Bi$_2$Se$_3$ Sensitized TiO$_2$ Nanotube Films for Photogenerated Cathodic Protection of 304 Stainless Steel Under Visible Light

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Abstract
Titanium dioxide (TiO$_2$) nanotube arrays coupled with a narrow gap semiconductor—bismuth selenide (Bi$_2$Se$_3$)—exhibited remarkable enhancement in the photocathodic protection property for 304 stainless steel under visible light. Bi$_2$Se$_3$/TiO$_2$ nanocomposites were successfully synthesized using a simple two-step method, including an electrochemical anodization method for preparing pure TiO$_2$ and a chemical bath deposition method for synthesizing Bi$_2$Se$_3$ nanoflowers. The morphology and structure of the composite films were studied by scanning electron microscopy, energy dispersion spectroscopy, X-ray photoelectron spectroscopy and X-ray diffraction. In addition, the influence of the Bi$_2$Se$_3$ content on the photoelectrochemical and photocathodic protection properties of the composite films was also studied. The photocurrent density of the Bi$_2$Se$_3$/TiO$_2$ nanocomposites was significantly higher than that of pure TiO$_2$ under visible light. The sensitizer Bi$_2$Se$_3$ enhanced the efficient separation of the photogenerated electron-hole pairs and the photocathodic protection properties of TiO$_2$. Under visible light illumination, Bi$_2$Se$_3$/TiO$_2$ nanocomposites synthesized by the chemical bath deposition method with Bi$^{3+}$ (0.5 mmol/L) exhibited the optimal photogenerated cathodic protection performance for 304 stainless steel.

Keywords: TiO$_2$, Bi$_2$Se$_3$, Stainless steel, Heterojunction, Photocathodic protection

Background
As important engineering materials, stainless steels have been widely applied to significant projects in numerous fields due to their excellent corrosion resistance. However, stainless steels can suffer serious corrosion when used in specific aggressive environments, such as acid environments, as well as under chloride-containing or high-temperature conditions [1–4]. Extensive research and applications of the traditional anti-corrosion method, including coatings [5, 6], use of a sacrificial anode [7] and impressed current cathodic protection [8, 9], have been developed during the past few decades. However, eco-friendly and long-lasting anticorrosion technology still remains a major objective. As a new anti-corrosion technology, photocathodic protection was first proposed by Yuan and Tsujikawa in 1995 [10] before receiving attention from corrosion researchers [11–14].

Titanium dioxide (TiO$_2$) is an important photoelectric material with good photoelectric conversion and photocatalysis properties and is widely used in catalysts [15], solar cells [16] and gas sensors [17] due to its low cost, non-toxicity and stable chemical properties. TiO$_2$ and TiO$_2$-based composites are used for photogenerated cathodic protection: a promising technique for corrosion prevention that has undergone rapid development in recent years [18–23]. However, the bandgap (3.2 eV) of TiO$_2$ restricts the photoresponse to only the ultraviolet region, which significantly depresses the utilization ratio of solar power. In addition, photo-induced charge carriers in bare TiO$_2$ nanoparticles show a very short lifetime due to the rapid recombination of photo-excited electron-hole pairs, which reduces the photocathodic protection effect of pure TiO$_2$ films. Thus, how to overcome the above deficiencies of TiO$_2$ has become a widely studied topic. Many studies have been conducted on compounding TiO$_2$ with
non-metal elements (F, N and S) \cite{12,24,25}, metal atoms (Fe, Co, Cu and Ce) \cite{26–29} and some narrow bandgap nano-semiconductors (Ag\textsubscript{2}O, ZnSe, WO\textsubscript{3}, CdS, Ag\textsubscript{2}S, CdSe and Bi\textsubscript{2}S\textsubscript{3}) \cite{30–36} to improve the carrier separation and light utilization of TiO\textsubscript{2}.

Bismuth selenide (Bi\textsubscript{2}Se\textsubscript{3}) is a direct bandgap layered semiconductor and important member of the V\textsubscript{2}VI\textsubscript{3} compound family. It has a high absorption coefficient in the visible and near-infrared light regions with a narrow bandgap (0.35 eV) \cite{37}. As an important n-type chalcogenide, Bi\textsubscript{2}Se\textsubscript{3} possesses many important characteristics, such as a high electrical conductivity \cite{38}, appreciable thermoelectric property \cite{39}, photosensitivity \cite{40}, electrochemical property \cite{41} and photoconductivity \cite{42}. Furthermore, Bi\textsubscript{2}Se\textsubscript{3} is a popular topological insulator \cite{43–45} and has the unique property of conductive surface states and insulating bulk states. High-quality Bi\textsubscript{2}Se\textsubscript{3} nanostructures have been prepared using a high vacuum physical deposition method, chemical vapour deposition, atomic layer deposition, pulsed laser deposition and a vapour-liquid-solid method, chemical vapour deposition, atomic layer deposition, pulsed laser deposition and a vapour-liquid-solid technique at high temperature \cite{44–49}. These synthetic methods for Bi\textsubscript{2}Se\textsubscript{3} require a difficult fabrication, leading to a high production cost. In this paper, the above problems are overcome by employing a low-cost and simple chemical bath deposition method for Bi\textsubscript{2}Se\textsubscript{3} nanoflower deposition on TiO\textsubscript{2}. The combination of a n-Bi\textsubscript{2}Se\textsubscript{3}/n-TiO\textsubscript{2} heterojunction as an efficient photoanode was applied to the photogenerated cathodic protection of 304ss for the first time. The morphology, structure and optical absorption property of Bi\textsubscript{2}Se\textsubscript{3}/TiO\textsubscript{2} nanocomposites were studied by scanning electron microscopy (SEM), X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS) and UV-visible (UV-Vis) diffuse reflectance spectra, respectively.

Methods

All of the chemicals used in this study were of analytical grade and used as received without further purification. All of the aqueous solutions were prepared using deionized water.

Preparation of TiO\textsubscript{2} Film

Ti foils (20 mm × 10 mm × 0.3 mm; > 99.9% purity) were polished using a mixture containing NH\textsubscript{4}F (2.25 g), H\textsubscript{2}O\textsubscript{2} (12.5 mL), H\textsubscript{2}O (30 wt%, 30 mL) and HNO\textsubscript{3} (68 wt%, 30 mL), and then, Ti pieces were cleaned with deionized water and ethanol. TiO\textsubscript{2} film was prepared on Ti foil by the anodic oxidation method reported in the literature \cite{50}. The Pt plate was chosen as the cathode, and the Ti foil was the anode at 20 V for 1 h in an ethylene glycol solution containing NH\textsubscript{4}F (0.22 g), H\textsubscript{2}O (4 mL) and ethylene glycol (40 mL) at ambient temperature. After that, the samples were rinsed with deionized water and ethanol. Finally, the specimens were annealed at 450 °C for 2 h and cooled in ambient air to obtain TiO\textsubscript{2} film.

Synthesis of Bi\textsubscript{2}Se\textsubscript{3} on the TiO\textsubscript{2} Film

The Bi\textsubscript{2}Se\textsubscript{3} was prepared by the chemical bath deposition method. In the experimental procedure, 8 mmol of nitrioltriacetic acid (H\textsubscript{3}NTA) and 0.4 mmol of Bi(NO\textsubscript{3})\textsubscript{3}·5H\textsubscript{2}O were added to deionized water (400 mL) to form the bismuth chelate, with a Bi\textsuperscript{3+} concentration of 1.0 mmol/L in the mixed solution. Two millimoles of ascorbic acid as the reducing reagent was added to the above solution, and then, ammonium hydroxide was cautiously added, dropwise, until the pH of the mixture was adjusted to approximately 8.6–8.9 and mixed solution appeared colourless and transparent. Finally, Na\textsubscript{2}SeSO\textsubscript{3} (20 mL, 30 mmol/L) was injected into the above solution. In all of the above experiments, the aqueous solutions were thoroughly stirred with a magnetic stirrer to obtain a homogeneous solution. Then, a TiO\textsubscript{2} substrate was immersed in the final solution (40 mL) in a beaker (100 mL). The beaker covered with cling film was then transferred into an oven heated to a temperature of 80 °C for 200 min to obtain the Bi\textsubscript{2}Se\textsubscript{3} nanoflower on the TiO\textsubscript{2} substrate. Finally, the sample was removed from the beaker and washed several times with deionized water and ethanol and then allowed to dry in ambient air. In this way, Bi\textsubscript{2}Se\textsubscript{3}-sensitized TiO\textsubscript{2} films were obtained and labelled with Bi\textsubscript{2}Se\textsubscript{3}/TiO\textsubscript{2}-1.0. For simplicity, different quantities of Bi\textsubscript{2}Se\textsubscript{3} on TiO\textsubscript{2} substrates are designated as Bi\textsubscript{2}Se\textsubscript{3}/TiO\textsubscript{2}-\gamma in this paper, where \gamma is the concentration of Bi\textsuperscript{3+} in the H\textsubscript{3}NTA and Bi(NO\textsubscript{3})\textsubscript{3}·5H\textsubscript{2}O solution. With the quantities of the other reagents held constant, Bi\textsubscript{2}Se\textsubscript{3}/TiO\textsubscript{2}-0.5 and Bi\textsubscript{2}Se\textsubscript{3}/TiO\textsubscript{2}-0.25 were obtained for Bi\textsuperscript{3+} concentrations of 0.5 mmol/L and 0.25 mmol/L, respectively. The influence of different quantities of Bi\textsubscript{2}Se\textsubscript{3} on the photoelectrochemical and photocathodic protection properties of the composite films was investigated in this paper.

Morphology and Composition Analysis

Scanning electron microscopy (SEM, Hitachi S-4800, Japan) was used to investigate the morphologies of the prepared films. Energy-dispersive X-ray spectroscopy (EDS, Oxford Energy 350 X-ray energy spectrum analyser) and X-ray photoelectron spectroscopy (XPS, Thermo Scientific ESCALAB 250Xi) were employed to determine the chemical composition of the Bi\textsubscript{2}Se\textsubscript{3}/TiO\textsubscript{2} nanocomposites. UV-Vis DRS (Japan Hitachi UH4150) was used to determine the light absorbance of the samples. The crystalline phase composition of the samples was characterised by an X-ray diffractometer (XRD, Germany Bruker AXSD8) using Cu K\textalpha radiation (\gamma = 1.54056 Å) from 10° to 80°.
Photoelectrochemical Measurements

As shown in Fig. 1, a coupling system comprising photolysis and electrolytic cells was used for the photoelectrochemical measurements, and a proton exchange membrane was used to link the two cells together. The photolysis cell contained a 0.1 mol/L Na₂S and 0.2 mol/L NaOH mixed solution, which played the role of a sacrificial agent for promoting the separation of electrons and holes [33, 51], while a 0.5 mol/L NaCl solution was used as the electrolyte for the electrolytic cell. In the electrolytic cell, a three-electrode system was adopted with a Pt foil as the counter electrode (CE), saturated calomel electrode as the reference electrode (RE) and 304ss as the working electrode (WE). Bi₂Se₃/TiO₂ nanocomposite samples placed in the photolysis cell were connected to a 304ss electrode immersed in the electrolytic cell by a copper wire. The light source in the visible light range was irradiated by a high-pressure xenon lamp (PLS-SXE 300 C, Beijing Perfectlight Company, China). The changes in the open-circuit potential (OCP) and photocurrent curves were measured using a Gamry potentiostat/galvanostat/ZRA system (GAMRY 3000, Gamry Instruments, USA) before and during light irradiation.

Results and Discussion

Characterization of Pure TiO₂ and Bi₂Se₃/TiO₂

Figure 2a shows typical top view and cross-sectional topographies for TiO₂ films prepared under the anodization method. The TiO₂ nanotube arrays show a nanoporous structure composed of well-ordered and high-density nanotubes with an average inner diameter and length of approximately 55 nm and 680 nm, respectively. As shown in Fig. 2b–d, the TiO₂ nanotube surfaces were successfully modified by Bi₂Se₃ via the chemical bath deposition method for different concentrations of Bi³⁺. For Bi₂Se₃/TiO₂-0.25, the Bi₂Se₃ nanoflakes were sporadically distributed and aggregated unevenly across the TiO₂ nanotubes (Fig. 2b). When the concentration of Bi³⁺ was 0.5 mmol/L, Bi₂Se₃ was composed almost entirely of flower-like patterns of piable ultrathin nanoflakes with a diameter of approximately 800 nm, without blocking the nozzle of the TiO₂ nanotubes or damaging them (Fig. 2c). Bi₂Se₃ nanoflowers that were observed to be evenly distributed on the surface of the TiO₂ showed an internal cross-linked structure for the ultrathin nanoflakes, which effectively prevented lamella aggregation and maintained a long-standing lifetime of the architectures, as shown in Fig. 2c. After the concentration of Bi³⁺ was increased to 1.0 mmol/L, the amount and diameter of the Bi₂Se₃ nanoflowers significantly increased, and the agglomeration of nanoflowers blocked the nanotubes, as shown in Fig. 2d. The corresponding EDS spectrum of the Bi₂Se₃/TiO₂-0.5 films shown in Fig. 2e revealed that the characteristic peaks for Ti, O, Bi and Se were marked with atomic percentages of Bi and Se of 0.9% and 1.3%, respectively. It is well known that the measurement error of EDS test is increased with the decrease of content of test element. So, it is acceptable that the atomic ratio of Bi and Se is close to 2:3.

Figure 3a shows the XRD spectra for pure TiO₂ (curve a) and Bi₂Se₃/TiO₂-1.0 nanocomposites (curve b). Aside from the Ti substrate peaks, the diffraction peaks at 25.38°, 38.03°, 48.01°, 54.05°, 55.17°, 62.71° and 70.44° were well matched with the lattice planes (101), (004), (200), (105), (211), (204) and (220) of anatase TiO₂, respectively (JCPDS 21-1272). Except for the TiO₂ peaks, the distinctive diffraction peaks at 29.35° and 74.90° were indexed to the lattice planes (015) and (0216) of the rhombohedral crystal Bi₂Se₃ (JCPDS 33-0214). However, there is no obvious peak of Bi₂Se₃/TiO₂-1.0 due to low content Bi₂Se₃ deposited on TiO₂ and the XRD spectra conformed to the SEM and EDS results. X-ray photoelectron spectroscopy (XPS) was used to further determine the chemical compositions and states of the Bi₂Se₃/TiO₂ nanocomposites. As shown in Fig. 3b, XPS revealed the existence of Bi, Se, Ti and O components in addition to C contaminants due to adventitious hydrocarbon contamination. Figure 3c shows the peak positions for Ti 2p at 458.7 and 464.5 eV, indicating that the titanium oxides mainly consisted of TiO₂ [52]. As illustrated in Fig. 3d, the O 1s semaphores matched with two Gaussian peaks: the maximum at the lower binding energy (530.0 eV) was attributed to the lattice oxygen (O₂) in Bi₂Se₃/TiO₂ nanocomposites and the second at the higher binding energy (531.5 eV) was derived from the adsorbed oxygen (O₁), including weak bonding oxygen or hydroxyl groups. The existence of O₁ was due to the generation of oxygen vacancies on the surface of the nanocomposites, which might improve the photoelectric
conversion properties of Bi$_2$Se$_3$/TiO$_2$ nanocomposites in photocathodic protection [53]. Figure 3e shows that the 4f$_{7/2}$ asymmetric peak for Bi resolved into two peaks (157.5 and 159.4 eV), with the Bi 4f$_{5/2}$ spectrum similarly divided into two bands at 162.8 and 164.7 eV, respectively. The positions of the lower peaks (157.5 eV and 162.8 eV) were in good agreement with those in Bi$_2$Se$_3$, with the higher peaks corresponding to bismuth oxide at 159.4 eV and 164.7 eV [54, 55]. It can be concluded that a handful of bismuth metal was oxidized during the synthetic process with Bi$_2$Se$_3$ modifying pure TiO$_2$. As shown in Fig. 3f, the two peaks were assigned to the 3d$_{3/2}$ and 3d$_{5/2}$ core levels of Se at 55.1 and 54.2 eV, respectively, indicating that Se existed in the form of Se$^{2-}$ [56].

Figure 4 shows the light absorption abilities of pure TiO$_2$ and Bi$_2$Se$_3$/TiO$_2$-1.0 nanocomposites. The characteristic absorption edge for pure TiO$_2$ was approximately 380 nm within the UV region due to the bandgap energy of anatase TiO$_2$ (3.2 eV) (curve a). Pronounced adsorption was observed for Bi$_2$Se$_3$/TiO$_2$ nanocomposites in the visible light region (350–800 nm) (curve b), with visible light absorption abilities higher than those of pure TiO$_2$ due to the incorporation of the Bi$_2$Se$_3$ nanoflower. This phenomenon can be ascribed to the fact that Bi$_2$Se$_3$ is excited under visible light due to its narrow bandgap (0.35 eV), with electrons and holes produced in its conduction band (CB) and valence band (VB). Therefore, the addition of Bi$_2$Se$_3$ effectively increases the visible light absorption capability of Bi$_2$Se$_3$/TiO$_2$ nanocomposites.

**Photocathodic Protection Performance of Pure TiO$_2$ and Bi$_2$Se$_3$/TiO$_2$**

As shown in Fig. 5, the OCP curves for 304ss coupled with pure TiO$_2$ and Bi$_2$Se$_3$/TiO$_2$ nanocomposite photoanodes
were measured under intermittent visible light, with the OCP response to illumination prompted and shifted to a negative potential for all of the coupled electrodes. At the initial phase of light on, the OCP for all of the coupled electrodes showed a negative shift over a short time, which was due to the transfer of the excited photoelectrons from the pure TiO$_2$ and Bi$_2$Se$_3$/TiO$_2$ nanocomposite to the 304ss electrode [1, 57]. Subsequently, the relatively stable OCP values can be attributed to the balancing rate between the creation and recombination of photogenerated electrons [32]. After switching off the irradiation, the OCP values for the Bi$_2$Se$_3$/TiO$_2$ nanocomposites returned to their original values at a slower speed compared to pure TiO$_2$. This phenomenon might be attributed to the electron pool effect of Bi$_2$Se$_3$/TiO$_2$ nanocomposites, which can store photoinduced electrons under light irradiation and slowly release these electrons without light irradiation. Under visible light irradiation, the OCP value for 304ss was approximately $-450 \text{ mV}$ when coupled with TiO$_2$ (curve a), and the OCP values for 304ss coupled with Bi$_2$Se$_3$/TiO$_2$-0.25 (curve b), Bi$_2$Se$_3$/TiO$_2$-0.5 (curve d) and Bi$_2$Se$_3$/TiO$_2$-1.0 (curve c) reached $-905 \text{ mV}$, $-996 \text{ mV}$ and $-958 \text{ mV}$, respectively. These results indicated that 304ss was cathodically polarized once coupled with Bi$_2$Se$_3$/TiO$_2$ nanocomposites and that a good cathodic protection for 304ss might be provided by the Bi$_2$Se$_3$/TiO$_2$ photoanodes. As shown in Fig. 5 d, the 304ss coupled to Bi$_2$Se$_3$/TiO$_2$-0.5 possessed most negative potential indicated that the best photocathodic protection performance for 304ss. This result might be because the active sites and light harvesting increased with the increasing Bi$_2$Se$_3$ content. However, an excessive amount of Bi$_2$Se$_3$ particles served as the recombination sites for electrons and holes, which hindered the charge transfer from the Bi$_2$Se$_3$/TiO$_2$ nanocomposites to 304ss.

As shown in Fig. 6, the photocurrent density vs. time curves for TiO$_2$ and Bi$_2$Se$_3$/TiO$_2$ nanocomposites showed a rapid and reproducible photoresponse under
intermittent visible light illumination, which reflected the photoelectric conversion performance of the materials. The photogenerated current was relatively small under visible light due to weak visible light absorption (curve a). However, the photogenerated current increased remarkably under visible light illumination following sensitization of TiO$_2$ by the Bi$_2$Se$_3$ nanoflower (curves b to d). The data implied that the Bi$_2$Se$_3$/TiO$_2$ nanocomposites were capable of utilizing visible light and that the heterojunction between TiO$_2$ and Bi$_2$Se$_3$ promoted the separation of photogenerated electrons and holes [58]. Furthermore, the photoelectrons produced in the conduction band of the Bi$_2$Se$_3$ nanoflower can be easily transferred to the more positive conduction band of the TiO$_2$ nanotubes under visible light illumination. After three irradiation intervals, the photocurrent maintained a relatively steady value and no photocurrent degradation was detected, illustrating the good photochemical stability of the Bi$_2$Se$_3$/TiO$_2$ nanocomposite films. For different concentrations of Bi$^{3+}$, the Bi$_2$Se$_3$/TiO$_2$ nanocomposites showed different intensities for the photocurrent response. In particular, the transient photocurrent density for Bi$_2$Se$_3$/TiO$_2$-0.5 (415 $\mu$A/cm$^2$) was higher than that for Bi$_2$Se$_3$/TiO$_2$-0.25 (85 $\mu$A/cm$^2$) and Bi$_2$Se$_3$/TiO$_2$-1.0 (160 $\mu$A/cm$^2$), indicating that Bi$_2$Se$_3$/TiO$_2$-0.5 possessed an ideal separation efficiency.

Fig. 4 UV-visible absorption spectra for TiO$_2$ (a) and Bi$_2$Se$_3$/TiO$_2$-1.0 (b)

Fig. 5 OCP for 304ss coupled with pure TiO$_2$ and Bi$_2$Se$_3$/TiO$_2$ nanocomposites in a 0.5 mol NaCl solution
for the photogenerated electron-hole pairs. The active sites and light harvesting were decreased because of the deficiency of Bi$_2$Se$_3$ nanoflowers on the Bi$_2$Se$_3$/TiO$_2$ nanocomposite films, while recombination sites for electrons and holes increased in the presence of an excessive amount of Bi$_2$Se$_3$ nanoflowers. Under visible light illumination, the largest photoinduced current density of the Bi$_2$Se$_3$/TiO$_2$-0.5 photoanode was consistent with the largest photoinduced potential drops illustrated in Fig. 5, further validating the optimal photocathodic protection performance of Bi$_2$Se$_3$/TiO$_2$-0.5 for 304ss.

Figure 7 shows the photoelectric conversion and transportation processes for the Bi$_2$Se$_3$/TiO$_2$ nanocomposites. Under visible light, Bi$_2$Se$_3$ nanoflowers can readily absorb photons as they contain adsorbed oxygen (O$_A$) and have a narrow bandgap width ($0.35$ eV). When the photons are absorbed by the Bi$_2$Se$_3$ nanoflowers, photoexcited electrons will be generated by excitation from the valence band (VB) of Bi$_2$Se$_3$ to the conduction band (CB) of Bi$_2$Se$_3$. The photoexcited electrons in the CB of Bi$_2$Se$_3$ are shifted to the CB of TiO$_2$, while the photogenerated holes in the VB of TiO$_2$ are transferred to the VB of Bi$_2$Se$_3$, and then are captured by S$^{2-}$ in the electrolyte to turn into S on the surface of photoanode film. When the photoexcited electrons exit the photoanode and transfer to 304ss, they will react with the oxygen gas and water to convert OH$^-$. Furthermore, Na$^+$ is transported from electrolytic cell to photolysis cell by proton

Fig. 6 Photocurrent density vs. time curves for pure TiO$_2$ and Bi$_2$Se$_3$/TiO$_2$ nanocomposites in 0.1 mol/L Na$_2$S and 0.2 mol/L NaOH mixed solution.

Fig. 7 Schematic representation of the electron transfer processes in Bi$_2$Se$_3$/TiO$_2$. 
exchange membrane, so that the coupling system is electrically neutral as a whole. As a consequence, the photogenerated charges are effectively separated and the recombination probability for photogenerated electron-hole pairs is reduced. Once 304ss receives photoexcited electrons from the Bi$_2$Se$_3$/TiO$_2$ nanocomposite through the wire, the potential of 304ss shifts negatively. Under visible light illumination, the Bi$_2$Se$_3$/TiO$_2$ nanocomposites can reduce the corrosion rate of 304ss. Therefore, the efficient separation of photo-excited electron-hole pairs in Bi$_2$Se$_3$/TiO$_2$ nanocomposites will accelerate the redox reaction and generate effective photocathodic protection for 304ss.

Conclusions

In this paper, TiO$_2$ nanotube arrays were prepared by the anodization method and Bi$_2$Se$_3$ nanoflowers were grown on TiO$_2$ nanotubes by chemical bath deposition. The Bi$_2$Se$_3$/TiO$_2$ nanocomposites showed a homogeneous distribution and ordered characteristics. Electrochemical tests for the nanocomposites and pure TiO$_2$ coupled with 304ss showed that the photogenerated cathodic protection performance of the Bi$_2$Se$_3$/TiO$_2$ nanocomposites was superior compared to that for pure TiO$_2$. The OCP value for 304ss coupled with Bi$_2$Se$_3$/TiO$_2$-0.5 showed a negative shift to $-996$ mV under visible light illumination due to the active sites and light harvesting of TiO$_2$ sensitized by Bi$_2$Se$_3$. By comparing the results of the electrochemical tests for three Bi$_2$Se$_3$/TiO$_2$ nanocomposites, the nanocomposite prepared using 0.5 mmol/L Bi$^{3+}$ in the electrolyte exhibited optimal performance.

Abbreviations

304ss: 304 stainless steel; CB: Conduction band; CE: The counter electrode; EDS: Energy-dispersive X-ray spectroscopy; H$_3$NTA: Nitrilotriacetic acid; OA: Adsorbed oxygen; OCP: Open-circuit potential; OL: Lattice oxygen; RE: The reference electrode; SCE: Saturated calomel electrode; SEM: Scanning electron microscopy; UV-Vis: UV-visible diffuse reflectance spectra; VB: Valence band; WE: The working electrode; XPS: X-ray photoelectron spectroscopy; XRD: X-ray diffraction

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Availability of Data and Materials

All datasets are presented in the main paper.

Authors’ Contributions

WCW performed the synthesis and characterization of Bi$_2$Se$_3$/TiO$_2$ films. XTW, NW and XBN took part in the synthesis. DZL, XL and QCZ participated in the characterization. WCW supervised the conceptual framework and drafted the manuscript. HL, XTW and YLH were participants in writing the manuscript. All authors read and approved the final manuscript.

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Ethics Approval and Consent to Participate

Not applicable.

Consent for Publication

Not applicable.

Competing Interests

The authors declare that they have no competing interests.

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References

1. Lin ZQ, Lai YK, Hu RG et al (2010) A highly efficient ZnS/CdS@TiO$_2$ photoelectrode for photogenerated cathodic protection of metals. Electrochim Acta 55:8717–8723
2. Ryan MP, Williams DE, Chater RJ et al (2002) Why stainless steel corrodes. Nature 415:770–774
3. Robertson J (1991) The mechanism of high-temperature aqueous corrosion of stainless-steels. Corros Sci 32:443–465
4. Hou B, Li X, Ma X et al (2017) The cost of corrosion in China. Npj Mater Degr 1:1–10
5. Abdulagatov AI, Yan Y, Cooper JR et al (2011) Al$_2$O$_3$ and TiO$_2$ atomic layer deposition on copper for water corrosion resistance. ACS Appl Mater Interfaces 3:4593–4601
6. Gonzalez MB, Saidman SB (2011) Electrodeposition of polypyrrole on 316L stainless steel for corrosion protection. Corros Sci 53:276–282
7. Jingling MA, Jiuba W, Gengxin LI et al (2010) The corrosion behaviour of Al-Zn-In-Mg-Ti alloy in NaCl solution. Corros Sci 52:534–539
8. Glass GK, Hassanein AM, Buenfeld NR (2001) Cathodic protection afforded by an intermittent current applied to reinforced concrete. Corros Sci 43: 1111–1131
9. Kear G, Baker BO, Stokes KR et al (2005) Corrosion and impressed current cathodic protection of copper-based materials using a bimetallic rotating cylinder electrode (BRCE). Corros Sci 47:1694–1705
10. Yuan J (1995) Characterization of sol-gel-derived TiO$_2$ coatings and their photoeffects on copper substrates. J Electrochem Soc 142:3444–3450
11. Subash R, Shihohara T, Mori K (2005) Modified TiO$_2$ coatings for cathodic protection applications. Sci Technol Adv Mat 6:501–507
12. Lei CX, Feng ZD, Zhou H (2012) Visible-light-driven photogenerated cathodic protection of stainless-steel by liquid-phase-deposited TiO$_2$ films. Electrochim Acta 68:134–140
13. Zhang W, Guo H, Sun H et al (2017) Constructing ternary polyaniline-graphene-TiO$_2$ hybrids with enhanced photoelectrochemical performance in photo-generated cathodic protection. Appl Surf Sci 410:547–556
14. Cui S, Yin X, Yu Q et al (2015) Polypyrrole nanowire/TiO$_2$ nanotube nanocomposites as photoanodes for photocathodic protection of Ti substrate and 304 stainless steel under visible light. Corros Sci 98:471–477
15. Zhang LW, Fu HB, Zhu YF (2008) Efficient TiO$_2$ photocatalysts from surface hybridization of TiO$_2$ particles with graphite-like carbon. Adv Funct Mater 18:2189–2198
16. Liu B, Aydil ES (2009) Growth of oriented single-crystalline rutile TiO$_2$ nanorods on transparent conducting substrates for dye-sensitized solar cells. J Am Chem Soc 131:3985–3990
17. Tang H, Prasad K, Sanjines R et al (1995) TiO$_2$ anatase thin-films as gas sensors. Sensors Actuat B-Chem 26:71–75
