Photogenerated cathodic protection of flower-like, nanostructured, N-doped TiO₂ film on stainless steel

Jing Li, Chang-Jian Lin *, Yue-Kun Lai, Rong-Gui Du

State Key Laboratory of Physical Chemistry of Solid Surface and Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China

1. Introduction

Titanium dioxide or titania (TiO₂) has attracted tremendous interest because of its unique optical and electrical properties, such as its excellent photoelectrochemistry and photocatalytic activity, and its good chemical stability [1–6]. Research into the photogenerated cathodic protection of metals coated by TiO₂ film or composites of nano TiO₂ with metallic or nonmetallic dopants under ultraviolet (UV) illumination has become significant [7–13] because of its sustainable corrosion protection performance. However, for practical applications, plain TiO₂ coating usually suffers from serious charge recombination problems. In addition, it is non-active both under visible light illumination and in the dark because of its large band gap. As such, the photoresponse and photocathodic protection activity of TiO₂ has room for vast improvement. Many efforts have been made to enhance the performance of TiO₂ as a photocatalyst under UV illumination and to extend its absorption and conversion capacity into the visible portion of the solar spectrum.

Improvement in the shifting of the optical absorption response of TiO₂ to the visible range has a profound positive effect on photogenerated cathodic protection. Recently, many research groups have found that TiO₂ doped with embedded metal atoms [14], transition metals [15], dye-sensitization compounds [16], or nonmetallic elements, such as nitrogen [17–20], carbon [21], sulfur [22], or iodine [23], co-doped with nitrogen and fluorine [24], showed photoelectrochemical responses in the visible light region and higher photocatalytic activity. Hexamethylenetetramine (C₆H₁₂N₄, HMT) has been utilized to fabricate N-doped TiO₂ [25–28] and to act as a structure-directing agent for the fabrication of ZnO [29,30] and CeO₂ [31] with certain nanofeatures. Recently, theoretical and experimental studies have shown that N-doped TiO₂ films are one of the most promising techniques to improve visible light response [32]. However, most of these studies are related to the visible-light photocatalytic activity of TiO₂ used in the field of pollutant degradation, environmental purification, and solar cells. Very few relevant studies were carried out on the photogenerated cathodic protection of metals.

Titania films with ordered nanostructures have aroused strong interest because of their potential applications in sensors, catalysts, and some devices [33–36]. They are used in the form of titania powders or thin films consisting of nanofeatures, such as tubes [37–39], rods [40,41], wires [42], needles [43], sheets [44], and flowers [45,46]. Such structures have an inherently high specific surface area synthesized through various physical, chemical, or electrochemical approaches. Recently, flower-like TiO₂ nanostructures with extremely large specific surface areas of 170–360 m² g⁻¹ prepared by hydrothermal treatment and low-temperature processing have been confirmed useful for the synthesis of crystalline TiO₂ with a high surface area [47]. However, most of the approaches involved, either templates or inconvenient reagents and complicated processes [48] or low-cost preparation of large-area films with ordered nanostructures, have remained virtually challenging. Furthermore, to the best of our knowledge, no report has been made on the photogenerated cathodic protection of such orderly nanostructured TiO₂ films.

© 2010 Elsevier B.V. All rights reserved.

* Corresponding author. Tel.: +86 592 2189354; fax: +86 592 2186657.
E-mail address: cjlin@xmu.edu.cn (C.-J. Lin).

0257-8972/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
Recently, we demonstrated that N-doped TiO$_2$ nanotube arrays can be prepared by a self-organized anodization because the photoanode was able to effectively provide a photogenerated cathodic protection for metals under regular sunlight illumination [28]. Likewise, the net-like, structured TiO$_2$ film prepared via a low-temperature hydrothermal reaction (140 °C) has been suggested to offer a distinct photogenerated cathodic protection for 316L stainless steel (SS) under white light illumination [49]. However, low-temperature synthetic routes that avoid an unwanted high-temperature annealing step are preferred because it can aid in realizing unique functional material architecture. Furthermore, the most important technical bottleneck in the practical application of a TiO$_2$ nanostructured film is maintaining sufficient negative potential shift under visible light and even in darkness. To enhance the photoabsorption of TiO$_2$ under visible light illumination and to increase its photocatalytic activity, an ordered, flower-like, nanostructured, N-doped TiO$_2$ film was fabricated by low-temperature hydrothermal synthetic routes in this study. Electrochemical characteristics and cathodic protection activity of 316-type SS coupled with flower-like N-TiO$_2$ films were investigated under ultraviolet–visible (UV–vis) light illumination and dark conditions in 0.2 M Na$_2$SO$_4$ and 0.5 M NaCl solutions. A comparative study was likewise made on flower-like, nanostructured, N-doped TiO$_2$ films obtained by a hydrothermal synthesis route and long TiO$_2$ nanotube (TN) array films prepared inorganic electrolyte by electrochemical anodization for the evaluation of photogenerated cathodic protection under visible light illumination and in the dark.

2. Experimental

2.1. Preparation of N-doped, flower-like, nanostructured TiO$_2$ films

Titanium foils were degreased by sonicating in acetone and anhydrous ethanol, rinsing in deionized (DI) water, and air-drying. The low-temperature growth of N-doped, crystallized TiO$_2$ thin films with flower-like top layers were prepared by a method described elsewhere [41,45]. Briefly, the Ti foil was reacted with 30 wt.% H$_2$O$_2$ solution, which contained 100 mg HMT and 1.0 mL concentrated nitric acid in a Teflon-sealed stainless steel autoclave with a 75% filling factor. Then, it was kept for up to 72 h in an oven maintained at 80 °C and subsequently air-cooled. The as-oxidized Ti plate was then rinsed gently in distilled water, air-dried, and then heated in air at 450, 550, and 600 °C for 1–2 h at 10 °C/min from room temperature. The annealed TiO$_2$ thin films were connected to a copper wire with a 1 cm$^2$ testing area exposed to air and the rest of the surface covered with an epoxy resin. The flower-like, N-doped TiO$_2$ film electrode was coupled with a 316L SS covered with epoxy resin by using conductive glue and a copper wire to expose only the front surface (1 cm$^2$).

2.2. Preparation of a TiO$_2$ nanotube electrode

Samples for anodization were cut from titanium foils (99.65% purity) with a thickness of 0.1 mm. Prior to the experiments, the samples were degreased by sonicating in acetone and anhydrous ethanol, and then rinsed in DI water and dried in a nitrogen stream. The titanium specimens were anodized with a platinum cathode in a mixture of 0.2 M Na$_2$SO$_4$ and 0.5 M NaCl solution, which contained 100 mg HMT and 1.0 mL concentrated nitric acid in a Teflon-sealed stainless steel autoclave with a 75% filling factor. Then, it was kept for up to 72 h in an oven maintained at 80 °C and subsequently air-cooled. The as-oxidized Ti plate was then rinsed gently in distilled water, air-dried, and then heated in air at 450, 550, and 600 °C for 1–2 h at 10 °C/min from room temperature. The annealed TiO$_2$ thin films were connected to a copper wire with a 1 cm$^2$ testing area exposed to air and the rest of the surface covered with an epoxy resin. The flower-like, N-doped TiO$_2$ film electrode was coupled with a 316L SS covered with epoxy resin by using conductive glue and a copper wire to expose only the front surface (1 cm$^2$).

2.3. Characterization of the nanostructured TiO$_2$ electrode

The surface morphologies and the thickness of the N-doped TiO$_2$ films were observed by a field emission scanning electron microscope (FE-SEM, Leo-1530) equipped with an energy disperse X-ray spectrometer (EDX). The structure of the samples was identified using an X-ray diffractometer (XRD) with a Cu-K$_\alpha$ radiation source (Phillips X'pert-MPD PW 3040). The surface chemical composition of the doped TiO$_2$ nanofilms was recorded by X-ray photoelectron spectroscopy (XPS, PHI Quantum 2000) with an Al-K$_\alpha$ radiation source. The binding energies were normalized to the signal for adventitious carbon at 284.8 eV. Quantitative analysis was carried out using the sensitivity factors supplied with the instrument. To minimize the side effect of having carbon as an additional dopant in the XPS experiment, the same experimental conditions were maintained with the instrument. The photoabsorption properties of the N-doped TiO$_2$ film samples were investigated by a diffuse reflectance UV–vis spectrometer (DRS, Varian, Cary 5000) in the wavelength range of 300–800 nm. The intensity of light irradiation was measured by a UV meter (Kimmon, PT-3000).

2.4. Photoelectrochemical characterization

Photoelectrochemical measurements were conducted using a Princeton Applied Research Model 263A potentiostat/galvanostat with an M5210 lock-in amplifier/chopper set-up (using a chopper frequency of 34 Hz) connected to an SBP 300 grating spectrometer with a LHX 150 W Xe lamp as the source of illumination; the measured intensity was 1.2 mW cm$^{-2}$. Photocurrent spectra were recorded in 0.2 M Na$_2$SO$_4$ solution in an electrochemical cell equipped with a quartz glass window. The photoelectrochemical characterization was carried out by measuring the electrode potential of the sample in the dark or under UV–visible light illumination conditions. A saturated calomel electrode (SCE) and a platinum foil served as reference electrode and counter electrode, respectively. The as-prepared annealed N-TiO$_2$ films coupled with the 316L SS cathode by conductivity glue and copper wire served as the working electrode. The test electrolyte was a 0.5 M NaCl solution. For the photopotential measurement, the sample was illuminated using a 150 W high-pressure Xe lamp. The photopotential was obtained when the electrode potential went down to a stable value under illumination. All experiments for the different specimens were done in triplicate to confirm the reproducibility of the measurements.

3. Results and discussion

3.1. Structure and morphology

Fig. 1 presents the typical FE-SEM images of TiO$_2$ nanotube arrays (Fig. 1a inset is the highly magnified image of Fig. 1a) obtained by electrochemical anodization and the variation of the surface morphology on the Ti plate after a low-temperature hydrothermal reaction at various durations. A compact amorphous TiO$_2$ layer, showing a porous nanostucture with an average pore size of about 50–60 nm, covered the Ti surface after 18 h of reaction (Fig. 1b). As seen in Fig. 1c, the typical flower-like cluster emerged after 24 h of reaction. Fig. 1d and e show the typical top-view and cross-sectional SEM images of the TiO$_2$ film morphologies obtained after 60 h of reaction at 80 °C. An overall view in Fig. 1d illustrates many flower-like TiO$_2$ aggregates sitting on top of the porous TiO$_2$ layer with an average pore size of about 240 nm. The bead-like TiO$_2$ inner layers were highly ordered and compact, and the thickness of the inner layers perpendicular to the Ti substrate was about 2.7 μm. The flower-like TiO$_2$ aggregates sitting on top of the bead-like TiO$_2$ porous layer formed two-level nanostructured TiO$_2$ films. A closer examination indicates that the flower-like TiO$_2$ aggregates were aligned in various directions (Fig. 1e). Each TiO$_2$ aggregate was about 2.3 μm in
diameter. The high-magnification images indicate that the flower-like aggregate consisted of TiO₂ nanorods with sizes of about 580 nm in length, which grew outward from a center point to give a roughly sphere-like outline. Based on the cross-sectional image of the dual structure, the inner (under) layer was condensed and compact. This kind of two level nanostructured TiO₂ films can be described as a dense layer deposited by layer growth and spherulitic crystallization behavior at the layer surface.

According to previous studies [41], the two steps of different layer growths of this dual structure could be attributed to the dissolution precipitation mechanism, assuming that the precipitation of the crystalline TiO₂ occurred mainly after the thorough dissolution of the amorphous one. In this case, the concentration of Ti(IV) ions was relatively high at the early precipitation stage. Solutions with higher Ti(IV) concentrations tended to precipitate TiO₂ in the anatase form at a given pH value. Thus, a nearly pure anatase inner layer was initially deposited on the titanium substrates, and then a mixture of anatase and rutile was obtained with decreasing Ti(IV) concentration.

The two-step growth of the dual structure could also be further elucidated in light of chemical dynamics: (1) the ready dissolution of the previously formed amorphous TiO₂ into the solution; (2) the deposition and precipitation of crystalline TiO₂ either on the titanium surface or in the solution through an inhomogeneous nucleation and growth process or a homogenous nucleation process [40]. A lower precipitation rate favored the formation of a layer of well-aligned TiO₂ nanorods. The growth of TiO₂ along the anatase (101)-axis seemed to be naturally favored in thermodynamics.

3.2. Chemical composition analysis

The XRD patterns of the as-prepared N-TiO₂ films were obtained by hydrothermal treatment at various durations and heat-treatment
at 450 °C for 1 h in air (Fig. 2). Except for peaks corresponding to the titanium substrate, all samples showed peaks at 2θ values of 25.3, 37.8, 48.2, 54.0, and 55.2°, which correspond to (101), (004), (200), (105), and (211) crystal planes of anatase TiO2 (JCPDS 21-1272), respectively. No other crystalline phase related to nitrogen was observed on N-doped samples. The intensity of these peaks increased slightly with a prolonged reaction time of 60 h. No significant structural change was observed during heat treatment.

Surface chemical compositions of N-doped species in flower-like TiO2 films were analyzed by XPS. Fig. 3a and b shows a comparison of the XPS survey spectra for non-doped and N-doped TiO2 samples and N1s high-resolution spectra of flower-like N-doped TiO2 films, respectively. In N-doped samples, a broad peak of N1s in the region of 396–405 eV with a maximum located at the bonding energy of 399.4 eV was clearly identified. This finding was in line with XPS results from previous reports on N-doping [25,50]. According to the binding energy (BE) of the reported N1s [45], one of the peaks at 399 eV could be attributed to a type of nitrogen in the N3− state that is probably bound to hydrogen or hyponitrite, whereas another peak at 396 eV could be assigned to the –NH species on the surface.

We also compared changes in the Ti2p region between non-doped TN, non-doped flower-like TiO2 films, and N-doped TiO2 samples. Fig. 3c shows that the Ti2p3/2 and Ti2p1/2 core levels of the N-TiO2 appeared at 457.2 and 463.5 eV, respectively. Binding energies of Ti2p3/2 and Ti2p1/2 after nitrogen doping decreased relative to the undoped TN (Ti2p3/2 appeared at 458.8 eV, whereas Ti2p1/2 appeared at 464.7 eV) and the undoped flower-like TiO2 films (Ti2p3/2 appeared at 459.5 eV, whereas Ti2p1/2 appeared at 465.3 eV). Chandra et al. reported that titanium atoms with a Ti2p3/2 BE of 459.9 eV and a Ti2p1/2 BE of 465.7 eV could be attributed to the octahedrally coordinated Ti(IV) [51]. The presence of Ti2p3/2 and Ti2p1/2 peaks either at 458.8 and 464.7 eV in undoped TN or at 459.5 and 465.3 eV in undoped TiO2 films thus confirmed that most of the titanium species present in our samples could be assigned to the tetrahedrally coordinated Ti(IV). This finding is identical with that reported by Mukhopadhyay et al. [52]. Negative shifts (Ti2p) in the BE of the N-doped TiO2 films indicate that the increase in electron density around titanium atoms can be attributed to nitrogen doping [53,54]. The formation of oxygen vacancies induced by nitrogen doping is responsible for the increase in electron density through a reduction of the valence state of Ti(IV) to Ti(III) or even Ti(I). The different electronic interactions of Ti with N anions cause partial electron transfer from nitrogen to titanium. At the same time, the electron density on Ti increases because of the lower electronegativity of nitrogen compared with oxygen. This further confirms that nitrogen was incorporated into the lattice and substituted for oxygen.

The lower BE of Ti2p in N-TiO2 shows that the electronic interaction of titanium with anions is considerably different than that of TiO2 [55], suggesting that the TiO2 lattice was considerably modified because of N-substitution. The lower BE of Ti2p in N-TiO2 could also be explained on the basis of covalency between titanium and nitrogen. Accordingly, if the electronegativity of the anion decreases, the percentage of ionicity likewise decreases. As a result, the electron density around the anion decreases as well, resulting in an increase in electron density around the cation. Our results on Ti2p core levels are consistent with that of Burda et al. [56].

Based on the O1S levels, peaks corresponding to oxygen in N-doped TiO2 shifted negatively by 1.0 eV in comparison with non-doped TiO2 TN (Fig. 3d). These results further confirmed the formation of O–Ti–N [57], in which partial electrons transferred from nitrogen to titanium and oxygen because of the higher electronegativity of oxygen compared to nitrogen. As such, nitrogen becomes electron-deficient, while both titanium and oxygen become electron-enriched. Furthermore, a broadening of the higher BE side at 531.5 eV (indicated by an arrow) was clearly visible in the case of the N-TiO2 sample. The results indicated that the presence of another type of oxygen could be attributed to the more covalent nature of N-TiO2. This might be due to the presence of oxygen and nitrogen from the same lattice units in TiO2.

The total concentration of nitrogen in the as-prepared sample was found to be ~3.51 at.%. Doping and heat treatment possibly led to the substitution of some oxygen sites by nitrogen. The nitrogen was not only successfully implanted in the N-doped, flower-like nanostructure but was also present in a chemically bonded state. The nitrogen ions substituted for oxygen atoms in the TiO2 lattice, and thus the corresponding nitrogen states were located above the valence band edge. As a result, higher photoelectrochemical efficiencies were expected under visible light irradiation.

3.3. Photoelectrochemical characterization

Fig. 4a shows a comparison of photocurrent spectra for the flower-like, two-level nanostructured N-TiO2 films annealed at 450 °C for 2 h (curve a) and the non-annealed N-TiO2 film (curve b) after 24 h of hydrothermal reaction recorded under a bias of 300 mV. The crystalline state of the N-TiO2 films after heat treatment showed a significant increase in photocurrent response in the UV region. Such response corresponded to an expected band gap for anatase at 3.5 eV, as well as a distinct photo absorption in the wavelength range of 650–700 nm (inset), which was much more enhanced than that of N-TiO2 films without heat treatment prepared using the same process. For example, the photocurrent of N-TiO2 films with a thickness of about 1.2 μm (Fig. 4a, curve a) was about 26 times greater than that for amorphous TiO2 films with a similar thickness in the same measuring condition (Fig. 4a, curve b). According to previous reports, such finding could be attributed to the semiconductor properties of TiO2 [58,59]. The highly crystalline structures offered unique advantages over amorphous architectures by providing a direct and rapid pathway for charge transport. This decreases the carrier path length, which, in turn, reduces recombination losses. In particular, amorphous flower-like TiO2 nanofilms without heat treatment showed a notable photoelectrochemical response (photocurrent value was about 500 nA) in the UV region (Fig. 4a, curve b). Such finding is in agreement with previous studies on the formation of crystalline metal oxide nanostructure films prepared without thermal annealing [45,60]. Furthermore, this result showed that the as-synthesized crystalline two-level nanostructured N-TiO2 films possessed better photoelectrochemical properties compared to TiO2 nanoparticle films prepared by a regular sol–gel method with annealing at high temperatures (500–600 °C) [28]. The annealed N-TiO2 nanofilm

![Fig. 2. XRD patterns of the N-doped TiO2 films formed by low-temperature hydrothermal method at 80 °C after reaction for various durations followed annealed at 450 °C. (a) 12 h; (b) 48 h; (c) 60 h. The peaks are annotated as A: anatase, T: Ti substrate.](image-url)
samples showed enhanced absorption in the visible wavelength range, with a broad absorption maximum centered in 625 nm at bias potentials of 100, 300, 500, 700 mV and 1 V after 18 h of hydrothermal reaction (Fig. 4b, curves a–e, respectively). However, for the pure TiO\textsubscript{2} flower-like nanofilms (curve f), no photocurrent was observed under visible light illumination at the same given bias potentials. A substantial sub-band gap photoresponse could be measured with an onset energy of approximately 2.0 eV, based on the empirical equation $E_g = \frac{1239.8}{\lambda_{\text{edge}}}$ [61].

Generally, the maximum photocurrent is a measure of the generation and subsequent collection of charge carriers. It correlates well with the surface area of the nanostructures. Meanwhile, the photoconversion efficiency depends on the separation processes of the photogenerated electron–hole pairs [62]. According to a previous report [63], a high energy conversion efficiency could be attributed to nanoporous TiO\textsubscript{2} electrodes that have large surface-to-volume ratios. With positive bias (vs. SCE), the Fermi level shifts to lower energies, which increases the driving force toward an efficient electron transfer, resulting in higher incident photon-to-electron conversion efficiency (IPCE) values. Notably, IPCE values will again decrease at a more positive bias. A similar dependence of IPCE on the applied bias has also been observed in another study [64]. Accordingly, an increase in photocurrent values with positive bias can also be attributed to an increase in charge collection efficiency because the photo-injected electrons are more efficiently withdrawn and transported to the back contact. The non-linear relationship between the dynamic photocurrent and the applied bias potential can be explained in this manner [65]: by illuminating the semiconductor with light energy greater than that of its bandgap, electron–hole pairs are generated on the electrode surface. A bias potential positive to the flat-band potential produces bending of the conduction band. Such reaction causes a more effective charge separation and increases the photocurrent that begins to flow, which likely promotes a better oxidative degradation process. Thus, the best bias potential for the maximum light-to-electricity conversion efficiency for the N-doped TiO\textsubscript{2} electrode is produced.

As seen in Fig. 4b, a decreased photocurrent was achieved at a lower bias of 100 mV and three more positive bias potentials of 500 mV, 700 mV, and 1 V. Since the electricity conversion efficiency (charge separation efficiency) reached its maximum at a bias of 300 mV, the photocurrent was considered higher and thereby presumed to be one of the critical point threshold bias potentials. A higher photoelectrochemical activity for the N-doped TiO\textsubscript{2} films could probably be attributed to its efficient separation of photogenerated electron–hole pairs under a suitable bias potential.

Such result implied that an efficient N-doping process may introduce significant amounts of defect states. The specific surface area of the films was estimated to be about 350 m\textsuperscript{2}/g [66], such that a high value of the specific surface area could provide the interlayer spacing with an effective surface for adsorbing species used in electrochemical reaction. A larger geometric surface area of the flower-like nanostructure entails the availability of a larger number of active sites for chemical reactions to occur and allows for more photogenerated holes to access a large number of species at the electrode/solution interface. Such active states of N can possibly narrow the band gap and act as traps for photogenerated electron-
hole pairs. In turn, this can lead to a significant increase of the photocurrent response in the visible range of the spectrum.

For normally grown TiO₂ films with a mixture of anatase and trace amounts of rutile phases, the mass fraction of anatase, \( W_a \), can be estimated using the following formula [41]:

\[
W_a = \frac{1}{1 + 0.8I_r/I_a}
\]

where \( I_r \) and \( I_a \) correspond to the X-ray integrated intensities of the (101) diffraction of anatase and the (110) diffraction of rutile, respectively. Considering the 60 h hydrothermal duration, for example, if the X-ray intensity of the abnormally strong (101) plane was assumed to be \( I_a \), then \( I_r = 1412.36 \) and \( I_a = 712.5 \), and the value of \( W_a \) could be calculated to be about 38.67% (Fig. 2a). The beard-like, nanoporous inner layers were comprised of two-fifth of the whole film in thickness (Fig. 1), suggesting that the estimated \( W_a \) was reasonable.

Moreover, given these data, the preparation process of low-temperature N-doping offered a large internal surface area in geometric and structural order. This was better than that expected for a net-like, nanostructured TiO₂ film obtained through the traditional low-temperature hydrothermal process [49]. Such condition indicated that the surfaces of N-doped, nanostructured films were rougher in nanoscale and therefore provided more surface sites for photoelectron adsorption. Similar results were found for N-doped TiO₂ nanotube arrays [28].

3.4. UV–vis absorption spectroscopy

A comparison of the optical absorption spectra for the nanostructured TiO₂ films in Fig. 5 provides the non-doped TiO₂ nanotube arrays as reference. The N-doped samples showed a much stronger photoabsorption from 470 to 650 nm compared to the pure TiO₂ nanotube layers (curve c) with predominant photoabsorption at the edge of 300 nm. This could be attributed to the randomly aligned nanoflowers on the surface, which caused more light absorption. The absorption edge of the N-doped TiO₂ nanolayers obtained after 12 and 60 h occurred at about 650 and 570 nm, and the corresponding band gap energy could be estimated to be 1.91 and 2.17 eV, respectively. These are in good agreement with our theoretical calculation as well as our previous studies [28]. Evidently, doping with nitrogen narrowed the band gap of TiO₂ and shifted the absorption edge of flower-like TiO₂ nanofilms to the visible light region. Such effect could probably be attributed to better scattering of the induced electron-hole pairs in the regular architecture [67] as well as the nitrogen and oxygen vacancies and electronic levels lying slightly below the conduction band edge [68, 69]. Nitrogen doping has been known to enhance the photocatalytic activity of TiO₂ under visible light illumination. The exact mechanism of the effects on the visible light activity of nitrogen incorporated into TiO₂, as well as the assignment of peaks for chemical states of N1s in the XPS, is still under debate [70, 71]. In the present investigation, the adsorption threshold of the TiO₂ flower-like film was remarkably stronger than that of the non-doped TiO₂ nanotube arrays. Therefore, the addition of certain amounts of HMT lead to the realization of nitrogen-doping.

3.5. Performance of photogenerated cathodic protection

The electrode potential responses of different samples were measured in 0.5 M NaCl solution against time when exposed to UV–vis illumination and in the dark. Fig. 6 shows the time dependence of the electrode potentials for 316L SS coupled with flower-like N-TiO₂ films prepared at different reaction times and the non-doped TN arrays under illumination and in the dark.

Fig. 6a shows a comparison of the response of the electrode potential of 316L SS coupled with flower-like N-TiO₂ films after a prolonged reaction time of 78 h (Fig. 6a, curve a) and the non-doped ordered TN array electrodes anodized at 25 V for 2 h (Fig. 6a, curve b), respectively, with and without UV light illumination. As expected on
Fig. 6. Time dependence of electrode potentials for 316L SS coupled with the flower-like TiO$_2$ films and TN films under dark and illumination conditions. (a) N-doped flower-like TiO$_2$ films (curve a) and non-doped TN arrays (curve b). (b) N-doped TiO$_2$ nanoporous films electrodes under visible light (curve c) and UV illumination (curve d).

The basis of recent publication [28], the potential of 316L SS coupled with the N-doped, flower-like TiO$_2$ film (curve a) immediately shifted negatively from +130 to −300 mV under UV irradiation (Fig. 6). Such potential switched promptly back to less negative values of about −300 mV relative to the rest potentials of N-TiO$_2$-coupled 316L SS in the dark after light was removed. These negative values of the electrode potential could last for a prolonged time of 5.5 h, implying the possibility of maintaining a complete cathodic protection for 316L SS even in the dark for a prolonged period. In the case of non-doped, ordered TN array films (curve b), the shift of the potential change of 316L SS was much less than that of 316L SS coupled with the N-doped, flower-like TiO$_2$ nanoarrays. The TN array has been one of the predominant materials used for the photoenergetic cathodic protection of metals under irradiation [28]. Herein, not only could the flower-like, structured TiO$_2$ film prepared by a low-temperature hydrothermal method effectively provide cathode protection for 316L SS in NaCl solution under UV illumination, its performance in some cases was even more superior than that of TN arrays observed in the dark.

Fig. 6b gives a comparison of the electrode potential of 316L SS coupled with the nanoporous, structured N-TiO$_2$ film electrodes prepared with a reaction time of 18 h and annealed at 450 °C under UV (curve d, $\lambda = 350$ nm), visible light (curve c, $\lambda = 550$ nm) illumination, and in the dark. The N-TiO$_2$ electrodes exhibited a photoeffect under both UV and visible light illumination. While under visible light, the electrode potential dropped immediately to a more negative value compared to the rest potential of N-TiO$_2$-coupled 316L SS in the dark (about −0.06 V). This resulted from the transference of the photo-generated electron–hole pairs in the regular, bead-like N-TiO$_2$ under the layers of the photoanode onto the surface of the 316L SS. Fig. 6b shows that the electrode potentials shifted to a more negative value of about −80 and −180 mV, respectively, after visible light illumination (curve c, $\lambda = 550$ nm) and UV illumination (curve d, $\lambda = 350$ nm). For curve c (Fig. 6b), after about 1 min of rapid drop to −180 mV, the electrode potential decreased immediately and stabilized at the photopotential of −150 mV (vs. SCE) for 1 h. After 4 min of illumination, when the visible light was removed, the electrode potential recovered only slightly. Interestingly, the negative electrode potential shift of 316L SS, coupled with the N-doped, flower-like TiO$_2$ film electrode, was maintained for a long period in the dark; that is, the photocathodic cathodic protection could last for a reasonable time even without any illumination. It can be inferred that the N-doping process in this method produce new states in the TiO$_2$ band gap, which could lead to a narrow band gap by mixing the N1s and O2p states and result in a strong visible light adsorption. For curve d (Fig. 6b), when the sample of 316L SS coupled with N-TiO$_2$ electrode was irradiated by UV, the electrode potential shifted to a more negative value. Then, the sample switched promptly back to less negative values than the rest potentials of N-TiO$_2$-coupled 316L SS in the dark because of fast charge recombination and stoppage of charge transfer after the light was removed. The TiO$_2$ nanotube film is known to exhibit excellent photocathodic cathodic protection to steel in the dark [28]. In this type of TiO$_2$ nanostructure, the trend of the electrode potential change of 316L SS was almost the same as that of 316L SS coupled with TN arrays prepared by electrochemical anodization. Herein, the flower-like, structured TiO$_2$ film derived from a hydrothermal reaction was likewise suggested to effectively provide cathodic protection for 316L SS in 0.5 M NaCl solution under irradiation. Notably, the electrode potential recovery was much more evident under UV irradiation (Fig. 6b, curve d) than that of N-doped photoanodes under visible light irradiation (Fig. 6b, curve c). This indicated that the N-doped TiO$_2$ films had more superior charge-storage property under visible light irradiation ($\lambda$>400 nm) than under UV illumination.

An optimal material structure could give rise to a larger specific surface area and more available surface active sites. Consequently, it could lead to a higher interfacial charge carrier transfer rate collected to maximize the quantum yield [72]. For the flower-like N-TiO$_2$ films, photogenerated charge carriers were usually separated more efficiently; the light scattered in the beard-like underlayers led to a more effective absorption. In this way, the surface recombination of e$^-$–h$^+$ pairs was hampered; the holes generated by a combination of light and thermal excitation could reach the surface without being lost in bulk recombination. Moreover, since the flower-like TiO$_2$ nanostucture had a large effective surface area in close proximity with the electrolyte [38,45], it enabled an efficient transport of photogenerated carriers to the redox species in the electrolyte. Therefore, the flower-like two-level nanostructured N-TiO$_2$ films exhibited an increased photocurrent and an effective photocathodic cathodic protection for a few hours even without illumination.

4. Conclusion

A novel, flower-like, two-level nanostructured, N-doped TiO$_2$ film was successfully synthesized via a low-temperature hydrothermal reaction (80 °C) and post-treatment. Its photoelectrochemical properties were investigated as photoanodes for photocathodic cathodic protection. A higher photoelectrochemical activity was observed for the N-doped TiO$_2$ films prepared for 12–78 h and annealed at 450 °C. A successful doping of nitrogen to the TiO$_2$ two-level nanostructured films provided a significant visible light response and led to a strong enhancement of photocurrent in both the UV and the visible range. This may be attributed to the doping modification of the states in the band gap of TiO$_2$ and the large effective surface area of the regular TiO$_2$.
nanostructure resulting in more photogenerated electron–hole pairs and an enhanced absorption of visible light. The electrode potential of SS coupled with N-doped TiO2 photoanodes in NaCl solution had a significantly negative shift under visible light illumination, and the potential negative shift of this electrode remained for a few hours even when illumination was turned off. The flower-like, nanostructured N-TiO2 film showed good photogenerated cathodic protection compared with TN arrays in the dark. Results indicate that the flower-like, two-level nanostructured, N-doped TiO2 films could be developed further as a feasible alternative material for photogenerated cathodic protection of metals under visible light irradiation or in the dark.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (50731004, 20620130427), and the National High Technology Research and Development Program of China (2009AAA03Z327).

References