

Research Article

Fabrication of TiO₂ Nanofilm Photoelectrodes on Ti Foil by Ti Ion Implantation and Subsequent Annealing

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The TiO₂ photoelectrodes fabricated on the substrate of Ti foils by Ti ions implantation and subsequent annealing at different temperatures were applied for water splitting. The size of TiO₂ nanoparticles increased with annealing temperatures, and the GIXRD patterns and Raman spectra demonstrate that the phase of TiO₂ turns to rutile at high temperature. The photoelectrochemical (PEC) and X-ray photoelectron spectroscopy (XPS) spectra of the valence band demonstrate that the samples annealed at 400 and 500°C show the n-type property. The sample annealed at 600°C shows the weak p-type TiO₂ property. For the sample annealed at 700°C, the negative photocurrent is main, which mainly performs the p-type property of TiO₂. The IPCE values indicate that the absorption edges are red shifted with the increase of annealing temperatures.

1. Introduction

The production of clean chemical fuels by solar conversion is an attractive and sustainable solution to the energy shortage. Since the solar water splitting on a TiO₂ photoelectrode was discovered by Fujishima and Honda [1], the hydrogen and electric power from water using solar energy has attracted considerable interest because it promises clean, environmentally friendly energy generation. The photoelectrochemical (PEC) reaction has emerged to convert solar energy into chemical energy [2, 3]. The PEC splitting of water into hydrogen and oxygen by the direct use of sunlight is an ideal method. As we know, a PEC cell is based on a semiconductor/liquid junction, where the minority charges generated on light absorption in the semiconductor are driven into the solution by the electric field at the junction, where they can drive a redox reaction [4–6].

In our previous work, we found that TiO₂ nanofilms can be formed on the surface of silica by the Ti⁺ ions implantation and subsequent annealing [7]. However, the substrate is nonconductive and the formed TiO₂ films cannot be used as photoelectrode. In order to acquire TiO₂ nanofilms on the substrate of Ti foil, we try to fabricate the TiO₂

by Ti ion implantation and subsequent annealing. The n-type properties of the as-prepared TiO₂ photoelectrode are detected at low temperatures of 400 and 500°C, while, for the samples annealed at 600 and 700°C, the current-potential curves show the property of p-type TiO₂. The photocurrent of the sample annealed at 500°C under UV-Visible light illumination with applied potential of 0.8 V (versus SCE) is 139.2 μA/cm².

2. Experimental

We used high purity (99.9%) Ti foils in our experiment, and the thickness of the Ti foil is 0.5 mm. High purity Ti foils were cleaned in a mixture of hydrofluoric acid, nitric acid, and purified water for 5 minutes and then implanted with Ti ions at an accelerate voltages of 20 kV, to the fluence of 3×10^{17} ions/cm² using a metal vapor vacuum arc (MEVVA) ion source implanter. The implanted samples were annealed at 400, 500, 600, and 700°C for 6 hours in oxygen atmosphere. The surface morphologies of the annealed samples were examined by scanning electron microscope (SEM, FEI Versa 3D). Raman scattering spectrum measurements were performed by a MicroRaman Microscope (Jobin-Yvon LabRAM

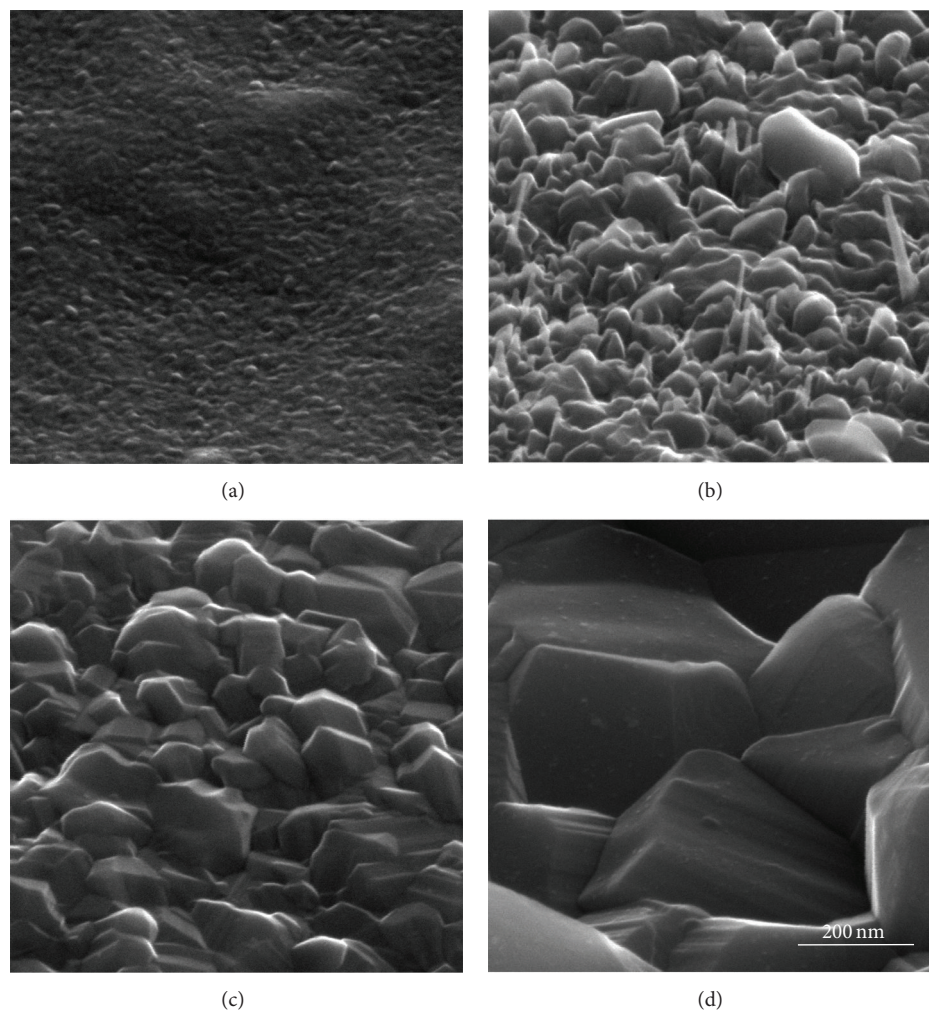


FIGURE 1: SEM image of the TiO_2 formed by Ti implanted into Ti foil and subsequent annealing at 400 (a), 500 (b), 600 (c), and 700°C (d) for 6 hours in oxygen atmosphere, respectively.

HR) using an Ar^+ laser (488 nm) as the excitation source to identify the crystalline phase of TiO_2 . The X-ray diffraction (XRD) patterns were obtained from a PANalytical X'pert MPD Pro diffractometer operated at 40 kV and 40 mA using Ni-filtered $\text{Cu K}\alpha$ irradiation (Wavelength 1.5406 Å). The chemical composition was obtained by X-ray photoelectron spectroscopy (Axis UltraDLD, Kratos) with monoaluminum $\text{K}\alpha$ radiation. The charge calibration was done by correcting Cls line of adventitious carbon setting to 284.8 eV to compensate the charge effect. UV-Vis diffuse reflection spectra (DRS) and monochromatic incident photon-to-electron conversion efficiency (IPCE) were detected to confirm the optical properties.

Photoelectrochemical measurements were carried out in a convenient three-electrode cell. Ti foils implanted by Ti ions onto a special designed electrode holder were used as the working electrodes. The surface areas exposed to electrolyte were fixed at 0.785 cm^2 . The PEC properties of all samples are characterized in $0.5 \text{ M Na}_2\text{SO}_4$ aqueous solution using three-electrode configuration with a Pt and an Ag/AgCl

electrode as a counter electrode and a reference electrode. An electrochemical workstation (CHI760D) and a 300 W Xe lamp ($100 \text{ mW}/\text{cm}^2$) as the solar irradiated simulator with light intensity set at $100 \text{ mW}/\text{cm}^2$ through an AM 1.5G filter were used for photocurrent-potential measurement. Incident photon-to-current conversion efficiency (IPCE) measurements were performed using a 300 W Xe lamp integrated with a computer-controlled monochromator, a photo chopper (PARC), and a lock-in amplifier used for photocurrent detection. IPCE measurements were performed in $0.5 \text{ M Na}_2\text{SO}_4$ aqueous solution as electrolyte, and the applied potential was controlled at 0.8 V versus Ag/AgCl reference electrode.

3. Results and Discussion

Figure 1 shows the SEM images of nanoparticles formed by Ti ions implanted into Ti foil and subsequent annealing at 400, 500, 600, and 700°C for 6 hours in oxygen atmosphere. In order to observe the nanoparticles clearly and present a three-dimensional image, we set the tilt angle to 52°. When

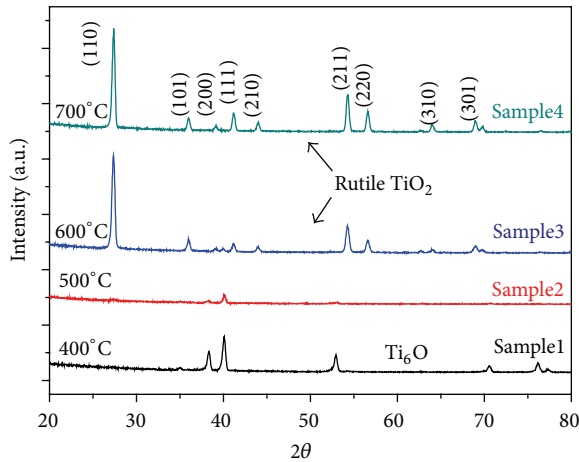


FIGURE 2: XRD patterns of TiO_2 , which are annealed at different temperatures.

the sample was annealed at 400°C , small titanium oxide nanoparticles were formed on the surface of the substrate, the average size of the nanoparticles is 25.8 nm, as shown in Figure 1(a). When the annealing temperature increases, the size of nanoparticles grows quickly. The average size of the nanoparticles grows to 93.3, 151.7, and 675 nm, for the annealing temperatures of 500, 600, and 700°C , respectively.

Figure 2 shows GIXRD patterns of the TiO_2 formed by Ti ions implantation into Ti foils and subsequent annealing at 400, 500, 600, and 700°C for 6 hours in oxygen atmosphere, respectively. It is found that the phase composition strongly depends on the annealing temperatures. With the increase of annealing temperature, the quality of titanium oxide changed from amorphous to rutile phase. The sample annealed at 400°C is Ti_6O . At the annealing temperatures of 600 and 700°C , the titanium oxide transfers mostly to rutile phase.

In order to confirm the ingredients of nanoparticles on the surface of the substrate, we show the Raman spectra of the TiO_2 films formed by Ti implanted into Ti foil and subsequent annealing. As shown in Figure 3, when the annealing temperature is 400°C , the Raman peak located at 140 cm^{-1} is the E_g mode of the TiO_2 in anatase phase [8, 9]. No Raman mode of the Ti_6O is found in the Raman spectra, which may be not in the range of the measurement. The anatase TiO_2 has not been detected in the XRD patterns due to its too fewer amount. With the increase of annealing temperature, two rutile Raman peaks appear at the 442 cm^{-1} (E_g) and 603 cm^{-1} (A_{1g}) [10, 11], which were the first-order Raman spectra of rutile TiO_2 . When the annealing temperature is 700°C , the second-order Raman peak at 234 cm^{-1} becomes stronger [12]. At the same time, the intensity of the E_g and A_{1g} modes became much stronger.

According to the SEM images, the GIXRD patterns, and the Raman spectra, we can conclude that the main content of nanoparticles on the surface of the samples annealed at 400°C is Ti_6O with small amount of TiO_2 nanoparticles. When the annealing temperature is 500°C the content of rutile TiO_2 is increased. As the annealing temperature increases to 600 and

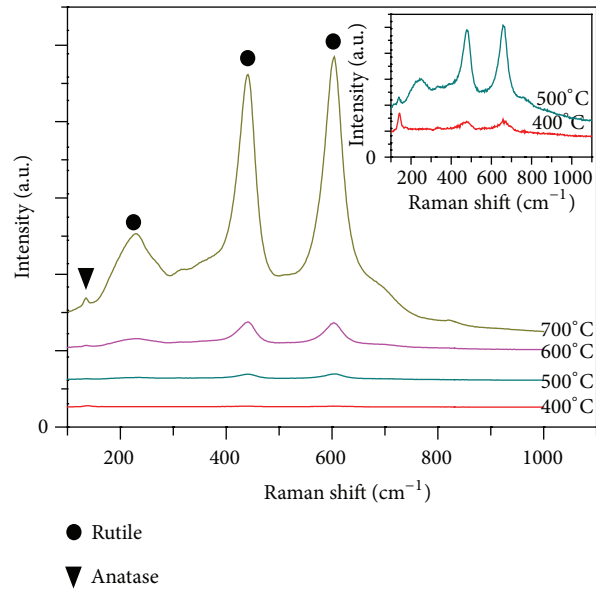


FIGURE 3: The Raman spectra of TiO_2 annealed at different temperatures.

700°C , the main particles are rutile TiO_2 . While annealing at low temperatures, implanted Ti atoms are slowly diffused out of the sample and are oxidized. Therefore, small TiO_2 particles are formed on the sample surface. Meanwhile, the near surface of substrate is also oxidized to Ti_6O . Under higher annealing temperatures, the implanted Ti atoms are easier to diffuse to sample surface and the size of TiO_2 particles grows. In order to confirm the formation of the TiO_2 films, XPS analysis was performed for the Ti-implanted sample to the fluence of 3×10^{17} ions/ cm^2 and annealed at 400, 500, 600, and 700°C for 6 hours. As shown in Figure 4, the binding energy of $\text{Ti}2p_{1/2}$ locates at 464.2 eV, and $\text{Ti}2p_{3/2}$ locates at 458.4 eV belong to the binding energy of Ti^{4+} .

In order to know the optical properties, we test the UV-Visible diffuse reflection spectra (DRS) and monochromatic incident photon-to-electron conversion efficiency (IPCE) of the TiO_2 films. As shown in Figure 5(a), with the increase of annealing temperature, the absorption of light from UV enlarged to visible light region. According to the GIXRD and Raman spectra, the main composition of the sample annealed at 400°C is Ti_6O . The broad absorption is possibly due to the absorption of Ti_6O . The size of TiO_2 nanoparticles increased with the annealing temperatures, and the high temperature easily caused the phase change of TiO_2 nanoparticles to rutile phase, which are the reason that the absorption edges are red shifted.

The IPCE values are shown in Figure 5(b); for the sample annealed at 400°C , the maximum IPCE is 2.9% at the absorption wavelength of 320 nm and is 6.94% for the sample annealed at 500°C . The highest IPCE for the sample annealed at 600°C is 2.8% at the absorption wavelength of 370 nm. The absorption edges are red shifted with the increase of annealing temperatures, indicating the formation of TiO_2 nanoparticles. The further red shift of the absorption

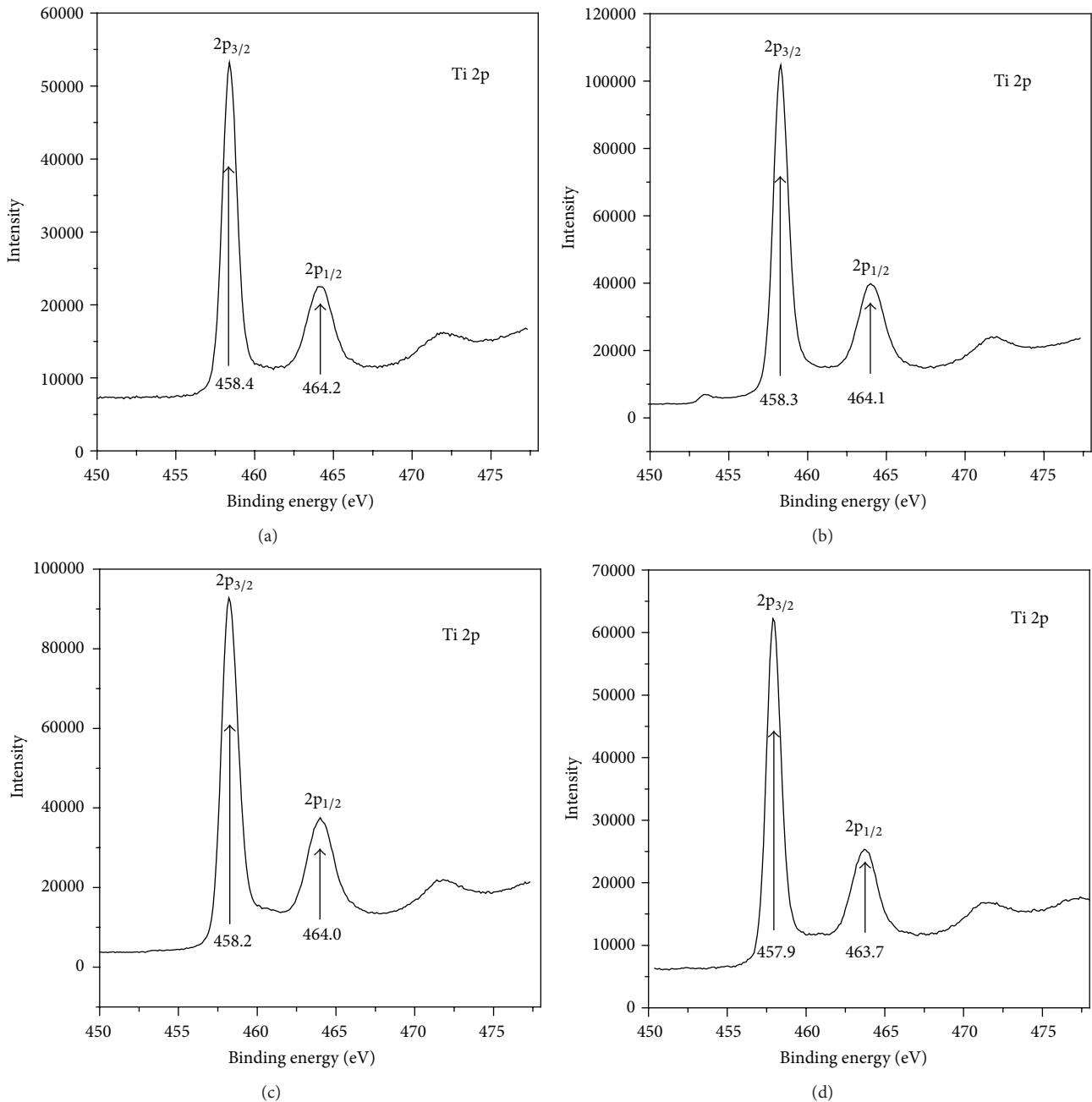


FIGURE 4: XPS spectrum of Ti 2p in the TiO_2 formed by Ti implanted into Ti foil and subsequent annealing at 400 (a), 500 (b), 600 (c), and 700°C (d) for 6 hours in oxygen atmosphere, respectively.

wavelength after annealing at 700°C is due to the increase of the sizes of TiO_2 nanoparticles.

Figure 6(a) shows current-potential curves in 0.5 M Na_2SO_4 aqueous solution under UV-Visible light illumination for TiO_2 formed by Ti ion implantation and subsequent annealing at 400, 500, 600, and 700°C. The samples annealed at 400 and 500°C were n-type Ti_6O . The photocurrent of the sample annealed at 500°C under UV-Visible light illumination with applied potential of 0.8 V (versus SCE) is $139.2 \mu\text{A}/\text{cm}^2$. The samples annealed at 400 or 500°C show positive photocurrent; they present n-type property.

For the samples annealed at 600°C, which have the negative photocurrent at the negative bias and have a positive photocurrent when they are at the positive bias, show the property of both the p-type and n-type TiO_2 . Thus, the sample annealed at 600°C has weak p-type property. For the sample annealed at 700°C, the negative photocurrent is main, which mainly performs the p-type property of TiO_2 . Because the substrate is Ti foils, the Ti ions are abundant and the Ti atoms were diffused to the surface and oxidized during annealing under oxygen atmosphere, and the Ti_6O was also gradually oxidized to TiO_2 with the increase of annealing temperature.

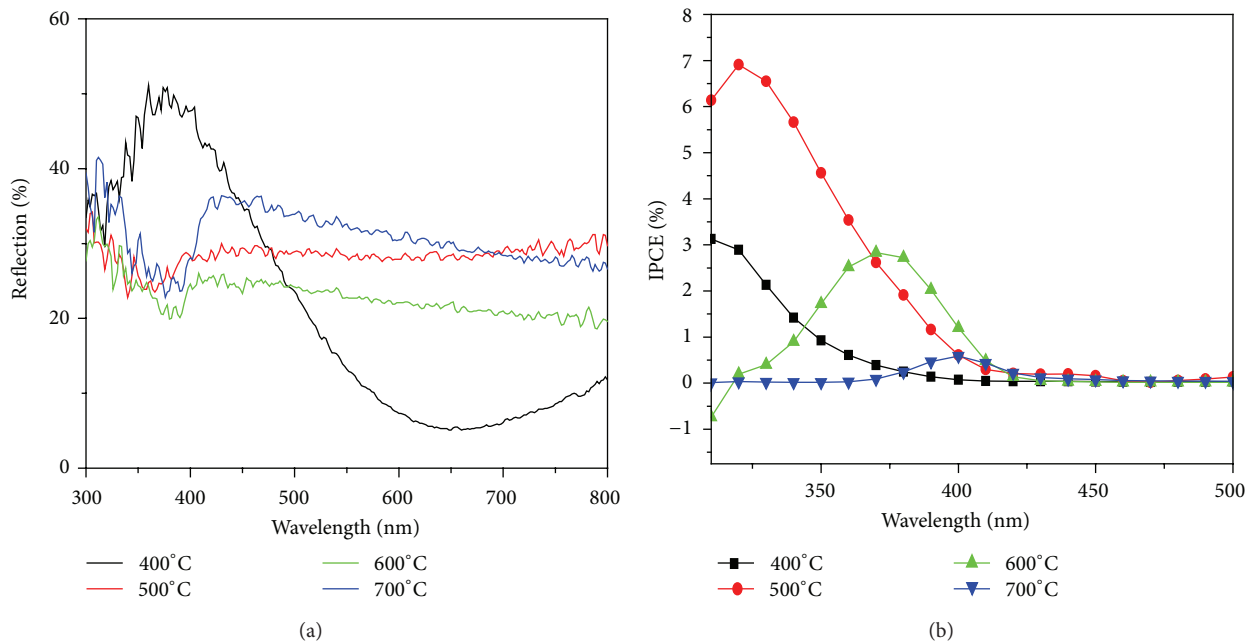


FIGURE 5: The UV-Vis diffuse reflection spectra (DRS) and monochromatic incident photon-to-electron conversion efficiency (IPCE) of the TiO₂ films formed by Ti implanted into Ti foil and subsequent annealing.

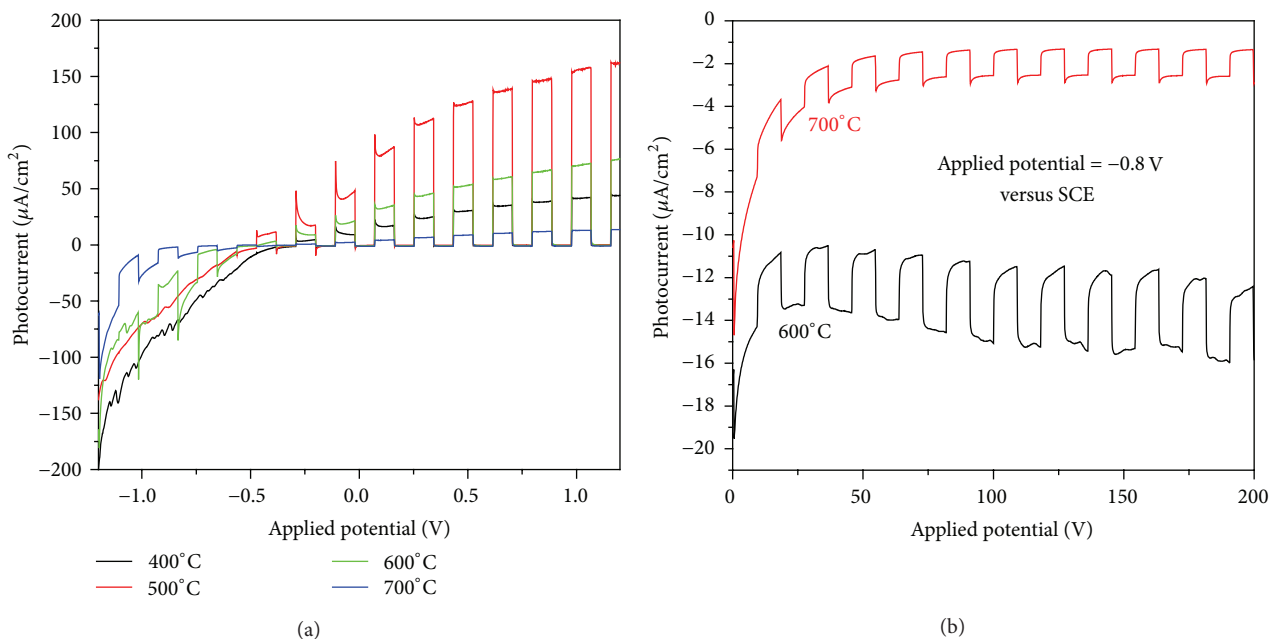


FIGURE 6: (a) The current-potential curves in 0.5 M Na₂SO₄ aqueous solution under simulated solar light for TiO₂ formed by Ti ion implantation and subsequent annealing at 400, 500, 600, and 700°C. (b) The i-t curve annealed at 600 and 700°C.

The samples annealed at 600 and 700°C are rutile TiO₂; some of the Ti ions locate in the interstitial positions, which lead to the property of p-type TiO₂. Figure 6(b) shows the photoelectrochemical measurement of the samples annealed at 600 and 700°C, which were operated by the amperometric i-t curve to evaluate their ability for photocatalytic water splitting under visible light illumination. The photocurrent

was 3.52 $\mu\text{A}/\text{cm}^2$ at 600°C and 1.60 $\mu\text{A}/\text{cm}^2$ at 700°C, with applied potential of -0.8 V (versus SCE).

Additional evidence of p-type TiO₂ is from XPS spectra of the valence band region. As shown in Figure 7, the valence band of TiO₂ that was annealed at 400°C (Figure 7(a)) starts from about 2.13 eV. In contrast, the valence band of TiO₂ starts from about 1.66 eV (Figure 7(c)). It means that

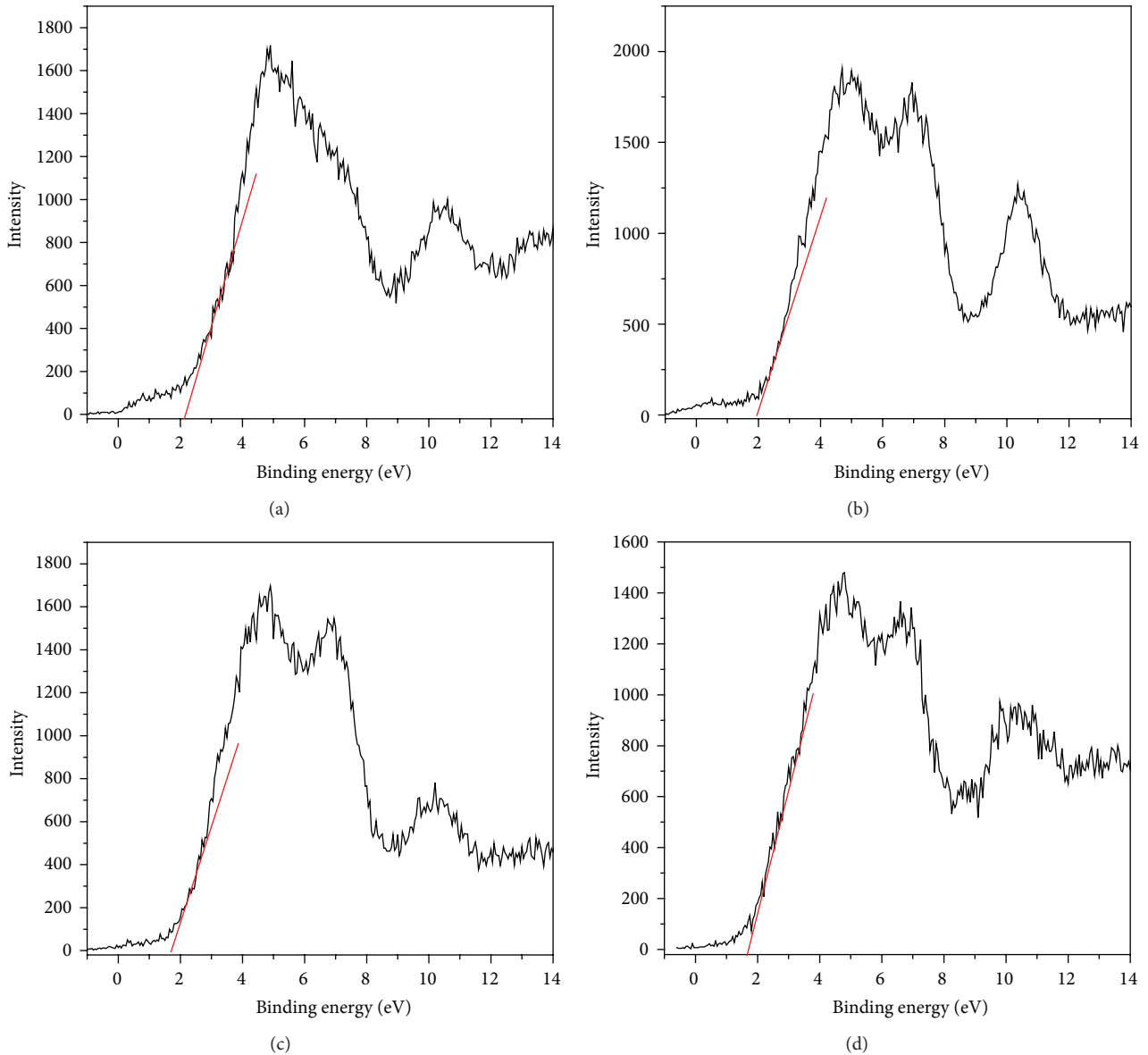


FIGURE 7: XPS spectra of the TiO₂ thin film at the valence band region, annealing at 400 (a), 500 (b), 600 (c), and 700°C (d) for 6 hours in oxygen atmosphere, respectively.

the Fermi level of TiO₂ (0.0 eV) is closer to the valence band of the sample annealing at 600°C; it is reported that the preparation of p-type TiO₂ using the thermal approach needs high temperature [13]. The XPS spectra prove the formation of p-type TiO₂.

4. Conclusion

The TiO₂ nanofilms were formed on the substrate of Ti foils as the photoelectrochemical (PEC) electrode. The size of TiO₂ nanoparticles increased with the increasing of annealing temperatures, and the GIXRD patterns and Raman spectra

demonstrate that the phase of TiO₂ turns to rutile at high temperature. The IPCE values indicate that the absorption edges are red shifted with the increase of annealing temperatures. The n-type properties of the as-prepared TiO₂ photoelectrode are detected at low temperatures of 400 and 500°C. For the samples annealed at 600 and 700°C, the photocurrent shows the property of p-type TiO₂.

Conflict of Interests

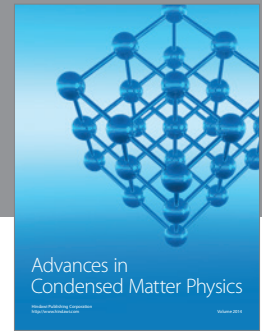
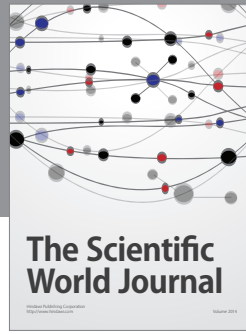
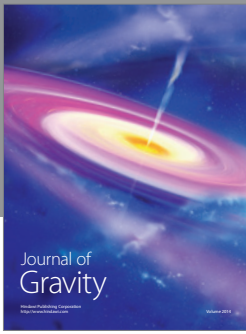
The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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