

Photovoltaic Properties of Titanium Dioxide Nanowires with Different Crystal Structures

WANG Xinyan¹, WANG Huan², YANG Xiaotian² and SU Xingguang^{1*}

1. College of Chemistry, Jilin University, Changchun 130012, P. R. China;

2. Jilin Provincial Key Laboratory of Architectural Electricity & Comprehensive Energy Saving, Jilin Jianzhu University, Changchun 130118, P. R. China

Abstract Titanium dioxide(TiO₂) nanowires with different crystal structures were successfully synthesized, and their charge transfer properties were further investigated by surface photovoltage(SPV), transient photovoltage(TPV) and surface photocurrent(SPC) techniques. The results reveal that both the surface states and the charge transfer rate of different TiO₂ nanowires are highly dependent on their crystal structures.

Keywords Nanostructure; Semiconductor; Photovoltage; Photocurrent

1 Introduction

One-dimensional(1D) nanostructures, such as nanowires, nanobelts, nanotubes and nanorod have interested some scientists due to their unique optoelectronic properties in a few past decades^[1–5], and they have considered them to be the optimal systems to investigate the dimensional- and size-dependent optical, electronic and mechanical properties of materials. Furthermore, 1D nanostructures are also expected to be one of the most important building blocks for fabricating electronic and optoelectronic nanodevices. Until now, the promising application in the fields of preparing nanolaser, nanotransistors, nano-optoelectronic sensor and chemical/biosensors has been proposed^[6–10].

Among them, titanium dioxide(TiO₂) with 1D nanostructures has been intensively studied because of its superior properties applied in the fields of photocatalysis, the preparation of gas-sensor, and solar energy conversion than those of conventional TiO₂ nanoparticles. For example, Lou *et al.*^[11] reported a large quantity of solvothermal syntheses of anatase TiO₂ nanowires, which exhibited excellent photocatalytic activity for the degradation of Rhodamine B. TiO₂ has also been proven to be beneficial to further improving the efficiency of dye-sensitized solar cells^[12] and the performance of gas sensors^[13]. Despite of these interesting results achieved, few studies have focused on the charge transfer properties of 1D TiO₂ nanostructures. And it is apparently of significant importance to further understand the charge transfer properties, which are expected to have effect on the optoelectronic performance of TiO₂ nanowires.

In this work, we systematically investigated the charge transfer properties of 1D TiO₂ nanowires with different crystal phases: anatase phase, mixed anatase/rutile phase and rutile phase by means of surface photovoltage(SPV), transient

photovoltage(TPV) and surface photocurrent(SPC) techniques. The results reveal that the charge transfer properties of the 1D TiO₂ nanowires are highly dependent on their crystal structures.

2 Experimental

2.1 Chemicals

Titanium(IV) isopropoxide(TTIP, 97% purity) and ethylene glycol(EG, anhydrous, 99.8% purity) were purchased from Sigma-Aldrich. All the chemicals were used as received without any further purification.

2.2 Synthesis

TiO₂ nanowire precursor was synthesized according to the reported protocol^[14,15]. Typically, 0.05 mL of TTIP was added in 10 mL of EG under the protection of nitrogen flow. After having been stirred for 30 min, the solution was heated to 170 °C and maintained at that temperature for 2 h in an oil bath. After that, the obtained white precipitate was washed with distilled(DI) water and ethanol, and centrifuged at 5000 r/min three times to remove the residual reagent and EG. The precipitate was first placed into a vacuum oven at 50 °C and left overnight and then calcinated at 500, 650 and 800 °C, respectively, for 2 h to obtain the samples with different crystal phases.

2.3 Characterization

The morphologies of the samples were obtained on a Schimadzu SSX-550 scanning electron microscope. X-Ray diffraction patterns were recorded on a Rigaku D/Max-2550 diffractometer with Cu K α radiation($\lambda=0.154056$ nm, 40 kV, 350 mA) in a range of 20°—80°(2 θ) at a scanning rate of

*Corresponding author. E-mail: suxg@jlu.edu.cn

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10°/min. SPV measurement was carried out on a commercial KP system(KP Technology Ltd., Scotland, UK) using a gold reference probe with a diameter of 1.8 mm, and the SPV signal was obtained by tracking the contact potential difference(CPD) between the sample and the probe. SPC and TPV measurements were obtained on the system, for which the details have been described elsewhere^[16].

3 Results and Discussion

TEM and XRD analyses were used to investigate the morphology and crystal structure of TiO₂ nanowires before and after calcination. It can be seen from the TEM image(Fig.1) that the obtained TiO₂ nanowires are tens of micrometers in length and few micrometers in width. The corresponding XRD pattern(Fig.2) shows that the sample is in an orthorhombic structure^[17]. The formation mechanism of TiO₂ nanowires, which is a generally accepted one is that TTIP would firstly react with EG to form titanium glycolates or mixed alkoxide/glycolate derivatives, and subsequently produce the one-dimensional nanomaterials composed of chainlike glycolate complexes during heating^[15].

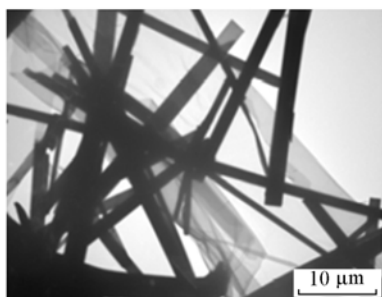


Fig.1 TEM image of the as-prepared TiO₂ nanowires before calcination

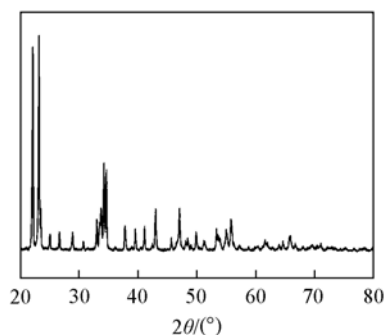


Fig.2 XRD pattern of the as-prepared TiO₂ nanowires before calcination

To obtain TiO₂ nanowires with different crystal structures (anatase phase, mixed anatase/rutile phase and rutile phase), further post heat treatments of TiO₂ nanowires at different temperatures(500, 650 and 800 °C) were carried out, respectively. The SEM images[Fig.3(A)—(C)] show that after having been calcinated, the nanowire structures of the samples are all well retained with the similar size(10 micrometers long, and few hundreds nanometers wide). The average values of the width and length for all the samples were calculated based on the SEM and TEM results(Table 1). It can be clearly seen that after the calcination of them, the widths and lengths of TiO₂

nanowires for all the samples are dramatically reduced due to the decomposition of titanium glycolates or mixed alkoxide/glycolate derivatives in the precursor to the TiO₂ during the calcination. The XRD results(Fig.4) indicate that at three different calcination temperatures, the crystal structures of the obtained samples exhibit anatase phase, mixed anatase/rutile phase and rutile phase, respectively, and for convenience, they are denoted as the samples a, b and c, respectively.

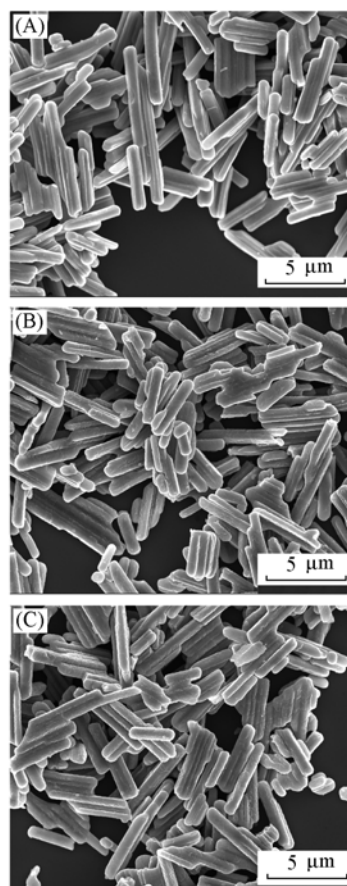


Fig.3 SEM images of TiO₂ nanowires annealed at 500 °C(A), 650 °C(B) and 800 °C(C) for 2 h, respectively

Table 1 Average values of the length and width of TiO₂ nanowires before and after calcination

Sample	Average value	
	Length/μm	Width/nm
Prepared-TiO ₂	31.3	1970
Annealed at 500 °C	9.5	625
Annealed at 650 °C	9.9	644
Annealed at 800 °C	9.3	673

The crystal sizes of the three samples calculated *via* the Scherer equation are in a range of 20—30 nm and quite different from the result obtained from the SEM image. This indicates that the TiO₂ nanowires with different crystal structures are all composed of small crystallites. Despite of the TiO₂ nanowires studied in our work being different from the single crystal TiO₂ nanowire, the mechanical interaction of the small crystallites in the TiO₂ nanowires should be strong enough due to the calcination treatment, which is expected to facilitate the charge transfer in TiO₂ nanowires with different

crystal structures.

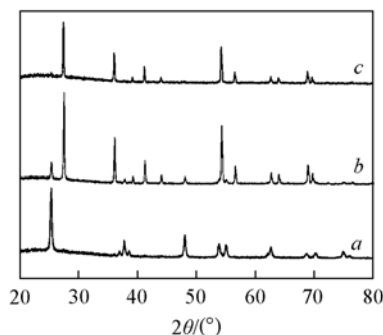


Fig.4 XRD diffraction patterns of the TiO₂ nanowires annealed at 500 °C(*a*), 650 °C(*b*) and 800 °C(*c*) for 2 h, respectively

We next investigated the photovoltaic properties of the obtained samples. Since the morphologies and crystallite sizes of the samples are similar, the differences of them in photovoltaic properties should be mainly attributed to the change of the crystal phase. Fig.5(A) shows the SPV results of the three samples. It is clearly seen that all the three samples exhibit the positive response.

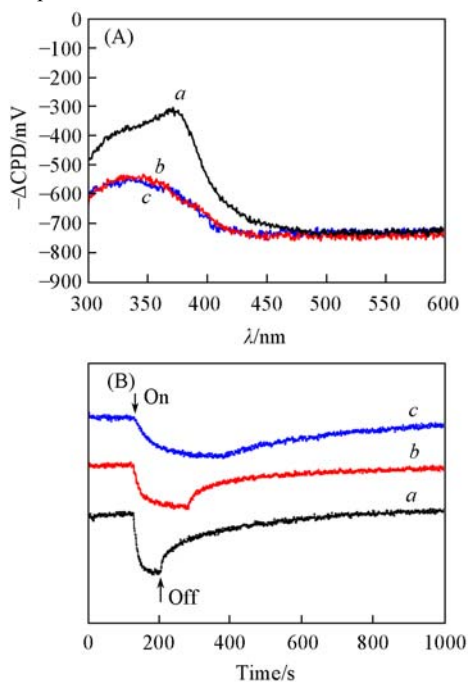


Fig.5 SPV spectra of the three different samples annealed at different temperatures for 2 h(A) and the contact potential difference(CPD) changes of the samples illuminated by the light of 370 nm(3.35 eV) during switching on and off(B)

Sufficient relaxation of the samples in the dark is shown by the stable dark CPD. *a*. 500 °C; *b*. 650 °C; *c*. 800 °C.

According to the rule of the generation of SPV signal, after the sample absorb the photons with enough energy, the electrons will be excited from valence band to the conduction band for the super band gap SPV, or from the surface states to the conduction band for the sub-band gap SPV, leaving holes trapped at surface states assumed to be O²⁻[17], which will result

in positive response. However, it should be noted here that SPV onset of sample *a* is red shift by about 60 nm compared with those of other two samples, while the SPV responses of samples *b* and *c* are similar. It has been well known that both the anatase and rutile crystal phases of TiO₂ belong to distorted octahedron class[18], and anatase is more distorted than rutile[19], which will result in more defects on the surface of the crystallites in the nanowire. Therefore, we attribute the red shift of the SPV response to the existence of more surface defects in sample *a* than in samples *b* and *c*.

Fig.5(B) displays the transient SPV spectra of the three samples under the illumination of light at 370 nm. When they were excited by the light at 370 nm(on), the time needed for the samples to reach the equilibrium of SPV was gradually prolonged with the change of the crystal structure from anatase phase to the mixed anatase/rutile and finally rutile. It is commonly recognized that the onset of SPV rate is determined by the intensity(*I*) of the built-in field in the materials which is thought to be correlated with the amount of surface states (O²⁻)^[17], thus, on the basis of the results shown in Fig.5(B), we propose the probable order of the intensity of built-in field in the TiO₂ nanowires with different crystal phases is $I_{\text{sample a}} > I_{\text{sample b}} > I_{\text{sample c}}$. Interestingly, for the relaxation process without the illumination of light(off) after the equilibrium of SPV response, the decay time was also gradually prolonged when the crystal phase of the samples was changed from anatase to rutile. The longer decay time means that fewer defects exist on the surfaces of the samples. Therefore, it is reasonable to conclude that the amounts(*n*) of the surface states are in the sequence of $n_{\text{sample a}} > n_{\text{sample b}} > n_{\text{sample c}}$.

Fig.6 represents the normalized TPV spectra of the three samples. As shown in Fig.6, all the samples possess two charge transfer processes: one is the quick process, in a range of 10⁻⁶—10⁻⁷ s, which is thought to be attributed to the time needed for the separation of photogenerated electron-hole pairs in the TiO₂ crystallites; the other is the slow process, in a range of 10⁻³ s, which is thought to be associated with the time of the photogenerated carriers transfer between the TiO₂ crystallites. The quick process reflects the time of the intrinsic photoinduced charge generation and separation of TiO₂, and it is likely independent on the crystal phase of the sample; while the slow process reflects the charge transfer properties in the sample.

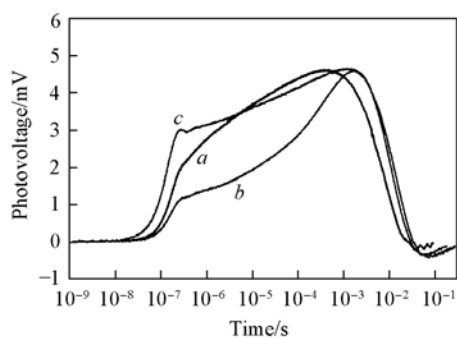


Fig.6 Normalized TPV spectra according to the fast charge transfer process of the samples annealed at 500 °C(*a*), 650 °C(*b*) and 800 °C(*c*) for 2 h, respectively

And as can be clearly seen, the time for the slow charge transfer process of the sample is prolonged as the crystal phase of the sample changes from anatase to rutile, demonstrating the different charge transfer rates in the samples with different crystal phases, and with the charge transfer rate (R) sequence of $R_{\text{sample a}} > R_{\text{sample b}} > R_{\text{sample c}}$, which is further proven by the SPC measurements (Fig. 7). As can be seen, the SPC signal is dramatically reduced as the crystal phase of the samples gradually changes from anatase to rutile.

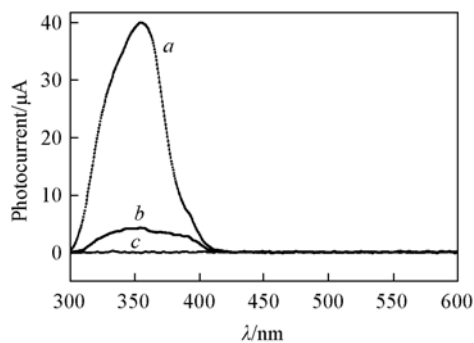


Fig. 7 SPC spectra of the samples annealed at 500 °C(a), 650 °C(b) and 800 °C(c) for 2 h, respectively

4 Conclusions

In conclusion, we have systematically studied the photovoltaic properties of TiO₂ nanowires with anatase, mixed anatase/rutile and rutile crystal phases and with similar morphology and size. The results show that both the amount of surface states and the charge transfer rate in the TiO₂ nanowires are gradually reduced with the changes of crystal phase from anatase to anatase/rutile and finally to rutile. These interesting findings may provide an insight into further optimization of

performance of TiO₂ nanowires based optoelectronic devices.

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