Enhanced Photoelectrochemical Activity of ZnO-Coated TiO\textsubscript{2} Nanotubes and Its Dependence on ZnO Coating Thickness

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Abstract

One-dimensional heterogeneous nanostructures in the form of ZnO-coated TiO\textsubscript{2} nanotubes (ZnO/TiO\textsubscript{2} NTs) were fabricated by atomic layer deposition of an ultrathin ZnO coating on electrochemical anodization-formed TiO\textsubscript{2} nanotubes (NTs) with the thickness of ZnO coating being precisely controlled at atomic scale, and the photoelectrochemical activity of the fabricated ZnO/TiO\textsubscript{2} NTs and the influence of ZnO coating and its thickness were studied. The structures of TiO\textsubscript{2} NTs and ZnO coatings were characterized by X-ray diffraction, Raman backscattering spectroscopy, and transmission electron microscopy. The photoelectrochemical activity was studied through the measurements of electrochemical impedance, flat-band potential, and transient photocurrent density. The TiO\textsubscript{2} NTs exhibit anatase structure, and the ZnO coatings are structured with hexagonal wurtzite. The photoelectrochemical activity of the ZnO/TiO\textsubscript{2} NTs is strongly dependent on the thickness of ZnO coating. ZnO/TiO\textsubscript{2} NTs with a thinner rather than a thicker ZnO coating exhibit better photoelectrochemical activity with reduced charge transfer resistance, increased negative flat-band potentials, and enhanced photocurrent densities. Under visible illumination, an increase of about 60\% in the photoelectrochemical activity is obtained for ZnO/TiO\textsubscript{2} NTs with an about 2-nm-thick ZnO coating.

Keywords: Photoelectrochemical activity, Heterogeneous nanostructure, TiO\textsubscript{2}, ZnO, ZnO-coated TiO\textsubscript{2} nanotube

Background

Titania (TiO\textsubscript{2}) and zinc oxide (ZnO) have recently attracted much attention because of their excellent optical, photoelectronic, and photoelectrochemical properties and consequently their potential applications in wide fields including photocatalytic reactions and photovoltaic processes [1–5]. Both metal oxides also have advantages of low cost, physical and chemical stability, nontoxicity, and ease of availability. In addition, TiO\textsubscript{2} and ZnO have similar band-gap energies (\textsim 3.22 eV for TiO\textsubscript{2} and \textsim 3.37 eV for ZnO) and are compatible to each other to compose heterogeneous materials. A variety of heterostructured materials composed of TiO\textsubscript{2} and ZnO (TiO\textsubscript{2}-ZnO) have been reported. Heterogeneous TiO\textsubscript{2}-ZnO materials exhibit improved individual and combined properties which are very distinct from those of the single constituting materials TiO\textsubscript{2} and ZnO and are promising for applications such as photocatalytic reactions and photovoltaic processes. Dye-sensitized solar cells using ZnO-coated nanocrystalline TiO\textsubscript{2} films as electrodes, for example, have shown enhanced conversion efficiencies [6]. In particular for heterostructured TiO\textsubscript{2}-ZnO, nanoscaled TiO\textsubscript{2} and ZnO are superior to bulk and film materials in their large surface-to-volume ratio for a large interface between TiO\textsubscript{2} and ZnO. Therefore, nanosized heterostructures constructed of nanoscaled TiO\textsubscript{2} and ZnO show better photoelectronic, photochemical, and photoelectrochemical properties. When used as a photocatalyst or a photoelectrode, for example, heterogeneous ZnO-TiO\textsubscript{2} nanostructures can provide improved performance due to the combination of the high activity of TiO\textsubscript{2} with the high electron mobility of ZnO. Furthermore, the alignment of the staggered band gaps of TiO\textsubscript{2} and ZnO is favorable for the separation of electrons and holes and consequently the suppression of electron-hole recombination [7, 8]. The staggered band alignment also results in an extension for

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spectral range of photoresponse, which allows an efficient use of light with a wide spectral band [9, 10]. Therefore, better electrochemical and photoelectrochemical properties and hence enhanced photocatalytic activities and increased photovoltaic efficiencies can be expected for the heterogeneous ZnO-TiO₂ nanostructures because of their improved charge conductivity, enhanced charged carrier separation, and extended photoresponse range [11, 12]. Of the diverse ZnO-TiO₂ nanoheterostructures, one-dimensional (1D) nanogeometry has received particular attention in the photocatalytic and photovoltaic applications due to its superior charge transport ability and short recombination pathway, which significantly suppresses the recombination of photogenerated electrons and holes [13–16]. The ultraviolet (UV) photoconductivity and photosensitivity of TiO₂-coated ZnO nanorods have been reported to be largely enhanced [17]. Using ZnO-sheathed TiO₂ as photoanodes, dye-sensitized solar cells have shown enhanced performance [18]. ZnO-coated TiO₂ nanotube (ZnO/TiO₂ NT) is one of the most studied 1D heterogeneous ZnO-TiO₂ nanostructures [16, 19–21]. However, the optimized photocatalytic activity and photovoltaic efficiency of heterogeneous TiO₂-ZnO materials including 1D heterogeneous ZnO-TiO₂ nanostructures are strongly dependent on the morphology and geometry.

In comparison to bare TiO₂ NTs, TiO₂ NTs covered by a thin ZnO coating usually present improved electrochemical and photoelectrochemical properties and are expected to have high quantum efficiencies for photocatalytic reactions and photovoltaic processes [16, 19–21]. As a nanoscaled heterostructure, it has been proved that the properties of ZnO/TiO₂ NTs are strongly dependent on the geometry and morphology of the heterogeneous nanogeometry, the crystal structure of TiO₂ and ZnO, and the interfacial quality between TiO₂ and ZnO. In the present work, ZnO/TiO₂ NTs were fabricated by atomic layer deposition (ALD) of a ZnO coating on the walls of electrochemically anodized TiO₂ NTs, and the thickness of ZnO coating was precisely controlled at a sub-nanometer level by varying the growth cycle of ZnO during the ALD process. The properties of the fabricated ZnO/TiO₂ NTs and their dependence on the ZnO coating thickness were studied for optimizing the electrochemical and photoelectrochemical activities.

**Methods**

The method and the equipment used for sample fabrication have been described previously [22]. Through an electrochemical anodization process, vertically aligned TiO₂ NTs were first formed on a polished Ti foil (99.99 % in purity, 0.1 mm in thickness). The formed TiO₂ NTs were annealed at 450 °C in air for 3 h. A thin ZnO coating was then deposited on the walls of the TiO₂ NTs by means of ALD using Zn(CH₂CH₃)₂ (diethylzinc (DEZ)) and deionized H₂O as zinc and oxygen precursors, respectively. The deposition of the ZnO coating was performed at 200 °C and the growth of the ZnO coating on the high-aspect-ratioed TiO₂ NTs was governed by self-limiting reactions [23, 24]

\[
\text{ZnOH}^+ + \text{Zn(CH₂CH₃)₂} \rightarrow \text{ZnO–ZnCH₂CH₃}^+ + \text{CH₃CH₃}.
\]

(1)

\[
\text{ZnCH₂CH₃}^+ + \text{H₂O} \rightarrow \text{ZnOH}^+ + \text{CH₃CH₃}
\]

(2)

The thickness of the deposited ZnO coating was precisely controlled by ALD growth cycles with 1 cycle of 0.5-s DEZ pulse, 2-s N₂ purge, 0.5-s H₂O pulse, and 2-s N₂ purge. Several sample groups of ZnO/TiO₂ NTs were prepared with the same TiO₂ NTs but different ZnO coating thickness. Two of them, one with a 10-cycle deposit of ZnO coating (referred as 10-cycle ZnO/TiO₂ NTs) and the other with a 25-cycle deposit of ZnO coating (referred as 25-cycle ZnO/TiO₂ NTs), were compared in this work for a study of the influence of ZnO coating thickness on the properties including photovoltaic activity. The obtained heterogeneous nanostructured ZnO-coated TiO₂ NTs samples were rinsed with deionized water and annealed at 450 °C for 30 min in air.

The sample morphology was examined by field-emission scanning electron microscopy (FESEM) with a Hitachi S–4800 microscope. The morphology and microstructure of the samples was characterized with a transmission electron microscope (TEM, Tecnai G² F20 S-Twin). The composition and thickness of the ZnO coatings were evaluated by Rutherford backscattering (RBS) method using a 2.0-MeV He⁺ beam at 165 ° scattering geometry. The He⁺ beam generated by a 9SDH-2 tandem accelerator at Fudan University was collimated to a diameter of 1.0 mm for RBS measurements. The structure of the samples was characterized by X-ray diffraction (XRD) with a Rigaku D/ max-γ B X-ray diffractometer using a Ni-filtered Cu Kα radiation. The sample structure was also characterized through the analysis of vibrational modes by means of Raman backscattering spectroscopy which was performed with a Jobin-Yvon LabRAM HR 800 UV micro-Raman spectrometer using a 325-nm He–Cd laser light to excite the samples. UV–visible absorption spectra of the samples were recorded with a UV–visible spectrophotometer (Shimadzu UV-350) using a diffuse reflectance integrating sphere.

Photoluminescence (PL) measurements were carried out at room temperature (300 K) and a reduced temperature of 20 K by exciting the samples with a nonpolarized 325-nm He–Cd laser beam, dispersing the emitted luminescence with a 0.5-m spectrometer (Spectra Pro 500i, Acton), and recording the PL spectra with an intensified
charge-coupled device (ICCD, iStar DH720, Andor). The spot size of the 325-nm laser beam exciting the samples for PL measurement is about 1 mm in diameter. The electrochemical properties of the samples were studied by electrochemical impedance and flat-band potential measurements using a Potentionstat/Galvanostat (EG & G, 273 A) and a two-phase lock-in amplifier (EG & G, 5210). In a three-electrode cell with a 0.5 M Na$_2$SO$_4$ solution, the impedance measurements were carried out at 0.0 V versus the reference electrode Ag/AgCl with frequencies ranging from 100 kHz to 0.1 Hz, and the flat-band potentials of the samples were determined from the Mott–Schottky plots obtained by measuring at 100 Hz with potentials scanning from 1.0 to 1.5 V at 50 mV/s. Linear-sweep cyclic voltammetry was performed at a potential ranging from +1.5 to −1.5 V versus Ag/AgCl in 0.5 M Na$_2$SO$_4$ at a scan rate of 50 mV/s. With an active area of 1 cm$^2$, the samples were used as photoelectrodes and subjected to intermittent irradiation of visible light (100 mW/cm$^2$) for photocurrent (PC) density measurements in the three-electrode cell in 0.5 M Na$_2$SO$_4$ using a CHI electrochemical analyzer (CHI 660A). A 500-W xenon lamp was used as the light source to provide visible light by removing infrared light with a quartz wafer filter and cutting ultraviolet (UV) light using a high-pass filter with a cutoff of 380 or 420 nm.

Results and Discussion

Figure 1 shows typical planar and cross-sectional FESEM images of the samples. Figure 1a indicates that highly ordered and vertically aligned TiO$_2$ NTs having an average diameter of ~60 nm and a wall thickness of ~15 nm were formed on Ti foil by electrochemical anodization process. Figure 1b, c shows the planar and cross-sectional FESEM images of ZnO-coated TiO$_2$ NTs fabricated by depositing 10 or 25 cycles of ZnO on TiO$_2$ NTs. It can be seen that the TiO$_2$ NTs are fully and uniformly covered by the ZnO coatings on the top and the side walls, even deep down to the bottom of the tubes. The ZnO-coated TiO$_2$ NTs have the same shapes as the bare TiO$_2$ NTs, but with slightly reduced tube diameters and thickened tube walls. Generally, the 25-cycle ZnO-coated TiO$_2$ NTs have smaller diameters and thicker walls than the 10-cycle ZnO-coated TiO$_2$ NTs.

Figure 2a shows the random RBS spectra of the bare TiO$_2$ NTs and the ZnO-coated TiO$_2$ NTs. Due to the nanosized tubular structure of the samples, the signals from the scattered helium atoms have no clear and steep edges. The signals attributed to O atoms in the samples are weak, and the resolution is limited by the overlap of its peaks on the base spectra of the heavy element Ti in the underlying Ti foil. The presence of TiO$_2$ NTs on Ti foil can be evidenced by the decreasing of the Ti signal near the Ti background edge. The salient peaks in the channel number ranging from 390 to 430 in the spectra of the ZnO-coated TiO$_2$ NTs are related to the contribution from Zn atoms in the ZnO coatings covering the TiO$_2$ NTs. The coverage of the TiO$_2$ NTs by ZnO coatings also results in further decreasing of the Ti signal near the Ti background edge. In comparison to the spectrum of the 10-cycle ZnO/TiO$_2$ NTs, the higher yield attributed to Zn in the spectrum of the 25-cycle
ZnO/TiO$_2$ NTs indicates the thicker ZnO coating of the 25-cycle ZnO/TiO$_2$ NTs. However, the thickness and the composition of the ZnO coatings cannot be calculated from the spectra shown in Fig. 2a because of the complicated profiles of the spectra taken from the nanosized tubular-structured samples. RBS analysis was also carried out on a ZnO film grown on a polished Si (100) substrate by ALD with 50-cycle deposit of ZnO with the other conditions remaining the same as for depositing ZnO coatings on the TiO$_2$ NTs. The RBS spectrum recorded for the ZnO film on Si is shown in Fig. 2b. The SIMNRA simulation [25] of this spectrum reveals that the ZnO film has a stoichiometric composition and a thickness of 10.25 nm, from which it is deduced that the thickness of 1-cycle deposit of ZnO is about 0.21 nm, consistent with the result obtained by spectroscopic ellipsometry performed for a ZnO thin film on a Si substrate deposited by the same method and conditions, which gave an estimated thickness of 0.225 nm for 1-cycle deposit of ZnO [26]. Therefore, the 10-cycle ZnO/TiO$_2$ NTs and 25-cycle ZnO/TiO$_2$ NTs can be estimated to have a ZnO coating of about 2.10 and 5.25 nm in thickness, respectively.

Figure 3a illustrates the XRD patterns of the bare TiO$_2$ NTs and the TiO$_2$ NTs covered by ZnO coatings. Besides the diffractions from the Ti foil (denoted by T), a prominent diffraction peak with 2θ at 25.22 is identified for the samples whether covered by ZnO or not. This peak is indexed to the (101) diffraction of anatase TiO$_2$ (denoted by A in Fig. 3a) (JCPDS 21-1272). For the bare TiO$_2$ NTs, in addition, a weak peak near 2θ = 27.40 can be recognized, which could be assigned to the (110) diffraction of rutile TiO$_2$ (denoted by R) (JCPDS 21-1276). The TiO$_2$ NTs are therefore of nearly tetragonal anatase phase with minor rutile phase. For the TiO$_2$ NTs covered by a 10-cycle deposit of ZnO, three additional peaks appear, which can be ascribed to hexagonal wurtzite ZnO (denoted by W) and are related to the diffractions from
the (100), (002), and (101) orientations of wurtzite ZnO (JCPDS: 36-1451), respectively. The multidiffractions reveal the non-oriented growth of ZnO on the TiO$_2$ NTs. For the TiO$_2$ NTs covered by a 25-cycle deposit of ZnO coating, the diffractions ascribed to wurtzite ZnO increase with a reduced peak width, indicating an improvement in the crystallinity of the ZnO coating with the coating thickness increasing. The above XRD results reveal that fabricated ZnO/TiO$_2$ NTs are constructed of tetragonal anatase TiO$_2$ NTs and hexagonal wurtzite ZnO coatings.

Raman backscattering measurements confirm the anatase structure of the TiO$_2$ NTs and the wurtzite structure of the ZnO coatings, as shown in Fig. 3b. The Raman spectrum taken from the bare TiO$_2$ NTs exhibits three distinct peaks located at 392, 514, and 633 cm$^{-1}$, respectively. They are attributed to the characteristic Raman reactive B$_{1g}$ mode, doublet A$_{1g}$/B$_{1g}$ mode, and E$_g$ mode of anatase TiO$_2$ [27, 28]. In addition, a broad band centered near 820 cm$^{-1}$ is resolved, which is attributed to the B$_{2g}$ mode of rutile TiO$_2$. In the Raman spectrum taken from the bare TiO$_2$ NTs, A and R in parentheses denote the anatase and the rutile phase of TiO$_2$, respectively. After being covered by a 10- or 25-cycle deposit of ZnO coating, the above TiO$_2$ modes are greatly suppressed and the Raman spectra are predominated by three strong backscattering peaks at 574, 1147, and 1720 cm$^{-1}$. The strongest peak at 574 cm$^{-1}$ is attributed to the polar optical mode associated with longitudinal optical (LO) phonons of ZnO [A$_1$(LO)], while the other two peaks at 1147 and 1720 cm$^{-1}$ are the overtones of A$_3$(LO) and result from 2- and 3-phonon scattering processes [A$_1$(2LO) and A$_1$(3LO)], respectively [29, 30]. The reduction in the measured Raman signals scattered from TiO$_2$ for the ZnO-coated TiO$_2$ nanotubes is mainly attributed to the absorption of the photons in the exciting 325-nm light by the ZnO coating.

The morphology of the ZnO/TiO$_2$ NTs and the crystal structure of the TiO$_2$ tubes and the ZnO coatings are further confirmed by TEM and high-resolution TEM examination, as shown in Fig. 4 which depicts representative TEM and high-resolution TEM images taken from the 25-cycle ZnO/TiO$_2$ NTs. The heterogeneous structure can be seen clearly from the images shown in Fig. 4a, b. We have measured the wall thickness of TiO$_2$ tube yielding ~15 nm which is consistent with the result obtained by FESEM, and the thickness of ZnO coating on the inner-wall of TiO$_2$ tube giving ~5 nm, consistent with that estimated by RBS. The high-resolution TEM image evidences the crystal structure of the TiO$_2$ tube and the ZnO coating. The interplanar spacings were determined for both TiO$_2$ and ZnO. We can see from Fig. 4b that TiO$_2$ is nearly single crystalline with interplanar spacing of 0.35 nm which is in agreement with $d_{101}$ of anatase TiO$_2$. Figure 4b also reveals several orientations of ZnO. Their interplanar spacings were determined to be 0.28, 0.26, and 0.25 nm, respectively, matching well with $d_{100}$, $d_{002}$, and $d_{101}$ of wurtzite ZnO. The crystal structure of the sample characterized by high-resolution TEM is in conformity with the XRD characterization.

The recorded UV–visible absorption spectra of the samples are displayed in Fig. 5. It can be seen that compared with the bare TiO$_2$ NTs, the ZnO-coated TiO$_2$ NTs exhibit an obvious red shift in the absorption edge, indicating that the ZnO coating on the TiO$_2$ NTs extends the photoresponse to longer wavelength, and the red shift increases with the ZnO coating thickness increasing. The red shift in the absorption edge of heterostructured materials composed of TiO$_2$ and ZnO has been reported and can be attributed to the staggered band gaps of TiO$_2$ and ZnO and the interface effect between TiO$_2$ and ZnO [9, 31, 32]. The red-shifted absorption edge and consequently the extended photoresponse...
region allow the ZnO-coated TiO$_2$ NTs to work in the visible region.

Figure 6a shows the PL spectra of the samples measured at 300 K. For the 25-cycle ZnO/TiO$_2$ NTs, an intense UV luminescence peaking at about 376 nm is observed, with very weak visible emission associated with defects such as oxygen vacancies [33, 34]. This UV luminescence is emitted from the ZnO coatings and corresponds to the room-temperature free exciton-related near-band-edge (NBE) emission of ZnO [30, 35, 36]. The intense UV ZnO NBE luminescence and the weak defect-related emission reveal the high quality of the ZnO coating and low concentration of defects. Aside from weak defect-related emission, in contrast, no obvious luminescence can be observed from the bare TiO$_2$ NTs and the TiO$_2$ NTs covered by a 10-cycle deposit of ZnO coating. The former is expected to have low probability of radiative recombination processes due to the indirect band energy structure of TiO$_2$ [37, 38]. For the latter, the light excitation of the ultrathin ZnO coating might be ineffective, and hence, the generation of electrons and holes in the ultrathin ZnO coating is limited due to its ineffective absorption of exciting photons. Additionally, the suppression of electron-hole recombination due to the efficient spatial separation of electrons and holes in the heterostructured ZnO/TiO$_2$ reduces the luminescence from the ZnO coating.

Generally, the PL from the sample becomes stronger at low temperatures. The inset in Fig. 6a compares the PL spectra of the 25-cycle ZnO/TiO$_2$ NTs measured at 300 and 20 K, respectively. At 20 K, the intensity of the UV ZnO NBE luminescence is increased about one order of magnitude for the 25-cycle ZnO/TiO$_2$ NTs as a result of the freezing of phonons and the quenching of nonradiative recombination processes at low temperatures [30, 35, 39]. The UV ZnO NBE luminescence at low temperature is still without the company of defect-related visible emission, but with a narrowed width as compared to that recorded at room temperature, as shown in Fig. 6b which illustrates the PL spectra recorded at 20 K. For the bare TiO$_2$ NTs, only the defect-related visible emission is observed. In addition to the defect-related visible emission, the PL of the 10-cycle ZnO/TiO$_2$ NTs includes a weak UV NBE luminescence from the ZnO coating with its intensity less than 2 % of
that of the 25-cycle ZnO/TiO$_2$ NTs. The comparison of the PL spectra of the ZnO-coated TiO$_2$ NTs with that of the bare TiO$_2$ NTs, measured at room temperature and low temperature, suggests that the visible emission is most probable associated with the defects in TiO$_2$ NTs. Moreover, the much weak PL from the 10-cycle ZnO/TiO$_2$ NTs as compared to that from the 25-cycle ZnO/TiO$_2$ NTs reveals a lower rate of radiative recombination of photogenerated electrons and holes in the 10-cycle deposit of ZnO than in 25-cycle deposit of ZnO, implying that ZnO/TiO$_2$ NTs with a thinner rather than a thicker ZnO coating have more efficient spatial separation of photogenerated electrons and holes and hence exhibit better photoelectrochemical activity as will be described below.

From the typical electrochemical impedance spectroscopy (EIS) Nyquist plots of the bare TiO$_2$ NTs and the heterogeneous structured ZnO-coated TiO$_2$ NTs illustrated in Fig. 7a, we can determine the charge transfer resistance ($R_{ct}$) of the samples when being used as electrodes. The charge transfer resistance of an electrode is one of the important parameters concerning the kinetics at the electrode. Compared to the bare TiO$_2$ NTs, the TiO$_2$ NTs covered by a 10-cycle deposit of ZnO present a decrease in $R_{ct}$, as implied by the smaller value of the arc diameter in the Nyquist plot, indicating that the transfer of charges across the interface between the electrode and the solution becomes easier. However, the presence of the 25-cycle deposit of ZnO on the TiO$_2$ NTs results in an increased $R_{ct}$, even higher than that of the bare TiO$_2$ NTs. The increase in $R_{ct}$ is probably attributed to a longer transport path for charges because of the thicker ZnO coating on the TiO$_2$ NTs and to a higher recombination rate of electrons and holes in the electrode, since the recombination rate in ZnO is higher than that in the TiO$_2$ [40].

Figure 8 shows the cyclic voltammetry curves obtained for the bare TiO$_2$ and the ZnO-coated TiO$_2$ NTs electrodes in the 0.5 M Na$_2$SO$_4$ solution at a scan rate of 50 mV/s. All the cyclic voltammograms show hysteretic shape characteristics, which suggests that electron charging/discharging occurs in the electrode/electrolyte interface, forming Faradic currents in the electrolyte. Moreover, the ZnO coating on TiO$_2$ induces a shift in the on-set potential of the cathodic current, consistent with the shift of flat-band potential, revealing that the ZnO coating plays a role as a blocking layer suppressing electron flow to the electrolyte. The shift of the on-set
potential is also attributed to the changes of the interface states or traps on TiO$_2$ surface covered by the ZnO coating.

Figure 9a illustrates the transient photocurrent responses of the ZnO-coated TiO$_2$ NTs used as photoelectrodes under intermittent illumination by light with a wavelength cutoff of 380 nm and compares with that of the bare TiO$_2$ NTs photoelectrode. Whether covered by a ZnO coating or not, the PC densities of the photoelectrode have a transient increase when the light on the electrode is turned on and decrease nearly to zero as soon as the incident light is turned off, demonstrating that the samples have a fast photoresponse speed and reasonably good photostability when used as photoelectrodes. Obviously, the coverage of the TiO$_2$ NTs by ZnO coatings results in an increase in PC density and hence an enhancement in photoelectrochemical activity compared with the uncovered TiO$_2$ NTs, and it seems that the increase of PC density and the enhancement of photoelectrochemical activity are nearly the same for the TiO$_2$ NTs covered by a 10- or 25-cycle deposit of ZnO coating. The increased PC density and the enhanced photoelectrochemical activity of the ZnO-coated TiO$_2$ NTs can be attributed to the nanotube-shaped TiO$_2$ structure which has a large effective surface area in close proximity with the ZnO coating and consequently results in an increase of diffusive transport of photogenerated electrons and holes. In the heterogeneous structure composed of anatase TiO$_2$ and wurtzite ZnO, in addition, an efficient spatial separation of photogenerated electrons and holes is expected, which also contributes to the increased PC density and the enhanced photoelectrochemical activity.

The enhanced photoelectrochemical activity of the ZnO-coated TiO$_2$ NTs can be better understood based on the staggered band alignment for the ZnO-coated TiO$_2$ NTs on Ti foil as delineated in Fig. 10. Although the band gap energies of ZnO and TiO$_2$ are similar (~3.37 vs ~3.22 eV), both the conduction band minimum (CBM) and valence band maximum (VBM) of ZnO lie a little above those of TiO$_2$ [45], making a type-II heterojunction with a work function of about 5.2 eV for ZnO [46] and that of about 5.1 eV for TiO$_2$ [47]. The contact between TiO$_2$ and the underlying Ti foil is ohmic by nature, as the work function of Ti (4.33 eV) is less than that of TiO$_2$. Therefore, when the nanoheterostructure is subjected to a positive bias, the electrons of the CB of ZnO can easily enter into the CB of TiO$_2$ and then collected by the metallic Ti foil, whereas the holes of the VB of TiO$_2$ can easily enter into the VB of ZnO. With excitation under light illumination, the photogenerated electrons in both TiO$_2$ and ZnO reach at the interface between TiO$_2$ and the Ti foil and are collected by the Ti foil, whereas the photogenerated holes reach at the ZnO surface where charge transfers occur between the electrolyte and the ZnO surface via electrochemical reactions.

The increased PC density and the enhanced photoelectrochemical activity can also be ascribed to a large number of photocurrent responses of the ZnO-coated TiO$_2$ NTs used as photoelectrodes under intermittent illumination by light with a wavelength cutoff of 380 nm and compares with that of the bare TiO$_2$ NTs photoelectrode. Whether covered by a ZnO coating or not, the PC densities of the photoelectrode have a transient increase when the light on the electrode is turned on and decrease nearly to zero as soon as the incident light is turned off, demonstrating that the samples have a fast photoresponse speed and reasonably good photostability when used as photoelectrodes. Obviously, the coverage of the TiO$_2$ NTs by ZnO coatings results in an increase in PC density and hence an enhancement in photoelectrochemical activity compared with the uncovered TiO$_2$ NTs, and it seems that the increase of PC density and the enhancement of photoelectrochemical activity are nearly the same for the TiO$_2$ NTs covered by a 10- or 25-cycle deposit of ZnO coating. The increased PC density and the enhanced photoelectrochemical activity of the ZnO-coated TiO$_2$ NTs can be attributed to the nanotube-shaped TiO$_2$ structure which has a large effective surface area in close proximity with the ZnO coating and consequently results in an increase of diffusive transport of photogenerated electrons and holes. In the heterogeneous structure composed of anatase TiO$_2$ and wurtzite ZnO, in addition, an efficient spatial separation of photogenerated electrons and holes is expected, which also contributes to the increased PC density and the enhanced photoelectrochemical activity.

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The increased PC density and the enhanced photoelectrochemical activity can also be ascribed to a large number
of electron-hole pairs formed under the illumination of the light around 380 nm the energy of whose photons is nearly resonant with the band gap of ZnO. As described above, however, the presence of the ZnO coatings on the TiO$_2$ NTs results in a red shift of absorption edge and allows the ZnO-coated TiO$_2$ NTs to absorb visible light. In order to investigate the influence of the ZnO coverage on the photoelectrochemical activity under visible illumination, PC measurements were also performed under intermittent visible illumination with a wavelength cutoff of 420 nm. Although the corresponding PC densities are generally lower than those obtained under the illumination with the wavelength cutoff of 380 nm, the ZnO-covered TiO$_2$ NTs present enhanced photoelectrochemical activities compared with the bare TiO$_2$ NTs. For the 10-cycle ZnO-covered TiO$_2$ NTs, in particular, a significant enhancement of photoelectrochemical activity is observed. The PC density increases from ~1.4 $\mu$A/cm$^2$ for the bare TiO$_2$ NTs to ~2.2 $\mu$A/cm$^2$ for the 10-cycle ZnO/TiO$_2$ NTs, as shown in Fig. 9b. An increase of nearly 60 % in photoelectrochemical activity is therefore obtained for the TiO$_2$ NTs covered by a 10-cycle deposit of ZnO, or by a 2.1-nm ZnO coating, compared with the bare TiO$_2$ NTs. In contrast, the 25-cycle ZnO/TiO$_2$ NTs just show a slight increase of PC density compared with the bare TiO$_2$ NTs. One of the factors unfavorable for the enhancement in the photoelectrochemical activity of the 25-cycle ZnO/TiO$_2$ NTs should be the thicker ZnO coating, which presents a longer pathway for the generated electrons to migrate to the TiO$_2$ surface and the generated holes to the ZnO surface, and hence increases the recombination of electrons and holes, not conducive to the separation of electrons and holes. Apparently, the higher photoelectrochemical activity of the 10-cycle ZnO/TiO$_2$ NTs is consistent with the suppressed recombination of electrons and holes in the heterogeneous nanostructures composed of TiO$_2$ NTs and ultrathin ZnO coating. The above results suggest that from the view of enhancing photoelectrochemical activity, ZnO coatings of about 2 nm in thickness are optimal for heterostructured ZnO/TiO$_2$ NTs [19, 40, 48, 49].

The bare TiO$_2$ NTs and ZnO-coated TiO$_2$ NTs show good stability in the photoelectrochemical properties. As an example, Fig. 11 shows the PC density of the 10-cycle ZnO/TiO$_2$ NTs for a longtime visible illumination. It is noted that no noticeable change is observed in the PC density after about one and a half hours of visible illumination of light with a wavelength cutoff of 420 nm and the 10-cycle ZnO/TiO$_2$ NTs photoelectrode still presents prompt and excellent transient photocurrent responses under intermittent illumination. It has been reported that unlike ZnO films, ZnO/TiO$_2$ NTs are stable in chemical properties and show excellent photo-stability [45].

**Conclusions**

Vertically aligned ZnO-coated TiO$_2$ NTs were fabricated by ALD deposition of ultrathin ZnO coatings on the walls of the TiO$_2$ NTs formed by electrochemical anodization of Ti foils. The TiO$_2$ NTs exhibit anatase structure while the ZnO coatings are structured with hexagonal wurtzite with precise thickness control at atomic scale for an investigation on the influence of ZnO coating and its thickness on the optical, electrochemical, and photoelectrochemical properties of the heterogeneous nanostructured ZnO/TiO$_2$ NTs. The fabricated bare TiO$_2$ NTs and the ZnO-coated TiO$_2$ NTs present fast photoresponse and good photostability. Compared with bare TiO$_2$ NTs, the presence of ZnO coatings significantly improves the electrochemical and photoelectrochemical activities due to the enhanced charge separation in the heterostructure composed of TiO$_2$ NTs and ZnO coatings, especially the TiO$_2$ NTs covered by a thinner ZnO coating of about 2 nm in thickness rather than a thicker ZnO coating. In comparison to the bare TiO$_2$ NTs, an increase of nearly 60 % in photoelectrochemical activity is obtained for the
TiO$_2$ NTs covered by an about 2-nm-thick ZnO coating under visible illumination with a wavelength cut-off of 420 nm.

Competing interests
The authors declare that they have no competing interests.

Authors’ contributions
HC prepared the samples, carried out the experiments, and drafted the manuscript. PL and XY participated in the experiments and manuscript writing. ZH and LS contributed to the result analysis and mechanism discussion. JS and NX characterized the sample structure and studied the optical and photoelectrochemical properties. JW conceived the research and revised the manuscript. All authors read and approved the final manuscript.

Acknowledgements
This work is supported by the National Natural Science Foundation of China (11275051). Acknowledgement is also made to the Municipal Natural Science Foundation of Shanghai (15ZR1403300).

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Received: 23 November 2015 Accepted: 14 February 2016
Published online: 24 February 2016

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