

## Enhanced photoelectrochemical activity of vertically aligned ZnO-coated TiO<sub>2</sub> nanotubes

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(Received 3 January 2014; accepted 18 January 2014; published online 6 February 2014)

Vertically aligned ZnO-TiO<sub>2</sub> hetero-nanostructures constructed of anatase TiO<sub>2</sub> nanotubes (NTs) and wurtzite ZnO coatings are fabricated by atomic layer deposition of ZnO coatings on electrochemical anodization formed TiO<sub>2</sub> NTs, and their photoelectrochemical activities are studied through photoelectrochemical and electrochemical characterization. Compared with bare TiO<sub>2</sub> NTs, the transient photocurrent increases to over 1.5-fold for the annealed ZnO-coated TiO<sub>2</sub> NTs under visible illumination. The ZnO-coated TiO<sub>2</sub> NTs also show a longer electron lifetime, a lower charge-transfer resistance and a more negative flat-band potential than the bare TiO<sub>2</sub> NTs, confirming the improved photoelectrochemical activity due to the enhanced charge separation. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4863852>]

Nanostructured TiO<sub>2</sub> and ZnO have recently attracted much attention because of their potential applications such as photocatalytic reactions and photovoltaic processes.<sup>1-3</sup> Both metal oxides have advantages of low cost, stability, nontoxicity, and ease of availability. In addition, the good compatibility between TiO<sub>2</sub> and ZnO allows them to be composed as a hetero-nanostructure. Compared with the single oxides, heterostructures constructed from nanostructured TiO<sub>2</sub> and ZnO can provide better performance when used as a photocatalyst or a photoelectrode due to the combination of the high reactivity of TiO<sub>2</sub> and the large binding energy of ZnO, as well as, the staggered band alignment of the formed heterostructures.<sup>4-6</sup> An extended range of photoresponse and an enhanced photoactivity can be achieved compared with the single metal oxides, which are most favorable for photocatalytic and photovoltaic applications.<sup>7-11</sup> Much work has been devoted to nano-scaled ZnO-TiO<sub>2</sub> heterogeneous structures, in particular, to one-dimensional hetero-nanostructures including nanotubes (NTs) and nanowires.<sup>8-11</sup>

In this work, we fabricated vertically aligned ZnO-coated TiO<sub>2</sub> (ZnO/TiO<sub>2</sub>) NTs by electrochemical anodization (EA) of Ti foils followed by atomic layer deposition (ALD) of ZnO. After morphology characterization, photoelectrochemical and electrochemical properties were studied in detail. Photocurrent (PC) density, electrochemical impedance spectroscopy (EIS), and flat-band potential were measured to understand the suppressed electron-hole recombination and the enhanced photoelectrochemical activity of the hetero-nanostructures composed of TiO<sub>2</sub> nanotubes and ZnO coatings and to obtain the improved photoelectrochemical performance.

TiO<sub>2</sub> NTs were first formed on Ti foil (99.99% in purity, 0.1 mm in thickness) by EA. The polished Ti foil was anodized at 0 °C in a two-electrode electrochemical cell using

the Ti foil as the working electrode and a graphite sheet as the counter electrode in 0.5 wt. % HF electrolyte at a voltage of 20 V for 40 min. The formed TiO<sub>2</sub> NTs were then annealed at 450 °C for 3 h in air. The annealed TiO<sub>2</sub> NTs were used as templates for the deposition of ZnO coatings by ALD (TFS200, BENEQ) using diethylzinc [Zn(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>, DEZ] as the metal precursor and de-ionized water (H<sub>2</sub>O) as the reactant. The ZnO coatings were typically deposited at 200 °C by several DEZ-H<sub>2</sub>O cycles in the sequence of 0.5-s DEZ pulse, 2-s N<sub>2</sub> purge, 0.5-s H<sub>2</sub>O pulse, and 2-s N<sub>2</sub> purge. One-cycle deposit of ZnO is approximately 0.2 nm in thickness when being deposited on a plane substrate. The obtained ZnO/TiO<sub>2</sub> samples were annealed at 450 °C for 30 min in air.

The sample morphology was examined by field-emission scanning electron microscopy (FESEM, Hitachi S-4800), revealing that highly ordered and vertically aligned TiO<sub>2</sub> NTs having an average diameter of ~60 nm and a wall thickness of ~15 nm were formed on Ti foil by EA, as shown in Fig. 1(a). Figure 1(b) shows the planar and cross-sectional FESEM images of ZnO/TiO<sub>2</sub> NTs fabricated by depositing 10 cycles of ZnO on TiO<sub>2</sub> NTs. It can be seen that the TiO<sub>2</sub> NTs are uniformly covered by the ZnO coatings, forming ZnO-coated TiO<sub>2</sub> NTs which have smaller diameters and thicker walls than the bare TiO<sub>2</sub> NTs. No changes in morphology were observed after annealing.

The sample structure was characterized by X-ray diffraction (XRD, Rigaku D/max-γ B X-ray), revealing that the fabricated ZnO/TiO<sub>2</sub> NTs are constructed from nearly tetragonal anatase TiO<sub>2</sub> and hexagonal wurtzite ZnO, as shown in Fig. 2(a), which is dominated by a prominent peak attributed to the (101) diffraction of anatase TiO<sub>2</sub> [A (101)] (JCPDS 21-1272) in addition to the peaks diffracted from Ti foil (denoted by T). Some weak diffraction from wurtzite ZnO (denoted by W) (JCPDS: 36-1451) also appear in the XRD patterns of the ZnO/TiO<sub>2</sub> NTs. Post-fabrication annealing resulted in an improvement in the structures of TiO<sub>2</sub> and ZnO, as revealed by the intensity increase of the diffractions.

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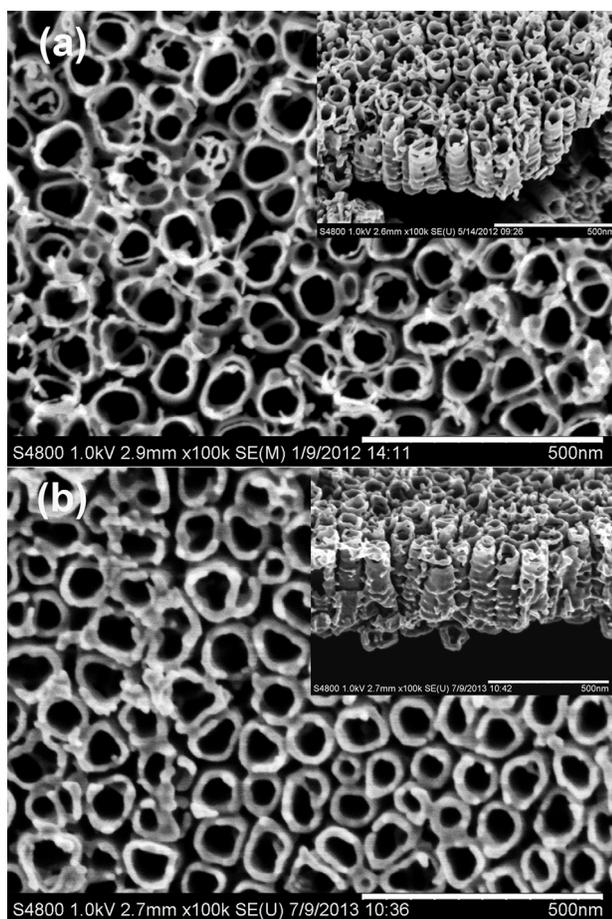


FIG. 1. Top-view and cross-sectional SEM images of bare TiO<sub>2</sub> NTs (a) and ZnO/TiO<sub>2</sub> NTs (b).

The crystal structures of TiO<sub>2</sub> and ZnO and the improvements in the structures were confirmed through the analysis of vibrational modes obtained by Raman scattering measurements (Jobin-Yvon LabRAM HR 800 UV) using a 325-nm He-Cd laser beam to excite the samples. As shown in Fig. 2(b), the Raman spectrum of the as-fabricated ZnO/TiO<sub>2</sub> NTs is similar with that of the bare TiO<sub>2</sub> NTs, both exhibit characteristic Raman modes of anatase TiO<sub>2</sub> (denoted by A).<sup>12</sup> For the annealed sample, however, the Raman mode associated with longitudinal optical (LO) phonons of wurtzite ZnO [A<sub>1</sub>(LO)], and its overtones [A<sub>1</sub>(2LO) and A<sub>1</sub>(3LO)] predominate the spectrum.<sup>13</sup>

With an active area of 1 cm<sup>2</sup>, bare TiO<sub>2</sub> NTs or ZnO/TiO<sub>2</sub> NTs were used as the working photoelectrode and subjected to the irradiation of visible light (100 mW/cm<sup>2</sup>) for PC measurements in a three-electrode cell in 0.5 M Na<sub>2</sub>SO<sub>4</sub> using a CHI electrochemical analyzer (CHI 660A). A Xe lamp was used as the light source to provide visible light by cutting ultraviolet (UV) light using a high-pass filter with a cutoff of 380 or 420 nm. Fig. 3 compares the transient photocurrent response of ZnO/TiO<sub>2</sub> over several on-off cycles of intermittent visible illumination with that of bare TiO<sub>2</sub>. For the as-fabricated ZnO/TiO<sub>2</sub> NTs, the photoelectrochemical activity is equal to or smaller than that of the bare TiO<sub>2</sub> NTs under the irradiation by 380-nm or 420-nm cutoff visible light, not as expected. After annealing, in contrast, a significant enhancement in photoelectrochemical activity is

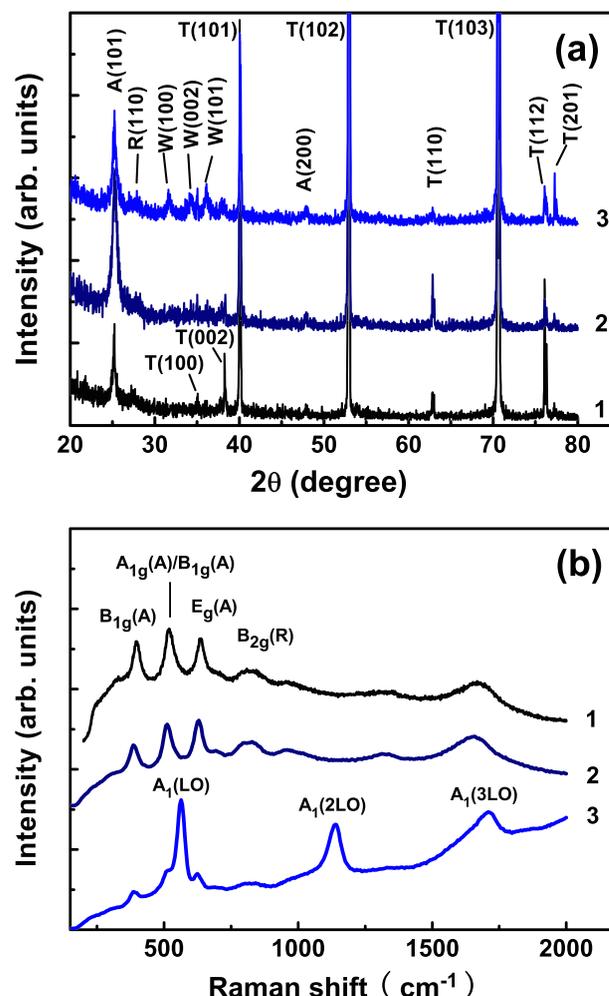


FIG. 2. XRD (a) and Raman spectra (b) of bare TiO<sub>2</sub> NTs (1), as-fabricated ZnO/TiO<sub>2</sub> NTs (2) and annealed ZnO/TiO<sub>2</sub> NTs (3).

observed, suggesting a more efficient separation of photo-generated electron–hole pairs. Post-fabrication annealing improved the quality of the interfaces between ZnO and TiO<sub>2</sub>, as well as the structures of ZnO and TiO<sub>2</sub>, which should be favorable for the transport and separation of photo-generated electrons and holes. Under the irradiation by 420-nm cutoff visible light, in particular, the PC density increases from  $\sim 1.4 \mu\text{A}/\text{cm}^2$  for the bare TiO<sub>2</sub> NTs to  $\sim 2.2 \mu\text{A}/\text{cm}^2$  for the annealed ZnO/TiO<sub>2</sub> NTs. The hetero-structured ZnO/TiO<sub>2</sub> NTs have therefore a photoelectrochemical activity of nearly 60% higher than that of the bare TiO<sub>2</sub> NTs. The transient PC density curves illustrated in Fig. 3 also demonstrate that the fabricated ZnO/TiO<sub>2</sub> NTs have a fast photoresponse speed and reasonably good photostability when used as photoelectrodes. Of more practical importance is the significant enhancement in the photoresponse to the light with longer wavelengths, indicating an extended region of photoresponse and a better match with solar spectrum due to the presence of ZnO coatings.

EIS and flat-band potential measurements were performed with a Potentionstat/Galvanostat (EG & G, 273 A) and a two-phase lock-in amplifier (EG & G, 5210). The impedance measurements were carried out at 0.0 V vs the reference electrode Ag/AgCl with frequencies ranging from 100

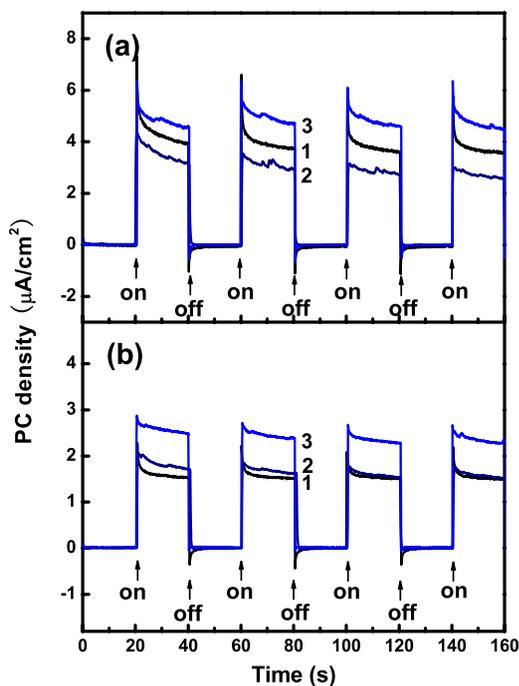


FIG. 3. Transient PC densities of bare  $\text{TiO}_2$  NTs (1), as-fabricated  $\text{ZnO}/\text{TiO}_2$  NTs (2), and annealed  $\text{ZnO}/\text{TiO}_2$  NTs (3) under visible illumination with cutoff of 380 nm (a) and 420 nm (b).

kHz to 0.1 Hz. Typical EIS Nyquist plots of the bare  $\text{TiO}_2$  NTs and the as-fabricated and annealed heterostructured  $\text{ZnO}/\text{TiO}_2$  NTs are illustrated in Fig. 4(a). It can be seen that with the presence of the ZnO coatings, the  $\text{ZnO}/\text{TiO}_2$  NTs present a decrease in charge-transfer resistance ( $R_{\text{ct}}$ ), as implied by the smaller value of the arc diameter in Nyquist plot compared to the bare  $\text{TiO}_2$  NTs.<sup>14</sup> The charge-transfer resistance controls the kinetics at the electrodes.<sup>15,16</sup> The smaller  $R_{\text{ct}}$  reveals the enhanced separation efficiency of photogenerated charge carriers for the  $\text{ZnO}/\text{TiO}_2$  NTs compared with the bare  $\text{TiO}_2$  NTs. With the  $R_{\text{ct}}$  decreasing, the transfer of charges across the interface between the semiconductor and the solution becomes easier, leading to the increase in the photocurrent, consistent with the results of the PC measurements.

The Bode phase plots in Fig. 4(b) show the characteristic frequency peak of the bare  $\text{TiO}_2$  NTs and the heterostructured  $\text{ZnO}/\text{TiO}_2$  NTs. According to the EIS model,<sup>17,18</sup> the lifetime ( $\tau_e$ ) of injected electrons can be deduced from the position of the low frequency peak through the expression  $\tau_e = 1/(2\pi f_{\text{max}})$ , where  $f_{\text{max}}$  is the frequency at the top of the low frequency arc. The frequency peak of the  $\text{ZnO}/\text{TiO}_2$  NTs moves to a lower frequency compared with that of the bare  $\text{TiO}_2$  NTs. That is to say, the electrons in the  $\text{ZnO}/\text{TiO}_2$  electrode have a longer lifetime ( $\sim 250 \mu\text{s}$ ) than those in the bare  $\text{TiO}_2$  NTs electrode ( $\sim 20 \mu\text{s}$ ). The longer lifetime is ascribed to the high electron mobility of the  $\text{ZnO}/\text{TiO}_2$  nano-heterostructure,<sup>19</sup> implying a lower recombination rate and an increased separation of charge carriers.

The flat-band potential was determined by the Mott-Schottky analysis method at a scanning rate of  $50 \text{ mV}\cdot\text{S}^{-1}$  with a potential range from  $-1.0$  to  $1.5 \text{ V}$  at  $100 \text{ Hz}$ . Fig. 4(c) displays the Mott-Schottky plots of the bare  $\text{TiO}_2$  NTs and

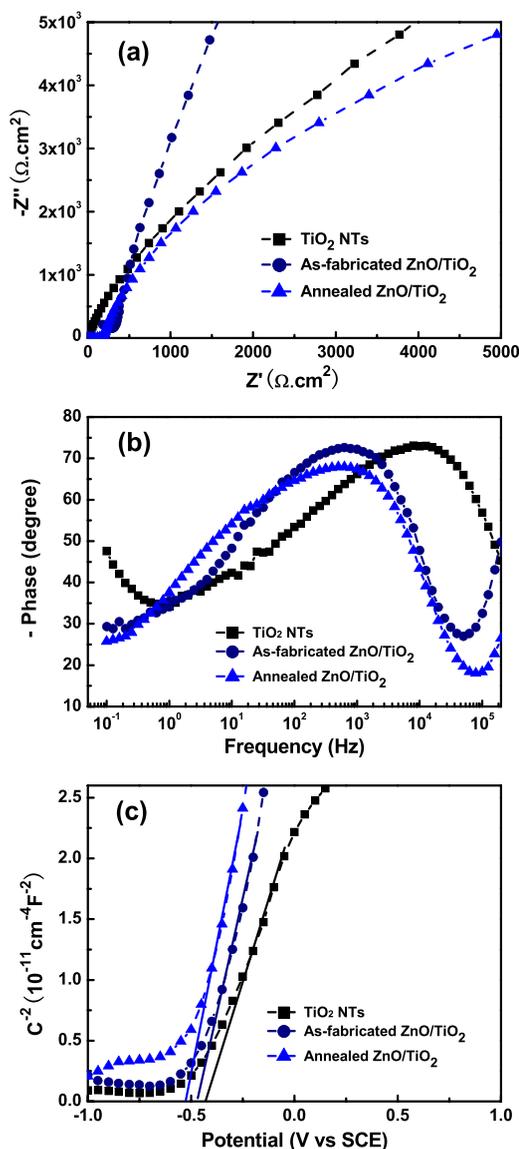


FIG. 4. Nyquist (a), Bode phase (b), and Mott-Schottky (c) plots of bare  $\text{TiO}_2$ , as-fabricated  $\text{ZnO}/\text{TiO}_2$  NTs and annealed  $\text{ZnO}/\text{TiO}_2$  NTs electrodes in  $0.5 \text{ M Na}_2\text{SO}_4$ .

the  $\text{ZnO}/\text{TiO}_2$  NTs. The flat-band potential ( $V_{\text{fb}}$ ) was determined by intersecting the tangent of Mott-Schottky curves with the potential axis.<sup>14</sup> Compared with the bare  $\text{TiO}_2$  NTs,  $V_{\text{fb}}$  shifts negatively for the  $\text{ZnO}/\text{TiO}_2$  NTs whether annealed or not. The value of  $V_{\text{fb}}$  for the annealed  $\text{ZnO}/\text{TiO}_2$  NTs shifts to  $-0.53 \text{ V}$  compared with  $-0.42 \text{ V}$  for the bare  $\text{TiO}_2$  NTs, revealing a smaller barrier for charge transfer in the heterostructured  $\text{ZnO}/\text{TiO}_2$  NTs, which is consistent with the above photoelectrochemical and electrochemical measurements. The  $V_{\text{fb}}$  plays an important role in photoelectrochemical performance. With a more negative  $V_{\text{fb}}$ , a higher open-circuit voltage can be expected when used as the photoelectrode in a photovoltaic device.

In conclusion,  $\text{ZnO}-\text{TiO}_2$  heterogeneous structures in the form of vertically aligned ZnO-coated  $\text{TiO}_2$  nanotubes were fabricated by atomic layer deposition of ZnO coatings on electrochemical anodization formed  $\text{TiO}_2$  nanotubes. The hetero-nanostructures are composed of anatase  $\text{TiO}_2$  nanotubes and wurtzite ZnO coatings. Compared with the

bare TiO<sub>2</sub> NTs, the transient photocurrent increases to about 1.6 times for the annealed ZnO/TiO<sub>2</sub> NTs under visible illumination, indicating an enhancement in the photoelectrochemical activity. This can be explained in terms of improved charge separation in the ZnO/TiO<sub>2</sub> NTs, which was confirmed by electrochemical characterization. The longer electron lifetime, the lower electron transport resistance, and the more negative flat-band potential of the heterostructured ZnO/TiO<sub>2</sub> NTs are favorable for electron transport with less diffusive hindrance, leading to the suppression in electron-hole recombination and the improvement in photoelectrochemical properties.

This work was supported by the National Basic Research Program of China (No. 2012CB934303), the National Natural Science Foundation of China (No. 11275051), and the Doctoral Fund of Chinese Ministry of Education (No. 20110071110020). The authors thank Professor X. L. Cui for her helpful discussion and Mr. P. Zhao for his assistance in measurements.

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