

Generic Synthesis of TiO₂ Based Nanocables by Using the Through-Hole TiO₂ Nanotube Arrays as Template

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In present work, large scale free-standing through-hole TiO₂ nanotube arrays have been synthesized via a facile method, which can be used as the perfect electrodeposition template for producing desired TiO₂ based nanocables. By completely consuming the Ti foil during anodization, large scale free-standing TiO₂ nanotube arrays can be synthesized without need to detach from the Ti substrate. Followed by a novel etching method, the through-hole nanotube arrays were easily obtained. We also demonstrated that, using this free-standing through-hole TiO₂ nanotube arrays as template, Cu/TiO₂ and Ni/TiO₂ nanocables have been conveniently synthesized by electrodeposition. Furthermore, semiconductors/TiO₂ nanocables also can be synthesized without principle limitation. This methodology can be used as the versatile tool to create a wide variety of TiO₂ based nanocables.

Keywords: TiO₂, Through-Hole Nanotube Arrays, Electrodeposition, Nanocables.

IP: 166.111.120.71 On: Sat, 21 Mar 2015 01:41:11
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1. INTRODUCTION

Recently, due to the precisely controlled morphology and potential applications, anodic TiO₂ nanotubes have attracted great interest in various areas, such as degradation of pollutants,^{1–3} hydrogen generation from photoelectrocatalytic,^{4,5} and dye-sensitized solar cells (DSSC).^{6–8} However, the performances of pure anodic TiO₂ nanotubes in those fields are quite limited because of its low exciton photo-generation and separation efficiencies. Thus, many efforts have been devoted to enhance its performances. Generally speaking, the performance of TiO₂ can be finely tuned by the shape/morphology, which determines the surface atomic arrangement and coordination, or by the compositions, which mediates the electronic structure.⁹ Moreover, extensive studies have revealed that in many applications, the composition mediation and thus the developing of TiO₂ nanotube arrays based nanocables would largely enhance its performance in many fields.¹⁰ For example, metal/TiO₂ nanocables can separate photogenerated excitors efficiently, which largely improved photocatalytic activity.¹¹ Furthermore, narrow band gap semiconductors/TiO₂ nanocables not only

can largely extend their light absorption range, also can significantly enhance the photo-conversion efficiency.¹² Therefore, novel TiO₂ based nanocables with desired properties are highly desired.

To obtain TiO₂ based nanocables, filling the nanochannels of the anodic TiO₂ nanotubes with secondary materials would be a convenient strategy. To anodic aluminum oxide (AAO) membrane, the “sister-material” of anodic TiO₂ nanotube arrays, the most powerful filling approach is based on electrodeposition, which applies to filling both metal and semiconductor.^{13,14} It is also desired to apply the strategy of electrodeposition to the anodic TiO₂ nanotube arrays. However, when polarized with a negative voltage, TiO₂ nanotube arrays would be in a forward-biased state due to the semiconductive nature,^{15,16} which means current passes freely, and resulting the deposition starts at the top surface of the nanotube layer. Many efforts have been carried out to overcome this difficulty, and adopt this convenient and effective electrodeposition method to fill anodic TiO₂ nanotubes. For example, Macak et al. reduce Ti⁴⁺ to Ti³⁺ at the bottom of the tubes and then electrodeposit Cu into the nanotubes.¹⁰ Mohapatra applied the pulsed electrodeposition method on filling the anodic TiO₂ nanotube arrays.¹⁷ However, those filling approaches are inconvenient and the obtained TiO₂ based nanocables are still quite short (less than 1 μm). Therefore,

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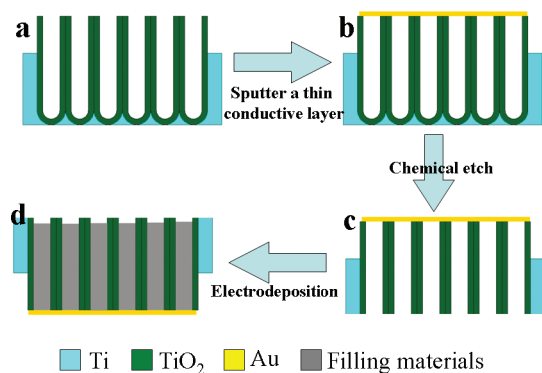


Fig. 1. Schematic representation for fabricating of TiO₂ based nanocables.

find a facile stratagem to obtain TiO₂ base nanocables is still a big challenge.

The through-hole TiO₂ nanotube arrays without closed bottoms, which could efficiently avoid the influence of the semiconductive nature and the electric leakage, could be used as the ideal electrodeposition templates. However, the through-hole TiO₂ nanotube arrays is thin, brittle and hard to handle,¹⁸ thus, few works using it as the electrodeposition template. Herein, we present a facile method to obtain large scale through-hole TiO₂ nanotube arrays, combined with electrodeposition approach, it is convenient to synthesis TiO₂ base nanocables. By totally anodized the Ti foil, large scale free-standing TiO₂ nanotube arrays with discontinued residual Ti layer can be obtained. Then, a thin layer of Au was sputtered onto the open side of the membrane, which can be used as not only the conducting layer, but also the supporting layer. By etching the residual Ti and closed bottom, the testtube-like nanotubes eventually becoming through-hole. The obtained through-hole TiO₂ nanotube membrane was a perfect electrodeposition template for secondary material filling. The schematic illustration of the filling procedure is shown in Figure 1. Herein, Cu, Ni/TiO₂ nanocables were demonstrately synthesized though the conveniently electrodeposition method. Besides metal, semiconductors also can be filled in without principle limitation. This methodology can be used as the versatile tool to create a wide variety of TiO₂ based nanocables.

2. EXPERIMENTAL DETAILS

In present study, all reagents were A.R. grade. Prior to anodization, the Ti foils were ultrasonically cleaned in acetone and distilled water, respectively, for 5 min. TiO₂ nanotubes were obtained by anodizing Ti foil in an electrolyte of 0.2 M NH₄F and 2 vol% H₂O in ethylene glycol at 60 V. The anodization process proceeded until the anodization current drops to zero. The as-prepared anodic TiO₂ nanotube arrays were carried out and washed with deioned water for several times and then dried in the air. Then, a thin layer of Au was sputtered on the opening end of the anodic TiO₂ nanotube arrays. After that, the dried

anodic TiO₂ nanotube arrays membrane was floated on the 1 wt% HF water solution while keeping the closed side down in the solution at room temperature (20 °C) to obtain through-hole TiO₂ nanotube arrays.

The electrodeposition of Cu was carried out in a two-electrode configuration with the through-hole TiO₂ nanotube arrays membrane as cathode and a graphite plate as anode. The electrolyte was prepared by dissolving 0.5 M CuSO₄ in deionized water. The electrodeposition of Cu was executed with a constant current of 0.5 mA cm⁻² at room temperature (20 °C).

The morphologies of the samples were examined by field-emission scanning electron microscopy (FE-SEM; FEI Sirion-200) and high resolution transmission electron microscopy (HRTEM; JEM-2010).

3. RESULTS AND DISCUSSION

As the Ti foil was only one side exposed to the electrolyte during the anodization process, thus, when the anodization current drops to zero, the Ti foil would be almost totally anodized to TiO₂ nanotubes. In this way, large scale free-standing TiO₂ nanotube arrays can be obtained conveniently. Figure 2(a) shows the digital camera image of the large-scale freestanding TiO₂ nanotube arrays obtained by totally consume Ti foil. The area of the membrane can reach several square centimeters. Furthermore, the membrane remains flat without curl when dried. Figure 2(b) shows the cross-sectional images of the free-standing TiO₂ nanotube. From which it can be seen that, after andoization, the thickness of the membrane increased to 100 μm. Figure 2(c) illustrates the top-surface SEM image of the anodic TiO₂ nanotube arrays, while Figure 2(d) shows the back. It can be seen that the average inner diameter of the nanotube is 130 nm with a wall thickness of 25 nm. And, the each anodic TiO₂ nanotube is testtube-like with

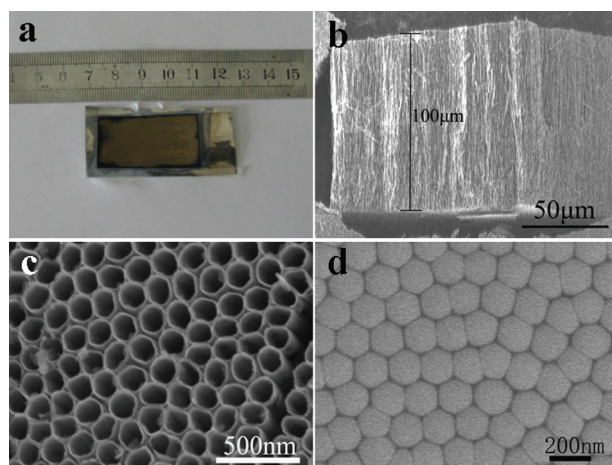


Fig. 2. (a) Digital camera image of the as-prepared large-scale free-standing TiO₂ nanotube arrays; (b) cross-sectional SEM image of the TiO₂ nanotube arrays; (c) and (d) top and back side SEM images of the TiO₂ nanotube arrays.

one end opened and the other closed. At the bottom of the anodic film, besides the closed ends, there also have a thin discontinuous Ti layer, which can be easily dissolved in next etching step.

It is well known that the free-standing anodic TiO₂ nanotube arrays is thin and brittle, when reaches through-hole, it is even harder to handle. In our case, before etching, a thin layer of Au were sputtered on the mouth-opening side of anodic TiO₂ nanotube arrays. Then, the membrane was put floating on the 1 wt% HF water solution while the mouth-opening side up. In this way, the residual Ti and closed bottoms can be etched gradually. Figure 3 illustrates the whole etching process. Firstly, the testtube-like TiO₂ nanotube arrays have been obtained after anodic oxidation (Fig. 3(a)). After two minutes etching, as seen from Figure 3(b), the remnant Ti and some parts of the bottoms of the nanotubes have been dissolved. Although many concaves formed on the bottom, it still closed. By prolonging the etching time to 4 minutes, the closed bottoms were partly opened and funnel like structures were formed (Fig. 3(c)). When the etching time reaches to 6 minutes (Fig. 3(d)), the closed bottoms can be totally etched and the free standing through-hole nanotubes can be obtained. When the etching time reaches 8 minutes, the long nanotubes would be broken into small pieces and the ordered array become chaos. Therefore, in present study, 6 min is be the rational etching time to obtain the through-hole TiO₂ nanotubes. In former reports, to obtain through-hole anodic TiO₂ nanotubes, two steps are necessary: firstly, detach the anodic TiO₂ nanotubes from the substrate; then, chemically etch the closed bottoms of the detached TiO₂ nanotubes.¹⁹ However, in our case, by completely consuming the Ti foil during anodization, detaching the anodic TiO₂ nanotube arrays from the substrate is not necessary. Furthermore, the sputtered Au layer can be used as not only the protecting layer making the mouth-opening side avoid from the corrosion of

etching solution, but also the conductive layer in the next step.

As an *n*-type semiconductor, TiO₂ could be polarized to a forward biased state under the negative voltage. Thus, when anodic TiO₂ nanotubes directly used in electrodeposition, the current would pass freely and make the electrodeposition starts at the top of the nanotube layers. Additionally, due to the testtube-like structure, the anodic TiO₂ nanotube arrays is prone to leakage currents at weak spots, which leads at sufficiently high cathodic pulses to distinct conductive paths and overgrowth on the top.²⁰ Using the Au conductive layer instead of closed bottom of TiO₂ as the start point of electrodeposition would be a effective method to solve those problems. During the electrodeposit process, the through-hole TiO₂ nanotubes with Au conductive layer were permeate with electrolyte. Due to the large difference in conductivity of Au and TiO₂, metal ions tend to nucleate on Au layer. Due to the confinement of the nanotube walls, the growth of nucleus would proceed along the axial orientation of the TiO₂ nanotubes. In this way, it is convenient to obtain TiO₂ based nanocables. Herein, we take Cu/TiO₂ nanocables as an example. Figure 4 shows the morphology of the Cu filled TiO₂ nanotube arrays. Figure 4(a) is the top-view FE-SEM image of the Cu filled TiO₂ nanotube arrays. Apparently, Cu has been electrodeposited into the nanochannel of TiO₂ nanotubes and the filling rate is close to 100%, indicating the forming of the Cu/TiO₂ nanocables. Figures 4(b) and (c) show the middle and lower part cross-section images of the fractured sample, which illustrate that the inner Cu nanowires are grown along with the outer TiO₂ nanotubes and well confined by its nanochannels. Figure 4(d) is the typical TEM image of the Cu/TiO₂ nanocables, from which the core-shell structure can be seen clearly. The EDS results further confirmed the success forming of Cu/TiO₂ nanocables.

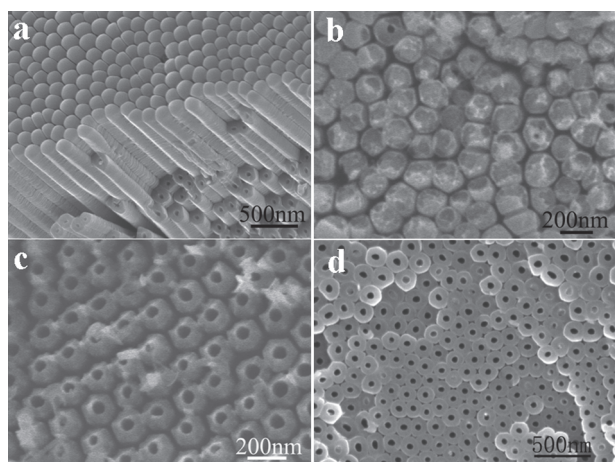


Fig. 3. Bottom SEM images of the TiO₂ nanotubes after different etching time. (a) 0 min, (b) 2 min, (c) 4 min, (d) 6 min.

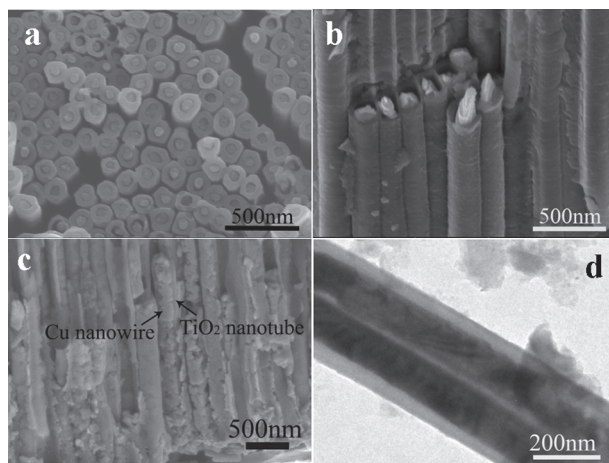


Fig. 4. Morphology of Cu/Ti nanocables: (a) top-view FE-SEM image of the Cu/Ti nanocables, (b), (c) cross-section FE-SEM image of the Cu/Ti nanocables, (d) TEM image of the Cu/Ti nanocables.

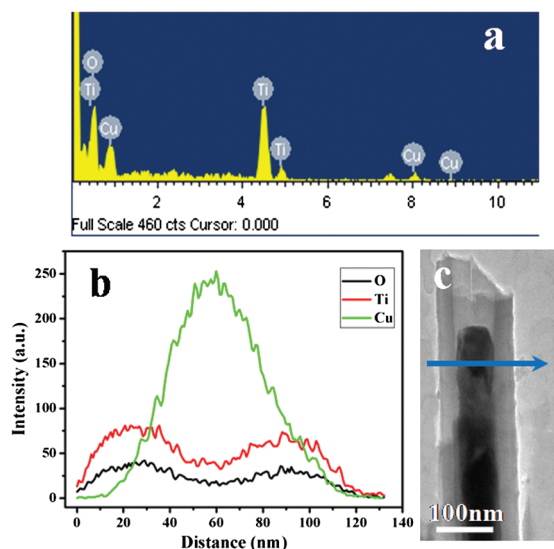


Fig. 5. (a) EDS spectrum of the Cu/Ti nanocables; (b) elemental line profiles acquired across the individual nanocable along the blue line as shown in (c).

Figure 5(a) shows the presentative EDS spectra of the Cu/TiO₂ nanocables. It can be seen that the nanocomposite composed of Ti O and Cu, no other element has been detected. Figure 5(b) presents the TEM EDS elemental line profiles acquired across the individual nanocable along the blue line as shown in Figure 5(c). The corresponding chemical concentration line profile of Ti and O shows two peaks, indicating the nanotube structure of TiO₂; the concentration line profile of Cu shows one peak, indicating the nanowire structure of Cu. The different elemental distribution confirms that the TiO₂ nanotube has been fulfilled with Cu, in another word, the nanocable structure of Cu/TiO₂ was confirmed. Furthermore, the peak width of Cu profiles line is approximately equals to the distance between two peaks of Ti and O profiles lines, indicating the closely connection between the core Cu nanowire and the out TiO₂ shell, which is benefit for electron transport between Cu core and TiO₂ shell. Besides Cu/TiO₂ nanocables, Ni/TiO₂ nanocables also have been synthesized simply by electrodepositing Ni into TiO₂ nanotubes. Furthermore, in our method, semiconductor/TiO₂ nanocables also can be obtained without principle limitation via semiconductor deposition. For example, it is possible to form CdS/TiO₂ and CdSe/TiO₂ nanocables to improve the solar energy conversion.

4. CONCLUSION

In conclusion, through-hole TiO₂ nanotube arrays have been synthesized via a facile method, which can be use as the perfect electrodeposition template, producing

any desired TiO₂ based metal/semiconductor composites. By completely consuming the Ti foil during anodization, free-standing TiO₂ nanotube arrays can be obtained without detaching TiO₂ nanotubes from the Ti substrate. A novel etching method that floating the as-prepared membrane on corrosive solution was developed to obtain through-hole nanotube arrays. Using the through-hole TiO₂ nanotubes as the template, the secondary materials can be conveniently filled in by electrodeposition. This method is highly expected to advance the synthesis of one dimensional TiO₂ based nanocables, which have great potential applications in many fields.

Acknowledgment: This work was supported by the National Natural Science Foundation of China (Nos. 61104205, 11074254, 51171176, 11204307).

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Received: 15 February 2014. Accepted: 17 February 2014.