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Preparation and photoelectric effect of Zn^{2+}-TiO_2 nanotube arrays

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Abstract: Zn^{2+}- TiO_2 nanotube arrays were prepared by anodic oxidation method. The current—time curves were used to investigate their growth mechanism. Scanning electron microscopy and X-ray diffractometry were applied to characterizing their structures and properties. The photoelectrochemical properties were studied by electrochemical impedance spectrum (EIS). The optimised working conditions for TiO_2 nanotube arrays were found to be pH 1, 0.5% HF (mass fraction), 20 V oxidation voltage and for 2 h. The produced sample was in anatase form, with length of 70−100 nm, thickness of 10 nm, uniform diameter and structure that does not collapse under the preparation conditions. The EIS results show that TiO_2 nanotube arrays prepared with 0.5% HF (mass fraction) present a low impedance and TiO_2 nanotube arrays loaded by Zn^{2+} could have a decreased resistance. This decrease could likely accelerate the transfer of carriers and even increase photoelectric conversion.

Key words: Zn^{2+}-TiO_2 nanotube array; anodic oxidation method; photoelectric effect; growth mechanism

1 Introduction

TiO_2 is an important inorganic functional material with good photoelectronic, photosensitive, gas sensing, and pressure-sensitive characteristics. It has recently attracted much attention in terms of its promising application prospects, such as in the fields of photoelectricity (for solar energy), electronics (types of sensors), and biology (bone growth)[1−3]. Highly ordered TiO_2 nanotube arrays fabricated by anodization constitute a material architecture that offers large internal surface area without a concomitant decrease in geometric and structural order. And the precisely oriented nature of the nanotube arrays makes them excellent electron percolation pathways for vectorial charge transfer between interfaces[4−5]. ZWILLING et al[6] prepared porous TiO_2 films by the anode oxidation method using a metal titanium sheet. This provided the research idea for preparing TiO_2 nanotube arrays. GONG et al[7] prepared TiO_2 nanotube arrays with the electrochemical anode oxidation method. The TiO_2 nanotube arrays with uniform distribution were previously prepared by the anode oxidation method, but the conversion efficiency still needed improvement[8−9]. During the procedure for improving the photoelectronic activity of TiO_2, various methods such as element doping[10−11], noble metal deposition[12], surface modification[13] and semiconductor composition[14], have been carried out. Among them, doping element into TiO_2 lattice is an effective way. And at present, nanotubes treated by loading modification have little report in photoelectric material fields. This study is based on the nanotube arrays treated by Zn^{2+} loading modification. $Zn(NO_3)_2$ was added during the oxidation process to load a certain amount of Zn^{2+} to the nanotubes. The influence of the oxidation voltage, temperature, time, electrolyte concentration, and content of Zn, as well as the photoelectric effect, on the structure and morphologies of the TiO_2 nanotubes was investigated. And the goal of this study is to prepare Zn^{2+}-TiO_2 nanotube arrays on Ti sheet and further investigate their photoelectric properties.

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2 Experimental

2.1 Materials

The materials used for this experiment were hydrofluoric acid (HF, AR), titanium foils (Ti), sodium sulfate (Na_2SO_4, AR), zinc nitrate [$Zn(NO_3)_2$, AR], isopropanol (C_3H_3O, AR), acetone (CH_3COCH_3, AR), and ethanol (CH_3CH_2OH, AR).

2.2 Synthesis

2.2.1 Synthesis of TiO_2 nanotube arrays

1) The titanium foils were anodized constantly at pH 4 with 1% HF (mass fraction, the same below if not mentioned) under different oxidation voltages. A potentiostat-galvanostat in a two-electrode setup was used to apply constant anodizing voltages of 15, 20, and 30 V typically for 2 h at 20 °C.

2) The titanium foils were anodized at a constant oxidation voltage of 20 V with 0.3%, 0.5%, 0.7%, and 1% HF at 20 °C. The increase rate of voltage was 0.1 V/s.

3) The titanium foils were anodized at a constant HF mass fraction of 0.5% in electrolyte systems with pH values of 1, 4, 7, and 9 at 20 °C.

Finally, the anodized samples were washed with de-ionised water, dried in air, and then calcined at 450 °C for 2 h.

2.2.2 Synthesis of Zn^{2+}-TiO_2 nanotube arrays

The titanium foils were anodized under conditions of 0.5% HF, pH 4, and an oxidation voltage of 20 V. The electrolytes contained 1.0% $Zn(NO_3)_2$. The anodized samples were washed with de-ionised water, dried in air after reacting for 2 h, and then calcined at 450 °C for 2 h.

2.3 Characterisation

The surface morphology and dimension characterisation of the anodized samples were observed on scanning electron microscope (SEM, JEOL JSM-6700F). The crystallographic structures of the produced nanotube arrays were characterised on X-ray diffractometer (XRD, Siemens D5000).

2.4 Photoelectric analysis

Photoelectric test was carried out with a three-electrode system, including a TiO_2/Zn^{2+}-TiO_2 nanotube arrays working electrode, a Pt counter electrode, and a saturated calomel reference electrode. A 0.1 mol/L Na_2SO_4 solution was used as the electrolyte solution. The electrochemical impedance was measured at room temperature on a CHI660C Electrochemical Workstation working under 8 W ultraviolet lamp（λ=365 nm）with 5 cm-distance between the lamp and electrode.

2.5 Analysis of growth mechanism of TiO_2 nanotube arrays

The titanium foils were anodized with 1.0% HF, an oxidation voltage of 5 V, and a duration of 20 min. A CHI660C Electrochemical Workstation with a three-electrode system, including a TiO_2/Zn^{2+}-TiO_2 nanotube arrays working electrode, a Pt counter electrode, and a saturated calomel reference electrode, was used to measure the current and voltage in order to analyze the growth mechanism of the TiO_2 nanotube arrays.

3 Results and discussion

3.1 XRD analysis

XRD was used to characterize the crystalline structure of the TiO_2 nanotube arrays. By comparing the two XRD patterns shown in Fig.1, it is easy to see that the crystalline structures of the TiO_2 nanotube arrays prepared in different electrolyte systems are not obviously different. The main diffraction peaks at 25.29° and 38.41° are indexed as the (101) and (004) reflections of the crystalline anatase phase.

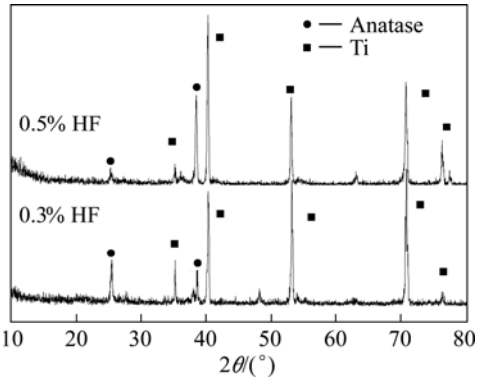

Fig.1 XRD patterns of TiO_2 nanotubes prepared with different electrolyte systems

The XRD patterns of pure TiO_2 and Zn^{2+}-TiO_2 nanotube arrays are shown in Fig.2. The pattern of the Zn^{2+}-TiO_2 nanotube arrays shows a diffraction peak at 56.70°, which is indexed as the (111) reflection of ZnO. The result demonstrates that Zn^{2+} has been loaded on the TiO_2 nanotube arrays, and ZnO is the main form of Zn^{2+} in the Zn^{2+}-TiO_2 nanotube arrays. Therefore, the half peak width of the sample increases and the lattice constant decreases. The patterns shown here have obvious diffraction peaks at 25.29° and 38.41°, indicating that those samples have a regular anatase crystal structure and the addition of Zn^{2+} has no effect on the crystalline lattice of the TiO_2 nanotube arrays.

3.2 SEM analysis of TiO_2 nanotube arrays prepared under different conditions

The SEM images of the TiO_2 nanotube arrays

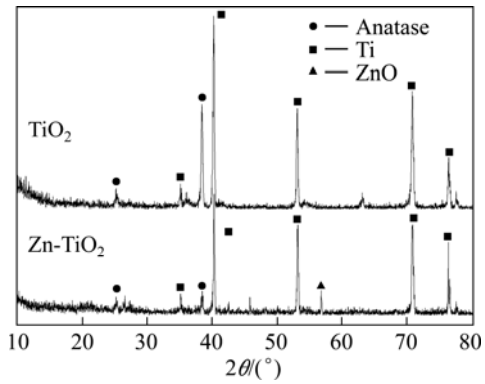

Fig.2 XRD patterns of TiO_2 nanotube arrays and Zn^{2+}-TiO_2 nanotube arrays

prepared on the surface of titanium in electrolyte systems with different PH values are shown in Fig.3. When pH=1, the nanotube arrays with diameter about 70 nm were uniformly distributed on the surface. However, the TiO_2 nanotube arrays have different lengths, creating an irregular arrangement. A TiO_2 nanotube arrays with a sponge structure can be obtained when prepared under pH 4. The reason for the phenomenon is the low mass fraction of H^+ in the reaction during its progress. And a low mass fraction of H^+ in the reaction leads to the decrease of the etching rate and creates an incomplete array structure. There are no nanotube arrays, but some corrosion pits appear in the electrolyte system with pH 7 (Fig.3(b)).

In the 0.5% HF reaction system, although the TiO_2 arrays have different lengths, it is obvious that the TiO_2 nanotube arrays have a better morphology, a regular arrangement, and an average tube diameter of 70 nm (Fig.4). Therefore, the formation rate and the dissolution rate of the TiO_2 nanotube arrays reach equilibrium when the mass fraction of HF is 0.5%.

Fig.5 shows that the nanotube arrays have different morphologies under different anodic oxidation voltages. When the anodic oxidation voltage is 20 V, the nanotube arrays have a regular arrangement, and the average tube diameter is about 80 nm. An unorganised arrangement is obtained when the voltage is 30 V. When it is 15 V, there are spots of nanotube arrays and some corrosion pits on the surface of titanium. The results exhibit that the anodic oxidation voltage has a significant influence on the morphology of the TiO_2 nanotube arrays. When the voltage is too low, there are no TiO_2 nanotube arrays generated, but rather some corrosion pits are formed. When it is too high, the nanotube arrays had an unorganised arrangement and easily collapsed.

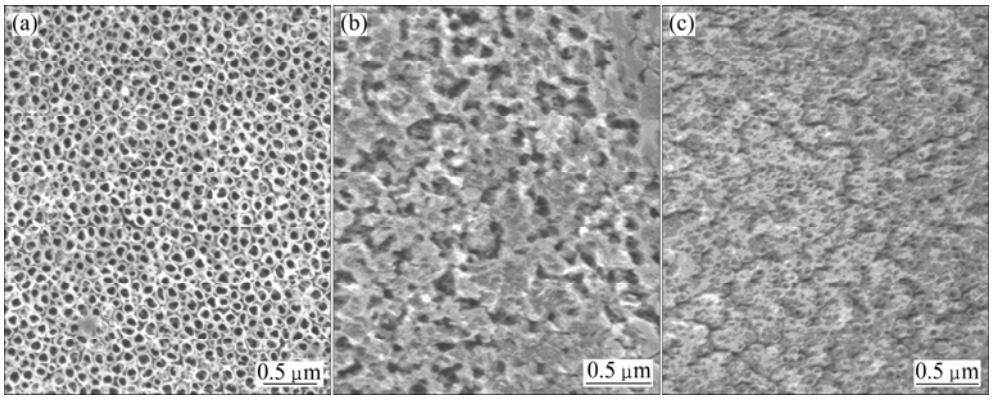

Fig.3 SEM images of TiO_2 nanotube arrays prepared in electrolyte systems with different pH values: (a) pH = 1; (b) pH = 7; (c) pH = 4

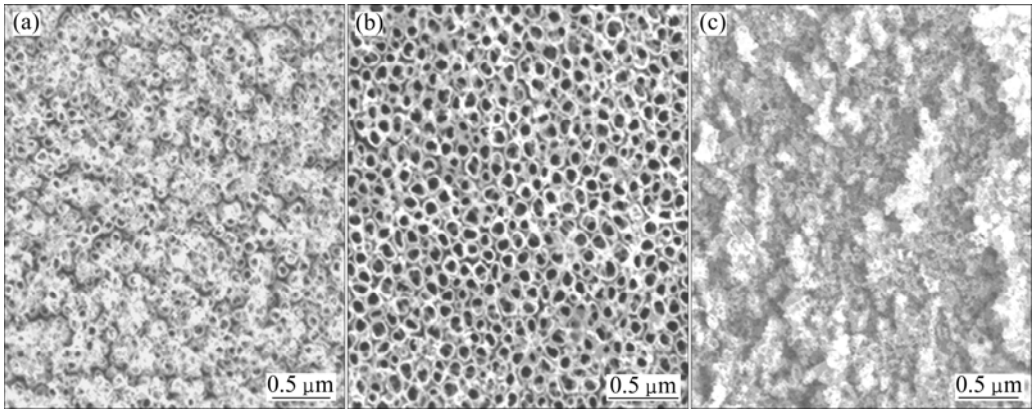

Fig.4 SEM images of TiO_2 nanotube arrays prepared in electrolyte systems with different mass fractions of HF: (a) 0.3% HF; (b) 0.5% HF; (c) 1.0% HF

Fig.6 shows the SEM images of TiO_2 and Zn^{2+}-TiO_2 nanotube arrays. It is obvious that the two morphologies are similar. The tube diameter is in the range of 70–100 nm, the tube wall is about 10 nm, and the TiO_2 nanotube arrays are homogeneously distributed on the surface of titanium. The results indicate that Zn^{2+} loading has little effect on the morphology of the Zn^{2+}-TiO_2 nanotube arrays.

3.3 Complex impedance analysis of TiO_2 nanotube arrays

The Nyquist diagrams (Fig.7) show that TiO_2 nanotube arrays prepared with 0.5% HF exhibit low impedance, which might have been influenced by the structure of the TiO_2 photoelectrodes. The SEM images of the TiO_2 nanotube arrays show that the nanotubes are distributed in a disordered fashion when the mass fractions of HF are 0.3% and 1.0%. A collapse even takes place at the mass fraction of 1.0%. All of these could increase the resistance of the array. When the mass fraction of HF is 0.5%, an orderly arrangement of the TiO_2 nanotube arrays is obtained. The order can reduce the interface resistance between the electrode and solution and be beneficial to the interface charge transfer. The general behaviour of the impedance spectra exhibited by the Zn^{2+}-TiO_2 nanotube arrays is similar to that of the TiO_2 nanotube arrays with 0.5% HF. TiO_2 nanotube arrays loaded with Zn^{2+} would not result in an increase of resistance. Some correspondences at low and high frequencies are revealed in Fig.8(a) and 8(b), respectively. It can be inferred that the response at high frequency is related to the interface between the electrode and the electrolyte, and the response at low frequency can be associated with the diffusion process of the carrier. Furthermore, TiO_2 nanotube arrays loaded by Zn^{2+} could decrease the resistance, which is likely to accelerate the transfer of the carrier and even increase the photoelectric conversion.

3.4 Current—time curve of TiO_2 nanotube array anodizing process

In the first few seconds of the anodic process, an exponential decay of the current occurs (Fig.9). Then the current increases slowly to a quasisteady state. The causes of the current drop are analyzed as follows. Initially, Ti^{4+} is produced by the reaction of Ti and HF. Then, Ti^{4+} is oxidized on the surface of the Ti foils. As the dense membranes of TiO_2 are formed on the surface of the Ti foils, a decrease in the anodic current takes place[15−16]. The oxide thickness increases with the increase of electric field intensity in the next stage. With the solubility of the TiO_2 in HF-containing electrolytes

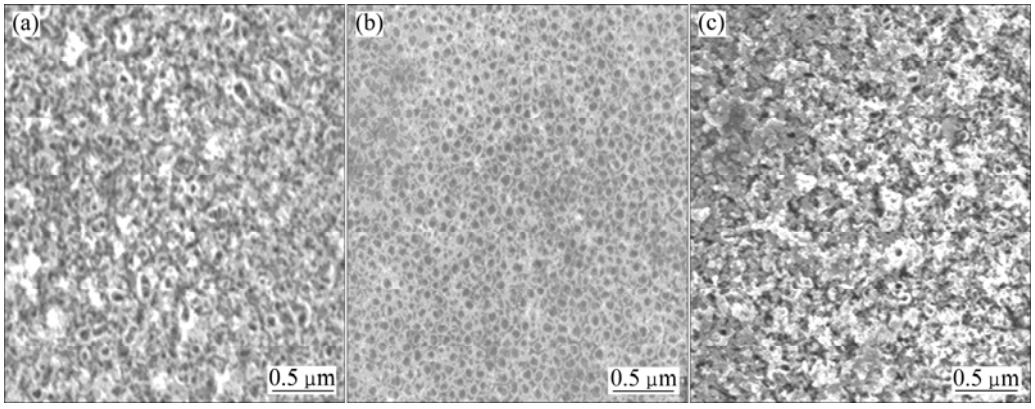

Fig.5 SEM images of TiO_2 nanotube arrays prepared at different voltages: (a) 30 V; (b) 20 V; (c) 15 V

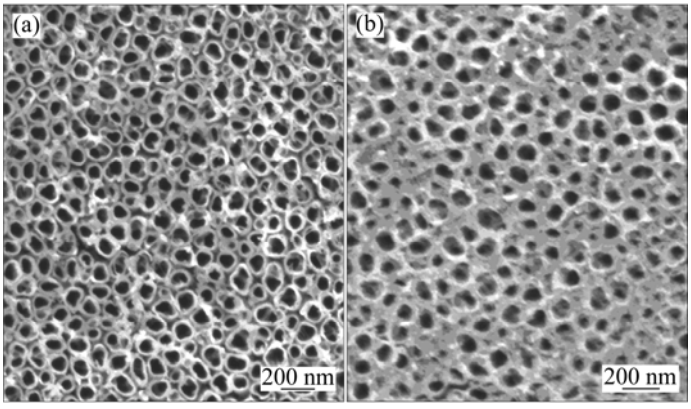

Fig.6 SEM images of TiO_2 (a) and Zn^{2+}-TiO_2 (b) nanotube arrays

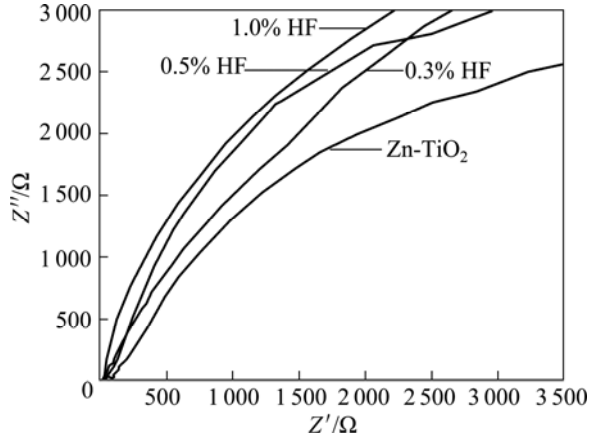

Fig.7 Nyquist diagrams of TiO_2 nanotubes

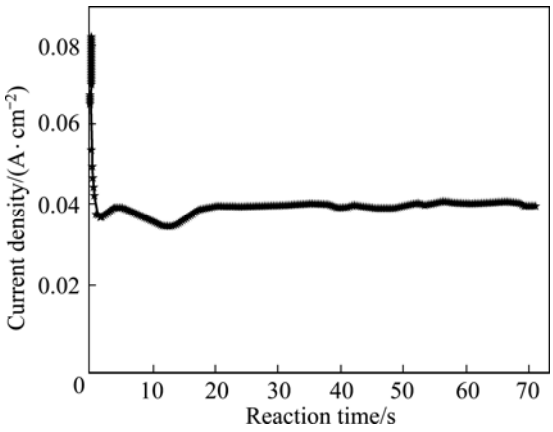

Fig.9 Anodic oxidation process of TiO_2 nanotube arrays

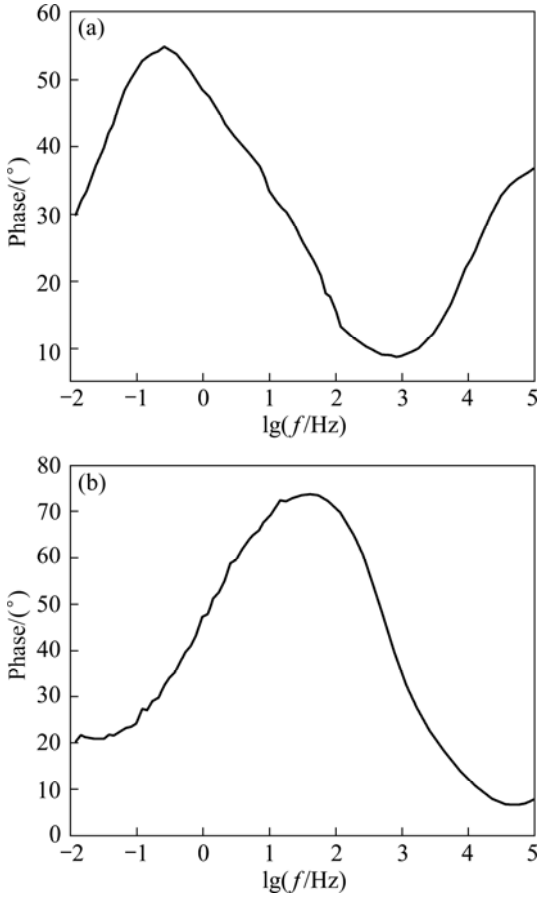

Fig.8 Frequency−phase of AC impedance diagram: (a) TiO_2 nanotubes; (b) Zn^{2+}-TiO_2 nanotubes

and the electric field, TiO_2 nanotubes with homogenous distribution could be formed on titanium oxide barrier with the disordered pore sites etched by HF. It is favorable for the transfer of Ti^{4+} from the oxide barrier to the solution during the process of the pitting cores to form titanium oxide nanopores, and Zn^{2+} is loaded on the TiO_2 nanotubes simultaneously. Due to all of these, the current starts to increase in the stage, leading to the random growth of TiO_2 nanopores. At the last stage, a more stable and regular self-aligned TiO_2 nanopore growth and dissolution equilibrium of Zn^{2+} were established; therefore, the current begins to decrease slowly again.

4 Conclusions

1) TiO_2 nanotube arrays with regular arrangements are obtained when the mass fraction of HF is 0.5%−1.0%, the pH value is 2−4, and the anodizing voltage is 20 V. The length of these tubes is 70−100 nm, and the thickness of these tubes is about 10 nm. Moreover, the adulterate of zinc does not affect obviously the array structure of the TiO_2 nanotubes.

2) It is known that the growth of the Zn^{2+}-TiO_2 nanotube arrays could be divided into three obvious phases in the preparation process. Firstly, a TiO_2 film is generated on the titanium substrate by HF acid etching. Secondly, the pitting and etching that occur on the oxide film result in microporous dent and microholes, which are evenly distributed in the basal surface gradually over time. Thirdly, nanotubes no longer elongate when the loading of Zn^{2+} and the current reach equilibrium. Finally, TiO_2 regions are dissolved through the pores among the holes and formed tubes.

3) According to the analysis on the complex impedance of nanotube arrays, it is obviously that TiO_2 nanotube arrays loaded by Zn^{2+} could decrease the resistance, which is likely to accelerate the transfer of the carrier and even increase the photoelectric conversion.

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