate into the interior of the spheres, leading to a further reaction to form porous structure in the inner part of the spheres. Meanwhile, the titania grains get a further growth and grow into interconnected nano-cluster. Eventually, the titania spheres consisting of interconnected nanocrystal and pores are obtained. Hence, it is suggested that this facile preparation strategy is suitable for the fabrication of porous anatase titania materials by complete hydrolysis and condensation from a partial hydrolysis precursor, and the original size could be also practically retained.

3　Conclusions

A facile template-free method was developed to synthesize porous anatase titania microspheres by simply treating the organic titanium precursor spheres in boiling water. The forming mechanism of porous structure and anatase nanocrystal is attributed to the complete hydrolysis and condensation of the precursor. This convenient strategy presents a new possibility for synthesis of porous anatase titania materials from an incomplete hydrolysis precursor.

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