Fabrication and correlation between photoluminescence and photoelectrochemical properties of vertically aligned ZnO coated TiO2 nanotube arrays

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ABSTRACT

We report on a study on the correlation between the photoluminescence and the photoelectrochemical properties of ZnO–TiO2 heterogeneous nanostructure composed of anatase TiO2 nanotubes and wurtzite ZnO coatings. Vertically aligned ZnO coated TiO2 nanotube (ZnO/TiO2 NT) arrays have been fabricated by atomic layer deposition of ZnO coatings on electrochemical anodization formed TiO2 nanotubes. The obtained ZnO/TiO2 NT arrays show higher photosensitivity to shorter wavelength light than to longer wavelength light. A reduction in photoluminescence and an enhancement in photoelectrochemical activity are observed for annealed ZnO/TiO2 NT arrays. ZnO/TiO2 NTs with thinner ZnO coatings rather than thicker ZnO coatings have better photoelectrochemical properties. Compared with bare TiO2 NT arrays, an increase in photocurrent of about 50 percent is obtained for the arrays of 450 °C annealed ZnO/TiO2 NTs with 10-cycle deposition of ZnO coatings under visible illumination with cutoff of 420 nm.

1. Introduction

By virtue of their high surface-to-volume ratio and superior optical, electronic and photoelectrochemical properties, nanostructured TiO2 and ZnO have recently attracted much attention because of their potential applications in photovoltaic processes, photocatalytic reactions, etc. [1–3]. Both metal oxides have also advantages of low cost, stability, nontoxicity, and ease of availability. Among various nanostructured TiO2, highly ordered tubular nanostructures i.e. TiO2 nanotubes (NTs) are of particular interest because of their larger surface area which increases the density of active sites for surface reactions and improves interfacial carrier transfer rates [4–6]. The aligned NT structure also dramatically improves charge transport properties, which greatly contributes to photoelectrochemical performance. TiO2 NT arrays have therefore been extensively studied as electrodes in photocatalysts [2,7–9] and solar cells [10–12]. ZnO nanomaterials have also been demonstrated to be promising when used in photocatalysts [13–15] and photovoltaics [16–18]. Due to their large band gaps (TiO2: ~3.2 eV, ZnO: ~3.4 eV), however, both TiO2 and ZnO normally only work under UV irradiation, thus restricting their practical applications.

The good compatibility between TiO2 and ZnO allows them to be composed to form a heterogeneous nanostructure. It has been proved that heterostructures composed of nanostructured TiO2 and ZnO can improve the quantum efficiency of photocatalysts and photovoltaics due to the combination of the high reactivity of TiO2 and the large binding energy of ZnO. Covering of a ZnO coating on TiO2 surface also increases the mobility of charge carriers ([TiO2: 0.5 cm2 V−1 s−1] < [ZnO: 200 cm2 V−1 s−1]). The process of electron and hole transfer between the corresponding conduction and valence bands can be improved and a better charge separation of photogenerated carriers can be achieved when compared with catalysts from a single metal oxide. In addition, an extension for spectral range of photoreponse can be expected due to the staggered band alignment of the heterostructures [19–21]. The improved electron and hole conductivity, the enhanced charged carriers separation and the extended photoresponse range, all facilitate an increase of solar conversion efficiencies and are most favorable for photocatalytic reactions and photovoltaic processes [22–25]. Much work has been therefore devoted to nano-scaled ZnO–TiO2 composites, in particular, to one-dimensional hetero-nanostructures such as ZnO modified TiO2 or TiO2 modified ZnO nanotubes (NTs) and nanowires [23–25].

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In the present work, we fabricated vertically aligned ZnO coated TiO$_2$ (ZnO/TiO$_2$) NTs by electrochemical anodization of Ti foil followed by atomic layer deposition (ALD) of ZnO on the TiO$_2$ NTs. After a detailed morphological and structural characterization, the correlation between the photoluminescence (PL) and the photoelectrochemical properties was studied by measuring PL and photocurrents to understand the suppressed radiative recombination and the enhanced charge separation of photogenerated carriers in the nano-heterojunction composed of TiO$_2$ NTs and ZnO coatings as well as to obtain better visible-light photoreponse and higher photoelectrochemical activity.

2. Experimental procedure

2.1. Sample fabrication

Two processes were applied to the fabrication of ZnO/TiO$_2$ NT arrays. Vertical aligned TiO$_2$ NT arrays were first formed on Ti foil (99.99% in purity, 0.1 mm in thickness) by electrochemical anodization which was performed in a two-electrode electrochemical cell using a Ti foil as the working electrode and a graphite sheet as the counter electrode separated by 1.3 cm. Before anodization, the Ti foil was chemically polished in a mixture of de-ionized water, HNO$_3$ and HF with the ratio of 5:4:1 (in volume) for 30 s to remove the surface oxide layer and then rinsed with de-ionized water. The polished Ti foil was anodized in 0.5 wt% HF electrolyte at a constant voltage of 20 V for 40 min to form TiO$_2$ NT arrays. The arrays were then annealed in a furnace at 450 °C for 3 h in atmospheric air to convert the formed amorphous TiO$_2$ into anatase. The annealed TiO$_2$ NTs were used as the template for the deposition of ZnO coatings by ALD (TFS200, BENEQ) using diethylzinc (Zn(C$_2$H$_5$)$_2$, DEZ) as the metal precursor for Zn and de-ionized water (H$_2$O) as the reactant. DEZ was kept at 18 °C and delivered into the deposition chamber with a high purity N$_2$ carrier gas flow. The ZnO coatings were typically deposited by several DEZ–H$_2$O cycles consisting of the sequence: 0.5 s DEZ pulse, 2 s N$_2$ purge, 0.5 s H$_2$O pulse, 2 s N$_2$ purge. A one-cycle deposit of ZnO was approximately 0.2 nm thick when deposited on a polished plane substrate. The deposition temperature and the working pressure were kept at 200 °C and ~1 Torr, respectively. The obtained ZnO coated TiO$_2$ NT arrays were rinsed with de-ionized water and annealed at different temperatures for 30 min in atmospheric air.

2.2. Structural characterization

The surface morphology of the prepared ZnO/TiO$_2$ NT arrays was examined by field-emission scanning electron microscopy (FESEM) with a Hitachi S-4800 microscope. The crystal structure was characterized by X-ray diffraction with a Rigaku D/max-γ B X-ray diffractometer using a rotating anode operating at 40 kV and 300 mA and Ni-filtered Cu K$_α$ radiation (λ = 0.15406 nm). The structure was also characterized through the analysis of vibrational modes by measuring Raman scattering spectra. These measurements were performed with a Jobin-Yvon LabRAM HR 800 UV micro-Raman spectrometer using 488 nm Ar$^+$ laser beam and 325 nm He–Cd laser beam to excite the samples.

2.3. Photoluminescence and photocurrent measurements

PL measurements were performed at room temperature by exciting the samples at normal incidence with a CW 325 nm He–Cd laser. PL spectra were recorded by collecting the emitted luminescence at normal direction with a 0.5 m spectrometer (Acton Research, Spectra Pro 500i) and an intensified charge-coupled device (ICCD, Andor Technology, iStar DH720) attached on the exit port of the spectrometer.

The photoelectrochemical properties were studied by measuring photocurrents in a three-electrode cell with 0.5 M Na$_2$SO$_4$ electrolyte using a CHI electrochemical analyzer (CHI 660A Instruments). With an active area of 1 cm$^2$, TiO$_2$ or ZnO/TiO$_2$ NT arrays were used as the working electrode and subjected to the irradiation of visible light with Ag/AgCl as the reference electrode and Pt foil as the counter electrode. A 500 W xenon lamp was used as the light source to provide two wavelength ranges of visible light by cutting ultraviolet light using high-pass filters with cutoff of 380 or 420 nm. The light intensity on the working electrode was 100 mW/cm$^2$.

Fig. 1. (a) Top-view and (b) cross-sectional SEM images of bare TiO$_2$ NTs, (c) top-view and (d) cross-sectional SEM images of ZnO/TiO$_2$ NTs with 50 cycles of ZnO coating.
3. Results and discussion

3.1. Morphology

Highly ordered and vertically aligned TiO$_2$ NT arrays were formed on Ti foil by electrochemical anodization, as shown in Fig. 1(a) and (b). The bare TiO$_2$ NTs have an average diameter of ~60 nm and a wall thickness of ~15 nm. FESEM examination reveals that the ZnO coatings deposited by ALD cover uniformly the TiO$_2$ NTs, both on the top and the inner walls of TiO$_2$ NTs, even deep down into the tubes, forming ZnO coated TiO$_2$ NT arrays. Fig. 1(c) and (d) shows the planar and cross-sectional FESEM images of the as-fabricated ZnO/TiO$_2$ NT arrays fabricated by depositing 50 cycles of ZnO on TiO$_2$ NTs. It can be seen that the ZnO coated NTs have smaller diameters and thicker walls than the bare TiO$_2$ NTs. Unless otherwise specified, the results described in this paper are obtained with the samples fabricated by depositing 50 cycles of ZnO on electrochemically anodized TiO$_2$ NTs. No changes in morphology were observed for the ZnO/TiO$_2$ NT arrays after annealing.

3.2. Structure

XRD was employed to characterize the crystal structure of ZnO/TiO$_2$ NT arrays as well as that of bare TiO$_2$ NT arrays. Fig. 2(a) illustrates the XRD patterns of the as-fabricated and annealed ZnO/TiO$_2$ NT arrays together with that of the bare TiO$_2$ NT arrays for comparison. The XRD pattern of the bare TiO$_2$ NT arrays exhibits three strong diffraction peaks indexed to the (101), (102) and (103) diffractions of Ti and three weak ones indexed to the (002), (110) and (112) diffractions of Ti, respectively. They are all diffracted by Ti foil and are denoted by T in Fig. 2 (JCPDS 44-1294). Besides, a prominent peak with 2θ at 25.22° and full width at half-maximum (FWHM) of 0.18° exists, is identified as a (101) diffraction of anatase TiO$_2$ (JCPDS 21-1272), denoted as A in Fig. 2. Additionally, a very weak diffraction near 27.40° is resolved, and can be assigned to the (110) diffraction of rutile TiO$_2$, denoted as R in Fig. 2. The TiO$_2$ NT arrays formed by electrochemical anodization are therefore composed of nanocrystallites with almost tetragonal anatase phase. After covered by ZnO, additional weak diffraction peaks appear, as indicated in XRD pattern 2 obtained for the as-fabricated ZnO/TiO$_2$ NT arrays. They can all be ascribed to hexagonal wurtzite ZnO corresponding to the (100), (002), (101) and (110) planes and are denoted by W in Fig. 2. The diffraction angles are somewhat larger than the standard values for bulk ZnO (JCPDS: 36-1451). Fig. 2(b) displays the magnified XRD patterns in the 2θ range from 30.0° to 38.5°. The multi diffractions of XRD pattern reveal a non-oriented growth of ZnO on the surface of TiO$_2$ NTs. The larger diffraction angles suggest imperfection in the crystal structure of ZnO. After annealing, the intensity of the diffractions ascribed to wurtzite ZnO generally increases with a reduced peak width as the annealing temperature increases, especially the (100) and (101) peaks, indicating an improvement in the crystallinity of ZnO after annealing. Compared with the as-fabricated ZnO/TiO$_2$ NT arrays, in addition, nearly all the diffraction angles of ZnO exhibit a small shift towards smaller values. The 2θ values of the ZnO (100) and (101) peaks shift from 32.17° and 36.46° for the as-fabricated sample to 31.64° and 36.10° for the annealed sample at 450 °C, respectively. They are smaller than the standard values for bulk ZnO, suggesting the presence of tensile strain in ZnO most probably due to the larger lattice constants of anatase TiO$_2$ than those of wurtzite ZnO. Using the well-known X-ray diffraction formula for hexagonal structure, the lattice constants of ZnO were determined to be $a = 0.326$ nm and $c = 0.522$ nm, respectively. The above XRD results indicate that the ZnO/TiO$_2$ NT arrays fabricated by atomic layer deposition of ZnO on electrochemically anodized TiO$_2$ NTs are composed of tetragonal anatase TiO$_2$ nanotubes and hexagonal wurtzite ZnO coatings.

Raman scattering measurement confirmed the tetragonal anatase structure of TiO$_2$ and the hexagonal wurtzite structure of ZnO for the fabricated ZnO/TiO$_2$ NT arrays. Tetragonal structure has six Raman active fundamental vibrational modes ($A_{1g} + 2B_{1g} + 3E_g$) [26,27]. For single crystal anatase TiO$_2$, these modes are located at 144 cm$^{-1}$ ($E_g$), 197 cm$^{-1}$ ($E_g$), 399 cm$^{-1}$ ($B_{1g}$), 513 cm$^{-1}$ ($A_{1g}$), 519 cm$^{-1}$ ($B_{1g}$), and 639 cm$^{-1}$ ($E_g$) [28,29]. At low temperatures, the assignment for the modes at 513 and 519 cm$^{-1}$ is not possible because of the overlap between the two modes in an experimental Raman spectrum [30]. Wurtzite ZnO has six Raman active phonon modes $E_2$ (low), $E_2$ (high), $A_1$ (TO), $A_1$ (LO), $E_1$ (TO) and $E_1$ (LO) [31–33]. Spectrum 1 in Fig. 3(a) was taken from the bare TiO$_2$ NT arrays with the excitation by 488 nm Ar$^+$ laser light. This spectrum exhibits five distinct peaks located at 144, 197, 392, 514, and 633 cm$^{-1}$. These peaks are close to those found in the bulk anatase TiO$_2$ [28,29] and can be assigned as characteristic Raman modes $E_g$, $E_g$, $B_{1g}$, $A_{1g}$/$B_{1g}$, and $E_g$, respectively, as shown in Fig. 3(a) where (A) denotes the anatase phase.

Fig. 3(a) also exhibits Raman spectra of ZnO/TiO$_2$ NT arrays. After being covered by ZnO coatings, all the anatase TiO$_2$ modes...
annealed ZnO/TiO$_2$ NTs (4) with 488 nm laser light (a) and 325 nm laser light (b).

laser light because of its indirect-band energy structure [35].

observed by optically exciting the bare TiO$_2$ NT arrays with 325 nm

2-phonon and 3-phonon scattering processes [A$_1$(2LO) and A$_1$

at 1147 and 1720 cm$^{-1}$

are still well resolved for the as-fabricated and annealed samples,

only resulting in intensity decrease. However, the vibrational

tubes and hexagonal wurtzite ZnO coatings.

An additional weak and broad band centered around 820 cm$^{-1}$

are still well resolved for the as-fabricated and annealed samples,

as Cu annealed ZnO/TiO$_2$ NTs (3), and 450 °C annealed ZnO/TiO$_2$ NTs (4) with 488 nm laser light (a) and 325 nm laser light (b).

Fig. 3. Raman scattering spectra obtained by exciting bare TiO$_2$ NTs (1), as-fabricated ZnO/TiO$_2$ NTs (2), 350 °C annealed ZnO/TiO$_2$ NTs (3), and 450 °C annealed ZnO/TiO$_2$ NTs (4) with 488 nm laser light (a) and 325 nm laser light (b).

And almost no visible luminescence can be recognized, suggesting

are still well resolved for the as-fabricated and annealed samples,

as Cu annealed ZnO/TiO$_2$ NTs (3), and 450 °C annealed ZnO/TiO$_2$ NTs (4).

Fig. 4. Room-temperature PL spectra of bare TiO$_2$ NTs (1), as-fabricated ZnO/TiO$_2$

NTs (2), 350 °C annealed ZnO/TiO$_2$ NTs (3), and 450 °C annealed ZnO/TiO$_2$ NTs (4).

3.3. Photoluminescence

Room-temperature PL spectra of the samples are shown in

Fig. 4. As expected, no obvious ultraviolet (UV) luminescence

corresponding to the near-band-edge (NBE) emission of TiO$_2$ was

excited by optically exciting the bare TiO$_2$ NT arrays with 325 nm

Fig. 4. Room-temperature PL spectra of bare TiO$_2$ NTs (1), as-fabricated ZnO/TiO$_2$

NTs (2), 350 °C annealed ZnO/TiO$_2$ NTs (3), and 450 °C annealed ZnO/TiO$_2$ NTs (4).

And almost no visible luminescence can be recognized, suggesting

the absence of oxygen vacancies [35]. In contrast, UV luminescence
centered at about 382 nm (equivalent photon energy of 3.246 eV)
was observed from the as-fabricated ZnO/TiO$_2$ NTs with the same
light excitation. This UV luminescence is emitted from the ZnO
coatings and corresponds to the room-temperature free exciton of
NBE emission of ZnO [34,36,37]. For the ZnO/TiO$_2$ NT arrays after
annealing at 350 °C for 30 min in air, the intensity of the UV NBE
emission decreases as compared with that of the sample without
annealing. The decrease in UV emission suggests a less efficient
radiative recombination of photogenerated electrons and holes
because of charge separation of photogenerated carriers in a type
II nano-heterojunction constructed from wurtzite ZnO and anatase
TiO$_2$. The interface between ZnO and TiO$_2$ was improved during
the post-fabrication annealing, which is favorable for the separa-
tion of photogenerated electrons and holes, resulting in the
suppression of radiative recombination of photogenerated carriers
and hence the reduction in PL intensity. For the ZnO/TiO$_2$ NT arrays
after annealing at 450 °C, the UV NBE emission becomes stronger
than that of the sample annealed 350 °C, which is probably due to
the improvement in the crystal structure of ZnO by high-
temperature annealing. However, the UV emission from the ZnO
coatings is still weaker than that of the as-fabricated ZnO/TiO$_2$ NT
arrays, suggesting that an enhancement of charge separation can
also be expected mainly due to the improved interface between
ZnO and TiO$_2$. It is worthwhile noting that for the prepared ZnO/
TiO$_2$ NT arrays either annealed or not, the visible defect-related
emission is very weak, indicating that few intrinsic defects such as
oxygen vacancies exist in ZnO and TiO$_2$ [35,38].

3.4. Photocurrent

The photoelectrochemical properties of the fabricated ZnO/TiO$_2$
NT arrays were investigated by measuring the photocurrents of
ZnO/TiO$_2$ NT arrays used as the electrode under intermittent
visible illumination and comparing with that of TiO$_2$ NT arrays
under the same illumination. Fig. 5(a) and (b) illustrates transient
photocurrent densities of TiO$_2$ NT arrays (curve 1) and ZnO/TiO$_2$
NT arrays (curves 2–4) over several on–off cycles of visible
illumination with the cutoff wavelengths of 380 and 420 nm,
respectively. By comparing both figures, it can be seen that the
prepared TiO$_2$ NT arrays and ZnO/TiO$_2$ NT arrays respond to the
light with wavelength longer than 420 nm less effectively than to
the light with wavelength shorter than 420 nm. Covering a TiO$_2$
nanotube with a ZnO coating constructs a nano-heterojunction
with type II staggered band alignment, in which the spatial
separation of the charge carriers will reduces the radiative
recombination of the photogenerated electrons and holes [19–21].

As a result, an enhanced photoresponse can be expected. However, it can be seen from Fig. 5 that the coverage of ZnO on the walls of TiO2 NT arrays does not result in an obvious enhancement in the photoresponse to visible illumination, but in a decrease of the photocurrent density, observations which were not expected. Only for the annealed ZnO/TiO2 NT arrays, a slight increase of photocurrent density is observed. With the illumination by visible light with 380 nm cutoff, the photocurrent density increases from ~3.8 μA/cm² for the bare TiO2 NT arrays to ~5.2 μA/cm² for the 450 °C annealed ZnO/TiO2 NT arrays. The increase in photocurrent density is however less (from ~1.4 μA/cm² to ~1.6 μA/cm²) under the illumination by visible light with 420 nm cutoff. As described above, post-fabrication annealing improved the interface between ZnO and TiO2 as well as the structures of ZnO and TiO2, which is favorable for the charge separation of photogenerated carriers and the suppression of radiative recombination of photogenerated electrons and holes. However, it seems that the enhancement in photoresponse by the coverage of ZnO on the walls of TiO2 NTs is not remarkable. One of the factors hampering the enhancement in photoresponse is probably due to a too large thickness of the ZnO coatings on the walls of the TiO2 NTs, which presents a long way for the generated electrons to migrate to the TiO2 surface and the generated holes to migrate to the ZnO surface, and hence is unfavorable for charge separation.

In order to effectively enhance the photoresponse, we fabricated ZnO/TiO2 NT arrays with thinner ZnO coatings on the walls of TiO2 NTs (10 cycles). This configuration exhibits a significant enhancement in photoresponse of ZnO/TiO2 NT arrays as compared with that of the bare TiO2 NT arrays. Fig. 6(a) and (b) compares the photocurrent densities of the ZnO/TiO2 NT arrays fabricated by depositing 10 cycles of ZnO (approximately 2 nm) on the walls of TiO2 NTs with those of the bare TiO2 NT arrays under the same illumination as for the measurements illustrated in Fig. 5. Although the photocurrent densities of the as-fabricated ZnO/TiO2 NT arrays are smaller or equal to those of the bare TiO2 NT arrays under the irradiation by 380 nm or 420 nm cutoff visible light, the photocurrent densities of the annealed ZnO/TiO2 NT arrays increase significantly. The enhanced photoelectrochemical properties should be attributed to the improved interface between ZnO and TiO2 as well as the improved crystal structures of ZnO and TiO2 due to annealing. The former facilitates the charge separation of photogenerated carriers, while the latter increases the mobility of photogenerated carriers. Under the irradiation by 420 nm cutoff visible light, in particular, the photocurrent density increases from ~1.4 μA/cm² for the bare TiO2 NT arrays to ~2.2 μA/cm² for the 450 °C annealed ZnO/TiO2 NT arrays. The photoresponsivity of the ZnO/TiO2 nano-heterostructures has thus a nearly 1.5-fold increase compared with that of bare TiO2 NTs, revealing an enhanced charge separation and a reduced radiative recombination of photoexcited electron–hole pairs in ZnO/TiO2 nano-heterostructure as compared with TiO2 NT. The transient photocurrent density curves illustrated in Fig. 6 also demonstrate that the vertically aligned ZnO/TiO2 NT arrays have a fast photoresponse speed and good photostability when used as electrodes. More important practically is the significant enhancement in photoresponse to the light with longer wavelengths, which reveals an extended region of photoresponse and a better match with the solar spectrum due to the presence of ZnO coatings on TiO2 NTs.

4. Conclusion

In summary, we have measured the photoluminescence and the photocurrents of ZnO coated TiO2 NT arrays to study the correlation between the photoluminescence and the photoelectrochemical properties of ZnO/TiO2 heterogeneous nanostructures. Vertically aligned ZnO/TiO2 NT arrays composed of tetragonal anatase TiO2 NTs and hexagonal wurtzite ZnO coatings were fabricated by atomic layer deposition of ZnO coatings on electrochemically anodized TiO2 NTs. The crystal structures of both ZnO coatings and TiO2 NTs and the interface between ZnO and TiO2 were improved by post-fabrication annealing. With a thin ZnO coating on TiO2 NT, the formed type II staggered band alignment constructed from the band structures ZnO and TiO2 facilatated the charge separation of photogenerated carriers, subsequently suppressed the radiative
recombination of photogenerated carries and enhanced the photo-
electrochemical properties. A reduction in photoluminescence and an
increase in photocurrent were observed for annealed ZnO/TiO2 NT
arrays due to the improvement in the interface between ZnO and TiO2.
The increased photocurrent also results from the improved crystal
structures of ZnO and TiO2. Compared with bare TiO2 NTs, the
photoelectrochemical activity increased to about 1.5-fold for 450 °C
annealed ZnO/TiO2 NTs with 10-cycle deposition of ZnO coatings on
TiO2 NTs under visible illumination with 420 nm cutoff.

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