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A One-step Electrochemical Method for the Production of $\text{TiO}_{2-x}\text{N}_x$ Nanotubes

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Abstract: Visible-light-active $\text{TiO}_{2-x}\text{N}_x$ nanotube arrays were synthesized in the electrolyte of ammonium fluoride (NH_4F) plus triethylamine ($\text{C}_6\text{H}_{15}\text{N}$) via anodic oxidation at 20V for 1 h. After annealed for 1 hour under 400 °C in the air, the anatase phase of TiO_2 appears. SEM showed the N-doping TiO_2 nanotube arrays have a length of about 120-150 nm and diameter of about 60 nm. XPS analysis implied that nitrogen was successfully introduced into TiO_2 lattice replacing oxygen atoms. The UV-Vis absorption spectra showed the absorption edge shift from 380 nm to 420 nm.

Keywords: Anodic oxidation; N doping; TiO_2 nanotubes

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Introduction

Titanium Oxide (TiO_2) is a large band gap semiconductor whose catalytic properties, relatively low cost and chemical inertness render it suitable for use in photocatalytic area [1-6] after the Honda-Fujishim's report in 1972 [7]. Despite its cost, making highly efficient photochemical cells using TiO_2 is a challenge unless two issues are addressed. The achievement of high-efficiency requires a suitable architecture that minimizes the recombination of the photogenerated electron-hole pairs by separating them quickly. Such architecture ought to have a high surface area in contact with the electrolyte species and a structure whose dimensions are smaller than the recombination length of charge carriers [8]. Titanium oxide nanotube is new form of TiO_2 nanostructure, which have larger specific surface area and better absorbability than other morphological TiO_2 nano material and had aroused much attention for their excellent properties of photoelectricity, catalysis, gas sensitivity, and the potential applications in areas such as solar cell [9], photocatalyst [10], solar water splitting

[11], gas sensors [12], and so on.

The second issue involves the large band gap of Titania (3.0-3.2 eV) compared to other oxides. This means that only about 5% of the sunlight (UV wavelengths) can be absorbed by TiO_2 and converted into useful chemical and electrical energy. Over the last decades, essentially two approaches were investigated in order to make the material more responsive to the natural solar spectrum. One approach is to sensitize TiO_2 with a suitable dye to construct an efficient solar cell [13, 14]. The other approach to obtain a good photocatalytic performance is doping with impurities, e.g. transition metals or other elements, including C, N, F, P and S. It was found that substitutional N-doping is the most promising path towards photocatalytic applications [15-17]. Nitrogen ions substitute oxygen atoms in the TiO_2 lattice and thus the corresponding N (2p) states are located above the valence band edge. Mixing of N (2p) states with O (2p) states results in a reduction of the band gap of the N-doped TiO_2 .

This work investigates ways to incorporate nitrogen atoms into titanium oxide nanotubes via a one-step

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electrochemical method and studies the resulting effect on the band gap and the photoelectron-chemical properties.

Experiments

Samples for anodization were cut from titanium foils ($w(N) \leq 0.012\%$, $w(C) \leq 0.02\%$, $w(Si) < 0.04\%$, $w(Fe) \leq 0.06\%$) with a thickness of 0.1 mm. Prior to experiments the samples were degreased by sonicating in acetone, isopropanol and methanol, rinsed in deionized water (DI) and dried in a nitrogen stream.

The anodization was carried out potentiostatically using a platinum counter electrode (99% purity). The titanium foil was attached to the anode, hence it is called anodic oxidation. The electrolyte (Potential of Hydrogen [pH] = 4.5) was made out of acid and base solutions, containing fluoride ions which are essential for the development of nanotube structure. For purposes of nitrogen doping, suitable nitrogen bearing ionic species were included in the anodization bath. Electrolytes were prepared from reagent grade chemicals. The species used including 1mol/L triethylamine ($C_6H_{15}N$) plus (0.5 wt%) ammonium fluoride (NH_4F). After the anodization was completed, the N-doped TiO_2 sample was annealed at $400^\circ C$ in the air ambient furnace for 1 hour.

XPS and SEM were used to confirm the presence of nitrogen in TiO_2 lattice and nanotubes respectively. Verifying these results, recorded Ultraviolet-Visible spectrum and tested photocurrent were compared to the normal TiO_2 photoresponse.

Results and discussion

XPS revealed shorter anodization periods to result in greater nitrogen incorporation. XPS showed that the greatest amount of doped nitrogen into TiO_2 was 6.2%, when anodized for 2 minutes at 20 V. But the film was too thin and nanotubes structure did not appear. After anodized for 60 minutes at 20 V, Scanning Electron Microscopy (SEM) showed formation of an interesting nanotubes structure appeared in $C_6H_{15}N$ plus NH_4F anodization bath.

From Fig. 1 we can see that TiO_2 nanotube arrays have a length of about 120-150 nm. The insets show the nanotubes after annealed at $400^\circ C$ in the air ambient furnace for 1 hour. It can be clearly seen from these images that the nanotube arrays kept their structural integrity after annealed at $400^\circ C$ with no significant morphological change. And TiO_2 nanotube arrays have diameter of about 60-70 nm with a tube-wall thickness of about 10-15 nm.

TiO_2 electrode structure was determined by X-ray diffractometer, Fig. 2 is XRD patterns of TiO_2 nan-

otubes annealed at $400^\circ C$, X-ray diffraction analysis revealed the presence of peaks at 2θ of 25.25° , 48.0° , 55.7° and 62.8° are typical peaks of TiO_2 . It is suggested that the amount of Nitrogen segregation in TiO_2 was not high enough to be detected by XRD. And X-ray diffraction analysis also revealed almost negligible amount of rutile was present.

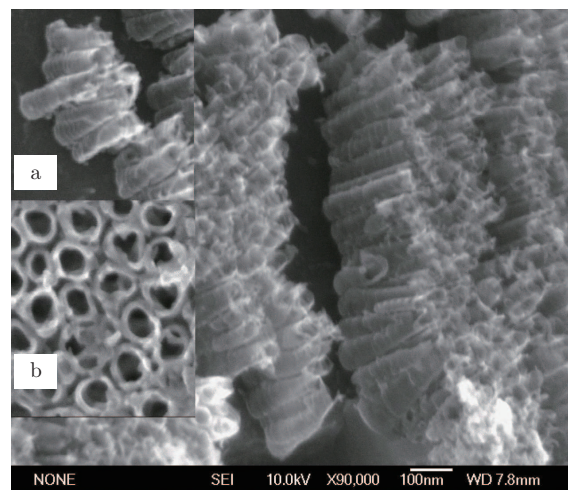


Fig. 1 SEM of TiO_2 nanotubes.

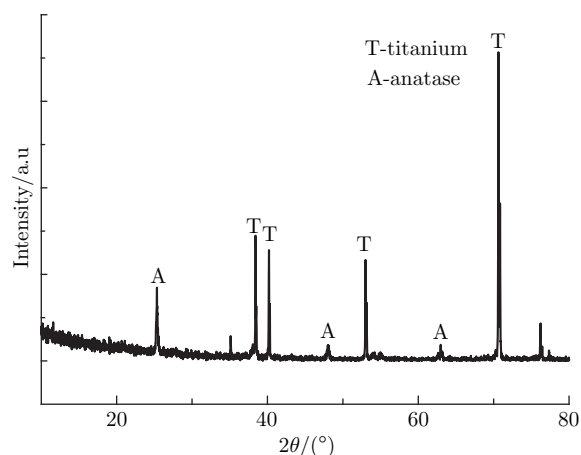


Fig. 2 XRD patterns of TiO_2 nanotubes annealed at $400^\circ C$.

Figure 3 shows the N1s XPS spectrum acquired for the N-doped nanotube layer formed as in Fig. 1. Clearly two different peaks can be observed. The peak at 400 ± 0.2 eV can be ascribed to γ -N state, which is molecularly chemisorbed N_2 and the other peak at 396 ± 0.4 eV corresponds to β -N state, which is essentially atomic N inform of mixed titanium oxide-nitride ($TiO_{2-x}N_x$). This indicates that the anodization in $C_6H_{15}N/NH_4F$ bath and then heat treatment indeed leads to the substitution of some oxygen sites by nitrogen. This finding is also well in line with XPS results from previous reports on N-doping [18, 19]. Literature [20] considered that the visible light absorption of N-doped TiO_2 arises from the N-induced mid-gap levels,

formed slightly above the top of VB. The substituted N is more important than the interstitial and surface chemical absorbed N_2 . They not only introduce mid-gap levels in the TiO_2 forbidden band, but also shift the VB edge.

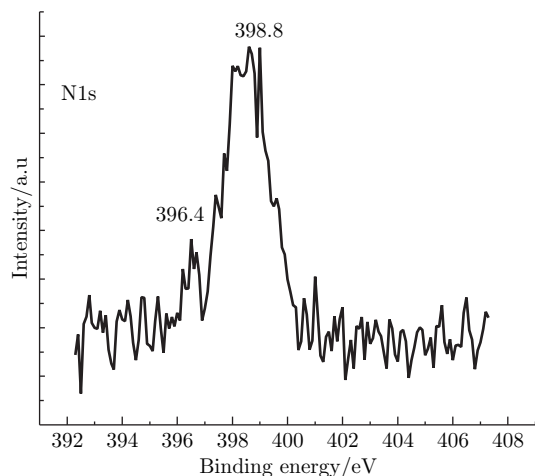


Fig. 3 N_{1s} XPS spectra of the N-doped TiO_2 nanotubes.

Nitrogen was successfully introduced into the TiO_2 lattice replacing oxygen atoms. As a result, a significant shift of TiO_2 band edge was seen from Ultraviolet-Visible (UV-Vis) Spectroscopy. Figure 4 shows the UV-Vis absorption spectra obtained from N-doped and undoped TiO_2 nanotube arrays. Compared with the spectra of the absorption edge was seen to shift appreciably from 380 nm to 420 nm in N-doped TiO_2 nanotube arrays. In addition, the color of $TiO_{2-x}N_x$ nanotube array is orange-yellow, and has shown the excellent visible light absorption in region from 400 to 800 nm.

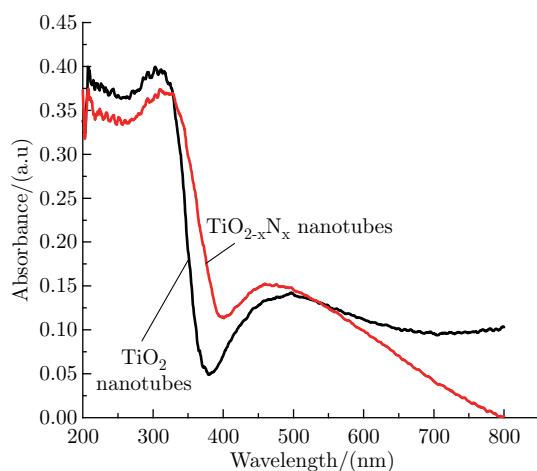


Fig. 4 UV-Vis absorption spectra of $TiO_{2-x}N_x$ nanotubes and TiO_2 nanotubes.

In order to investigate the influence of applied potential on the photocurrent magnitude, a series of experiments were carried out in a conventional three-electrode

configuration with a platinum gauze as a counter electrode and with Ag/AgCl (1 M KCl) reference electrode at room; the electrolyte for these measurements was 0.1 mol/L Na_2SO_4 . Figure 5 shows I_{ph} for the N-doped samples as a function of applied potential (vs. Ag/AgCl electrode) under visible light emitted from 150 W Xe-arc lamps. Clearly, the higher the applied potential, the higher the photocurrent of the N-doped sample. The shape of the increase is in quite good agreement with the Gartner model that predicts $I_{ph} \propto (U - U_{fb})^{0.5}$ behaviour [21]. As it can be expected, for the undoped sample, essentially no I_{ph} is detected over the entire investigated voltage range.

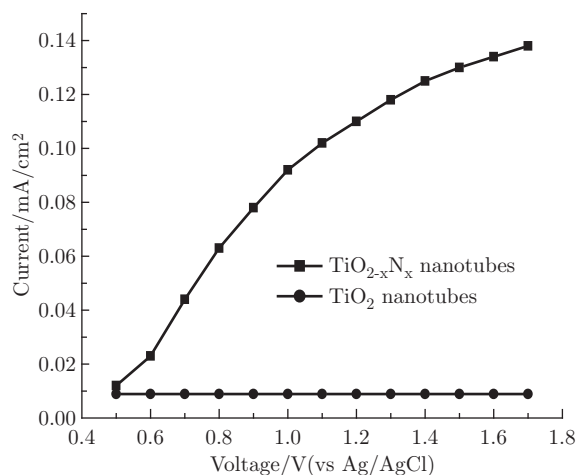


Fig. 5 Dependence of I_{ph} on the applied potential for undoped and N-doped TiO_2 nanotube arrays under visible light.

Conclusion

Nitrogen was successfully incorporated into titania nanotubes by use of nitrogen bearing species ($C_6H_{15}N/NH_4F$) in the anodization bath. This incorporation of nitrogen reduced the band gap of TiO_2 as measured by Ultraviolet-Visible absorption spectroscopy and extended the photo response of titania into the visible by 40 nm.

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