NH$_4$F/H$_3$PO$_4$体系中阳极氧化法制备 TiO$_2$ 纳米管阵列

李纲 刘中清* 王磊 卢静 张昭*
(四川大学化学工程学院, 成都 610065)

摘要：以价廉的 Ni 板代替常用的 Pt 片为阳极，纯钛为阴极，采用电化学阳极氧化法制备
NH$_4$F-H$_3$PO$_4$ 体系中制备出 TiO$_2$ 纳米管阵列。详细研究了制备参数(溶液酸度，氟离子浓
度，外加电压和氧化时间)对所获纳米管阵列形貌的影响。采用场发射扫描电镜
(FE-SEM) 和 X 射线衍射(XRD)对样品的形貌和晶相结构进行了表征。在最优化的条件
下，可以获得形貌规整，表面干净，有序的
TiO$_2$ 纳米管阵列。纳米管阵列的平均管径为 60 nm，管长约 530 nm。采用阳极氧化法制备的
纳米管阵列是非晶态的，经 400 ℃热处理 2 h 后，可以转变为锐钛矿相。实验结果还发现，
经过热处理后，纳米管阵列变得更为有序，管径扩大至约 95 nm。

关键词：TiO$_2$；纳米管阵列；Ni 阴极；电化学阳极氧化

Fabrication of TiO$_2$ Nanotube Arrays via Electrochemical Anodization in NH$_4$F/H$_3$PO$_4$ Electrolyte Solution System

LI Gang LIU Zhong-Qing* WANG Lei LU Jing ZHANG Zhao*
(College of Chemical Engineering, Sichuan University, Chengdu 610065)

Abstract: TiO$_2$ nanotube arrays were fabricated by anodization of titanium in aqueous electrolyte solution of NH$_4$F+H$_3$PO$_4$ using a Nickel sheet of low cost as cathode instead of conventionally used noble Platinum. The effects of preparation parameters, i.e., concentration of H$_3$PO$_4$ and F$^-$, applied voltage and anodization time, on the morphology of as-prepared nanotube arrays were systematically studied. Field emission scanning electron microscope(FE-SEM) and X-ray diffraction(XRD) analysis were carried out to characterize the morphology and structure of the samples. The results showed that the self-ordered TiO$_2$ nanotube arrays with an average pore size of 60 nm and a length of 530 nm could be obtained under optimum conditions. The as-prepared nanotube arrays were amorphous and transformed into an anatase crystal structure after being annealed at 400 ℃ for 2 h. It was also found that the freshly-prepared nanotube arrays got more ordered after calcination, with a pore size of ca. 95 nm.

Key words: titania; nanotube arrays; nickel cathode; electrochemical anodization

Since Gong and co-workers pioneered the work of fabrication of TiO$_2$ nanotube arrays by anodization of titanium in HF in 2001[1], more and more attention has been given to titania nanotube arrays. It has been commonly recognized that an enhanced photocatalytic activity [2] and solar-to-electric energy conversion efficiency [3] can be obtained for TiO$_2$ nanotube arrays, owing to its large surface to volume ratio, unique optical and electronic characteristics as well as a superior physical topology. To date, many attempts have successfully been conducted for the preparation of TiO$_2$ nanotube arrays, including sol-gel template method [4],

*通讯联系人。E-mail: 301qzl@vip.sina.com, zzhang@scu.edu.cn。

第一作者：李纲，男，27 岁，博士生，研究方向：纳米材料制备与环境光催化。
liquid phase deposition process[5] and electrochemical anodization approach.[6-9] Among them, anodization strategy is considered to be the most ideal way to form TiO$_2$ nanotube arrays. This is due to the fact that the process is very simple, the thickness and morphology of such a nanotubular titania film can be easily manipulated by tailoring the anodization conditions[10], e.g. applied potential, anodization duration and electrolyte composition. Furthermore, the as-prepared titania nanotube arrays have good mechanical adhesion strength with the Ti substrate. It is beneficial to the electrochemical catalysis or photo-electrochemical catalysis because of the excellent electronic conductivity of Ti substrate[11].

Although lots of literatures related to the preparation of titania nanotube arrays have been reported in the past years, there still exist two major problems required to be solved. For one thing, Pt electrode is usually preferentially selected as the cathode due to its excellent electrochemical property while an electrochemical anodization process is performed[12,13]. However, the expensive costs limit its usage on a large-scale. Thus, it is desirable to obtain excellent anodized materials by using cheap cathode instead of Pt. For another, it is still a challenge to fabricate well-ordered TiO$_2$ nanotube arrays without precipitate or debris on the surface, resulting from the hydrolysis of TiF$_6^{2-}$ during the anodization process.

Very recently, Grimes and co-works reported on the effect of the cathode material in controlling the morphology and properties of the TiO$_2$ nanotube arrays fabricated in aqueous and ethylene glycol electrolytes solution containing NH$_4$F and H$_3$PO$_4$ for the first time[14]. In this study, they proposed that some less-expensive cathode materials could be used as the candidates instead of Pt. However, the detailed preparation parameters for fabrication of well-order titania nanotube arrays with clean surface were not systematically investigated. In the present study, thereby we focused on the influences of preparation conditions on fabrication of self-aligned TiO$_2$ nanotube arrays by anodization of titanium in an aqueous electrolyte solution of NH$_4$F-H$_3$PO$_4$ using a cheap Ni foil of Pt-group element as cathode.

1 Experimental section

1.1 Fabrication of TiO$_2$ nanotube arrays

All chemicals in the experiments were analytical reagent and were used as received. All the solutions were prepared with distilled water. Titanium foil of high purity(99.6%, thickness 0.5 mm) with a size of 30 mm x 20 mm was used as starting materials for preparation of titania nanotube arrays. Prior to anodization, the foil was mechanically polished to a mirror image with 500$^0$ and 1200$^0$ silicon carbide abrasive paper successively, followed by rinsed with distilled water and dried in ambient air. After that, an electrically insulated copper wire was attached on the backside using carbon electric conductive adhesive, followed by thoroughly sealed with a mixture of rosin and paraffin except for a working area of 600 mm$^2$ exposed to the electrolyte solution. Finally, the as-obtained electrode was chemically etched by soaking in a mixture of HF and HNO$_3$(HF:HNO$_3$=H$_2$O=1:4:5 in volume) for 30 s to eliminate the flaws resulting from polishing process. So far, a working electrode was obtained.

An anodization process was conducted in a conventional two-electrode configuration with vigorous magnetic stirring, in which the Ti foil was used as the anode and a Ni sheet with a size of 80 mm x 30 mm was served as the cathode. The distance between the two electrodes was 40 mm during all of the experiments. 0.05–0.4 mol·L$^{-1}$ NH$_4$F together with 0.05–2.0 mol·L$^{-1}$ H$_3$PO$_4$ were used as electrolyte solution. The anodizing voltages were kept constant during the whole process supplied by a DC power supply. The entire course of anodization was conducted at room temperature(23 $^\circ$C).

After anodization, the samples were taken out from the electrolyte solution immediately and rinsed with a mass of distilled water, then dried at ambient atmosphere. Subsequently, the as-synthesized nanotube arrays were calcined at 400 $^\circ$C for 2 h with a heating rate of 5 $^\circ$C·min$^{-1}$ in air.

1.2 Characterization of as-formed and annealed TiO$_2$ nanotube arrays

The morphology of the samples was observed using
an Inspert F field emission scanning electron microscope (FE-SEM, FEI Corporation). It was noted that the cross-sectional images were obtained by observing mechanically fractured samples. The phase purity and crystal structure of the obtained products were examined by X-ray diffraction (XRD) using a Philips X’ Pert PRO diffractometer equipped with Cu Kα radiation in the 2θ range 20° to 80°, employing a step size of 0.03°. The accelerating voltage was set at 40 kV with 40 mA flux.

2 Results and discussion

2.1 Effect of concentration of phosphoric acid on the morphology of as-fabricated nanotube arrays

Fig.1 shows the FE-SEM images of titanium oxide that were anodically prepared in 0.2 mol ·L⁻¹ NH₄F electrolyte solution addition with different H₃PO₄ concentrations at a voltage of 20 V for 10 h. Only few pores can be seen on the surface from the top-view of Fig.1 (a1), whereas large parts of the residential areas were covered by oxide film when the concentration of H₃PO₄ was 0.05 mol ·L⁻¹. Meanwhile, it was apparent that no discernible tube structure emerged from the cross-sectional view of Fig.1 (a2). As the H₃PO₄ concentration increased to 0.6 mol ·L⁻¹, a marked rise of the porosity on the surface was observed in Fig.1(b1). As it can be seen from the cross-sectional view in Fig.1 (b2), discrete and tubular structure was obvious. However, the surface was covered with a white precipitate layer. Further increasing the concentration up to 2.0 mol ·L⁻¹, continuous and porous, tubular and well-ordered titania nanotube arrays with a average pore size of 60 nm, tube wall of 50 nm and a length of about 530 nm were obtained, as shown in Fig.1 (c1) and 1(c2). The results indicated that the H₃PO₄ concentration had an important influence on the fabrication of TiO₂ nanotube arrays. As for this point, it can be well explained from the formation mechanism of TiO₂ nanotube arrays via anodization method proposed by some specialists[13-17]. It is well known that the growth mechanism involves the following two principal reactions:

\[ \text{Ti} + 2\text{H}_2\text{O} \rightarrow \text{TiO}_2 + 4\text{H}^+ + 4\text{e}^- \]  \hspace{1cm} (1)
\[ \text{TiO}_2 + 4\text{H}^+ + 6\text{F}^- \rightarrow \text{TiF}_6^{2-} + 2\text{H}_2\text{O} \]  \hspace{1cm} (2)

In the initial stage, a compact oxide film on the Ti

![Fig.1 FE-SEM images of top-view and cross-sectional view of titanium oxide that were anodically prepared in 0.2 mol ·L⁻¹ NH₄F electrolyte solution addition with different H₃PO₄ concentrations at a constant voltage of 20 V for 10 h](image)

(a) 0.05 mol ·L⁻¹; (b) 0.6 mol ·L⁻¹; (c) 2.0 mol ·L⁻¹
substrate was formed. After that, a subsequent dissolution of TiO₂ oxide film took place under the assistance of electric field and chemical acid. Clearly, the acidity of the electrolyte solution played a key role in forming tube structure. When a low concentration of H₃PO₄ was introduced, the equation (2) would be difficult to proceed. So it was not surprising that ordered nanotube arrays didn’t form. On the other hand, TiF₆⁻ would easily hydrolyze at a relative high pH value, resulted in the formation of white debris or precipitate on the surface of nanotube arrays. Thus, it would be favorable for formation of clean and well-ordered nanotube arrays under appropriate solution acidity.

2.2 Effect of F⁻ concentration on the morphology of as-fabricated nanotube arrays

FE-SEM images of titanium oxide that were anodically prepared in 2.0 mol · L⁻¹ H₃PO₄ electrolyte solution addition with different concentrations of NH₄F at a constant voltage of 20 V for 10 h are presented in Fig.2. It was clear that porous-like morphology was formed for the sample anodized in 0.05 mol · L⁻¹ NH₄F (Fig.2(a)), the phenomenon of adjacent pores sharing a tube wall was also observed, showing a characteristic similar to AAO template[18]. The discrete porous feature, however, was apparent for the other three samples prepared in 0.1, 0.2 and 0.4 mol · L⁻¹ NH₄F, respectively (see Fig.2(b), Fig.1(c1) and Fig.2(c)). It was noted that their surface morphology was changed and the pore size ranged from 130 nm to 85, 60 and 45 nm with the increasing of F⁻ concentration from 0.05 mol · L⁻¹, to 0.1, 0.2 and 0.4 mol · L⁻¹, correspondingly. Moreover, the porous structure obtained in 0.2 mol · L⁻¹ NH₄F was the best ordered in our experiment, suggesting that there existed an appropriate value for F⁻ concentration. Such a close correlation between morphology and F⁻ concentration was attributed to the dissolution action of fluorine ions. It is believed that stresses exist in the as-formed compact passive oxide layer due to the volume change by anodization Ti[19]. When low concentrated fluorine ions were used, in other word, the limited amount of F⁻ in the electrolyte was not enough to etch the whole oxide layer and selective dissolution preferentially took place on the breakdown site of high energy. Thereby, irregular and sponge-like pores sharing a same tube wall were grown discretely on local areas(see Fig.2(a)). With the increasing of F⁻ concentration, more breakdown sites could be corroded on the whole surface homogenously and synchronously. Meanwhile, the inter-pore regions could be also attacked by the abundant F⁻ ions [20]. Thus, unlike Fig.2(a), a discrete and tubular structure emerged. Moreover, the higher the concentration of F⁻ ions, the smaller the pore size was.

![FE-SEM images of top-view of titanium oxide that were anodically prepared in 2.0 mol · L⁻¹ H₃PO₄ electrolyte solution addition with different concentrations of NH₄F at a constant voltage of 20 V for 10 h](image)

**Fig.2** FE-SEM images of top-view of titanium oxide that were anodically prepared in 2.0 mol · L⁻¹ H₃PO₄ electrolyte solution addition with different concentrations of NH₄F at a constant voltage of 20 V for 10 h

2.3 Effect of applied voltage on the morphology of as-fabricated nanotube arrays

Fig.3(a)–3(c) depict the FE-SEM images of titanium oxide that were anodically prepared in 0.2 mol · L⁻¹ NH₄F electrolyte solution together with 2.0 mol · L⁻¹ H₃PO₄ at different voltages for 10 h. As evident from the picture of Fig.3 (a), only a compact oxide layer can be seen at a voltage of 5 V, when the applied voltage was settled at
10 V, sponge-like pores were apparent (Fig.3 (h)). However, no obvious tubes can be found from the cross-sectional view (not shown here) at a potential lower than 10 V. As compared to the regular and tubular feature prepared at a voltage of 20 V (Fig.1 (c)), a higher voltage of 30 V would result in the appearance of aggregation of particles with sub-micro scale derived from smaller grains of ca. 20 nm (Fig.3(c)). The changes of morphology as a function of the applied voltages could be ascribed to two factors. For one reason, the collapse of the pore walls would happen before the formation of channels from adjacent discrete pores at a certain voltage because the electrochemical etching rate increased with the elevated voltage. For another reason, when the voltage was applied at 30 V, the Ti-O bond undergone much stronger polarization and was more easily weakened than that at a relatively low potential upon the effects of electric field, promoting the dissolution of the metal oxide more quickly\(^\text{[20]}\). So an over-low or over-high potential was not perfected for fabrication of self-organized TiO\(_2\) nanotube arrays.

(a) 1 h; (b) 3 h; (c) 6 h

Fig.4  FE-SEM images of top-view and cross-sectional view of titanium oxide that were anodically prepared in 0.2 mol·L\(^{-1}\) NH\(_4\)F electrolyte solution together with 2.0 mol·L\(^{-1}\) H\(_3\)PO\(_4\) at 20 V for various durations
2.4 Effect of anodization time on the morphology of as-fabricated nanotube arrays

Fig. 4(a)–4(c) show the FE-SEM images of titanium oxide that were anodically prepared in 0.2 mol·L⁻¹ NH₄F electrolyte solution together with 2.0 mol·L⁻¹ H₃PO₄ at a constant voltage of 20 V for various reaction time. For different durations from 1, 3, 6 h (Fig. 4) to 10 h (Fig. 1(c)), there was no significant change of the morphologies of the as-prepared nanotube arrays. The pore size and length of the nanotube arrays with ridged tube wall were not varied along with the variations of times, maintaining 60 nm in diameter and approximate 530 nm in length. It has been well recognized that the fabrication of TiO₂ nanotube arrays is a result of the competition between pore formation and dissolution of oxide layer by F⁻[19,22]. When the equilibrium is achieved, the length of the nanotube arrays will alter no more. Usually, such a process is rapidly reached less than 1 h in an acidic aqueous electrolyte solution containing F⁻[23]. This was why these as-prepared nanotube arrays exhibited nearly a similar morphology in our experiment.

2.5 Effect of anneal treatment on the crystal structure and morphology of as-fabricated nanotube arrays

In order to investigate the influence of anneal treatment on the crystal structure and morphology of the as-fabricated nanotube arrays, a heat treatment at 400 °C for 2 h was carried out. From the XRD pattern (Fig. 5(a)), only diffraction peaks of Ti can be observed, indicating that the nanotube arrays were amorphous. However, after calcination, some distinct peaks except for Ti occurred, which could be well indexed to TiO₂ of anatase crystal structure (Fig. 5(b)).

It can be seen from the FE-SEM image (Fig. 6) that the nanotube arrays got more ordered after calcination, with a mean pore size of ca. 95 nm much larger than that of without heat treatment, which was in striking contrast to the occurrence of a smaller pore size after calcination reported in elsewhere[24]. This was probably attributed to the shrinkage of the tube wall originating from the thermal treatment process.

![XRD patterns of the nanotube arrays](image)

Fig. 5 XRD patterns of the samples before and after heat treatment

(a) before heat treatment; (b) after heat treatment

Fig. 6 FE-SEM images of the nanotube arrays calcined at 400 °C for 2 h

3 Conclusions

In summary, we systematically investigated the influences of preparation parameters, including H₃PO₄ and F⁻ concentration of the solution, applied voltages and durations, on the morphologies of the titania nanotube arrays by anodization of Ti in a electrolyte
solution of NH₄F + H₃PO₄ using a cheap Ni sheet as cathode material in this paper. It was found that the concentration of phosphoric acid and F⁻ together with applied voltages played a key role in the fabrication of regular nanotube arrays, whereas the effect of anodization time was negligible when the duration was in a range of 1 h to 10 h. Under the optimum conditions, that was, in 0.2 mol·L⁻¹ NH₄F with addition of 2.0 mol·L⁻¹ H₃PO₄ electrolyte solution and at a voltage of 20 V for 10 h, continuous, porous, uniform and tubular structure could be achieved. The average pore size, length and tube wall thickness of the nanotube arrays were 60, 530 and 50 nm, respectively. The as-fabricated nanotube was amorphous and could transform to anatase crystal structure after being calcined at 400 °C for 2 h. The nanotube arrays with anneal treatment had a much better well-ordered architecture in comparison with that of non-thermal treatment. The pore size was enlarged to ca. 95 nm, which was probably due to the shrinkage of the tube wall under the heat treatment process.

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