Long-Term Photoelectrochemical Cathodic Protection by Co(OH)$_2$-Modified TiO$_2$ on 304 Stainless Steel in Marine Environment

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The long-term photoelectrochemical cathodic protection by Co(OH)$_2$-surface modified TiO$_2$ of anatase nanotubes and rutile type, prepared by anodic oxidation has been studied in aqueous 3.5 wt% NaCl solution. Electrochemical measurements have been used to evaluate the photoelectrochemical protective properties of both Co(OH)$_2$-modified TiO$_2$ coupled with 304 stainless steel in 3.5 wt% NaCl solution under illumination and in the dark. Morphologies, crystal structures, surface compositions, and light response range of both Co(OH)$_2$-surface modified TiO$_2$ films before and after immersion were characterized, respectively, by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), UV-Vis spectrophotometry. The results show that the photogenerated electrode potential of both types of TiO$_2$ films modified with Co(OH)$_2$ is more negative affording protection of 304 stainless steel than that of the non-modified TiO$_2$ under illumination. These TiO$_2$ films provide a long period (12 h) of protection. The anatase-TiO$_2$ nanotube film always shows a better protection performance than rutile-TiO$_2$ film.

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In recent years, photocatalysis has been broadly used in solar cells, for degradation of pollutants, splitting of water, air purification, and corrosion protection of metals.\textsuperscript{1,2} The latter application has attracted our attention because of its environmental advantages.

In 1990s, Tsuchikawa and Yuan\textsuperscript{3} first proposed the method of photoelectrochemical cathodic protection of metals by photocatalytic materials. They reported the more negative corrosion potential of TiO$_2$-coated 304 stainless steel or carbon steel under UV irradiation than that of bare steel. The TiO$_2$ coating plays the role of providing electrons like a sacrificial anode in cathodic protection. Subsequently, Fujishima et al.\textsuperscript{4} studied the mechanism of the photoelectrochemical cathodic protection of TiO$_2$-WO$_3$ in 3 wt% NaCl solution with pH = 5. So far, TiO$_2$ protection of metals using sunlight has been a focus of great attention as a possible means for converting solar energy to electrical energy by generating the required negative electrode potential. Photoelectrochemical cathodic protection has become an active research field of metal corrosion protection. It has attracted numerous studies and yielded new technologies.\textsuperscript{5-13}

Many metal oxides and sulfides, such as TiO$_2$,\textsuperscript{4,9} ZnO,\textsuperscript{14} SnO$_2$,\textsuperscript{15} and CdS,\textsuperscript{16} have been investigated as common photocatalyst materials. TiO$_2$ is most widely used in current applications because of its environmental advantages. Corrosion is a gradual and long-term destruction of materials. Therefore, it is important to study long-term protection efficiency, including photoelectrochemical one. Unfortunately, it is difficult to find published results for long-term performance of TiO$_2$, and thus the long-term performance is not clear now.\textsuperscript{10,12} The long-term behavior of photocatalytic materials in photoelectrochemical cathodic protection is worth much attention. Also, it is difficult to reach the minimum protection potential of metal in marine environment. What’s more, the photocatalytic material itself is not stable: the photogenerated charges composite easily, leading to inhibited photoelectric conversion efficiency, thus auxiliary hole-scavengers solution such as Na$_2$S and Na$_2$SO$_3$ have been applied in many published results to improve the electrochemical protection.\textsuperscript{14,15,24-25} Sun et al. realized the protection of Q235 and 304 stainless steel in 3.5 wt% NaCl solution by ZnO in solution with added Na$_2$S+NaOH solution.\textsuperscript{6} Lin et al. studied the protection of 403SS in 0.5 M NaCl solution by ZnS/CdS@TiO$_2$ in Na$_2$S+NaOH solution.\textsuperscript{8} With the hole-scavengers solution, the photocatalytic material shows a good protection performance. But the scavengers will lose efficiency in long-term service, and most importantly they are not useful under practically relevant conditions and cannot be applied in marine environments. So most photocatalytic materials cannot achieve protection in a simple 3.5 wt% NaCl solution.

Many approaches have been tried, like modification of crystal surface and surface defects,\textsuperscript{26,27} semiconductor composites,\textsuperscript{28} transition metal ion doping,\textsuperscript{29} and surface modification by catalyst promoter deposition,\textsuperscript{30} to improve the photocatalytic activity of photocatalyst materials themselves. Doping, for example, enhanced the visible light absorption, modified the electronic structure and narrowed the bandgap of TiO$_2$ and was first studied by Asahi et al.\textsuperscript{31} Different from doping, Zhang et al. reported that g-C$_3$N$_4$ modified with cheap and easily available Co(OH)$_2$ on its surface significantly restrained the recombination rate of the interface charge carriers by providing the oxidative half reaction sites, and accelerated the oxygen evolution kinetics.\textsuperscript{32} Loading catalyst promoter is becoming a new attractive way to improve the photocatalytic activity of photocatalysts themselves, and it doesn’t change the position of energy bands.\textsuperscript{33,34} However, most of the promoters are noble metals that can’t be used widely. So the application of low-cost catalyst promoters like Co(OH)$_2$ becomes necessary. It is also easy to deposit. Co(OH)$_2$ played an excellent role in photocatalytic water oxidation\textsuperscript{32} and supercapacitor materials,\textsuperscript{40,43} but hasn’t been studied in photoelectrochemical corrosion protection. Hence Co(OH)$_2$ modification of the surface of TiO$_2$ films to protect
metals is studied, and the performance of this modified TiO₂ films in 3.5 wt% NaCl solution has been measured.

In the present study, anodic oxidation has been chosen as fabrication method to produce both anatase TiO₂ nanotubes and rutile TiO₂ thin films. Both films have been superficially modified with Co(OH)₂ layers. Short-term and long-term photoelectrochemical behavior and protection mechanism with 304 stainless steel in aqueous 3.5 wt% NaCl solution were studied by electrochemical methods. A 3.5 wt% NaCl solution simulating marine environment has been used in this work. This solution is close to the real application environment and meaningful to explore the photoelectrochemical performance. Before and after exposure changes of morphologies, crystal structures, surface compositions, and light response range of both Co(OH)₂-modified TiO₂ films after modification were characterized, respectively. The improvement of photoelectrochemical behavior of TiO₂ films by Co(OH)₂ surface modification is discussed.

Experimental

Preparation of Co(OH)₂-surface modified TiO₂ films.—Anodic oxidation, an attractive method to form metal oxide nanostructures on metal substrates, has become a mature chemical fabrication technique. A layer of uniform and compact TiO₂ nanotubes on the surface of a Ti matrix could be grown by anodic oxidation. Therefore, an anatase TiO₂ nanotube-array film was formed. Subsequently the top amorphous nanotube-array film could be easily removed through ultrasonic treatment, and a nanotube-free compact amorphous rutile TiO₂ film was exposed. Both as-prepared films were heated at sufficient temperatures, respectively, and anatase TiO₂ nanotubes and rutile TiO₂ films were obtained.

Finally a successive ionic layer adsorption and reaction method has been used to deposit Co(OH)₂ nanoparticles on both annealed TiO₂ films. The TiO₂ films were immersed in an aqueous solution of Co(CH₃COO)₂, deionized water, an aqueous solution of NaOH and deionized water, respectively, until the deposition of the desired amount Co(OH)₂ nanoparticles was finished. In this way the Co(OH)₂ surface modification of TiO₂ materials was obtained.

Preparation of TiO₂ electrodes and 304 stainless steel electrode.—Prior to the experiments, the titanium samples with the TiO₂ films were cut into about 5 mm × 5 mm, fastening to the copper wire. Edges and back of the titanium sheet were covered with resin-paraffin mixture (1:1) to ensure that only the front surface was exposed to corrosive solution. The 304 stainless steel electrodes were also prepared in the same size and same covering; all electrodes were measured in 3.5 wt% NaCl solution simulated seawater environment.

Characterization of TiO₂ films.—Surface and cross section morphologies of TiO₂ films before and after exposure to corrosive solution were examined with scanning electron microscopy (SEM, INPECT F50, FEI, USA). The deposited Co(OH)₂ nanoparticles were examined with transmission electron microscopy (TEM, Tecnai G2 F20, USA). The crystalline structures were studied via X’pert X-ray diffractometer (XRD, X’pert PRO, Panalytical, Netherlands) using Cu-κα radiation at 40 kV, with 2θ ranging from 10° to 90°. The surface chemical compositions analysis was performed using X-ray photoelectron spectroscopy (XPS, ESCALAB250, Thermo VG, USA) with Al Kα radiation. Photoabsorption properties were investigated by a diffuse reflectance UV-vis spectrometer (V-770, JASCO, Japan) in the wavelength range 200–900 nm.

Photoelectrochemical characterization.—Photoelectrochemical measurements were conducted with a potentiostat Autolab PGSTAT302N (Metrohm Autolab, The Netherlands) to measure open circuit potentials (OCP) (Fig. 1a). With the electrochemical noise (ECN) module, changes of photogenerated potential and current for both photocatalytic TiO₂ films in dark and under light illumination conditions were recorded (Fig. 1b). For OCP measurements as shown in Fig. 1a the TiO₂ film samples and the 304 stainless steel were electrically coupled, connecting to working electrode; a platinum was connected to counter electrode. In Fig. 1b, the TiO₂ films and the 304 stainless steel were connected to working electrode and counter electrode (the groudwire was used as counter electrode here so that the electrons could flow from TiO₂ films to 304 stainless steel), respectively. All reported potentials measured in the experiment are relative to a KCl-saturated silver/silver chloride electrode (Ag/AgCl), connecting to reference electrode. All electrodes were measured in 3.5 wt% NaCl solution simulated seawater environment at room temperature. The light was a 300 W Xe lamp (PLS-SXE 300, Beijing PerfectLight Co. Ltd); the measured intensity with an AM1.5 filter to simulate the sunlight was 100 mW cm⁻². All experiments began after a stable OCP was observed. To analyze and evaluate the photoelectrochemical protection performance of the as-prepared photoanodes, the photocurrent density changes between TiO₂ films and 304 stainless steel electrodes were measured in the natural state without/with illumination, respectively. Illumination-induced photopotential changes of the TiO₂ films were recorded with respect to the reference electrode.

To explore the influence of Co(OH)₂ surface modification and long-term performance on the TiO₂ films on photoelectrochemical protection, a short cycle experiment was done of 600 s duration alternating between 300 s with illumination and 300 s without. A long-term experiment for 12 h under illumination was done and the photoinduced current and potential changes were analyzed. This may be useful to find ways to improve the preparation process so as to provide a theoretical basis for photocatalytic cathodic protection in marine environment.

Figure 1. Schematic diagram of Autolab electrochemical test system for measuring (a) open circuit potential and (b) photogenerated potential and current of TiO₂ films.
Micromorphologies.—The macroscopic morphology of the anatase TiO$_2$ nanotubes film is blue-gray, uniform and smooth. Fig. 3 shows the SEM images of the prepared TiO$_2$. The anatase TiO$_2$ grew in the form of one-dimensional nanotubes, continuously and uniformly distributed with clearly vertical growth. The nanotubes are approximately 150 nm in diameter (Fig. 3a surface) and 5 μm in length (Fig. 3c cross section morphology). The inset in Fig. 3a shows Co(OH)$_2$ forms spherical particles, approximately 3 nm in diameter adsorbed on a nanotube. It has been proved that nano-material shows excellent conductive properties and obvious quantum size effect, especially one-dimensional nanotubes with high specific surface area as well. Photo-generated electrons can move easily and fast in this structure, which helps to improve the light absorption of photocatalytic material in return. The nanotube structure provides a large number of surface reaction sites, resulting in higher solar energy conversion efficiency, which improves the electrochemical protection performance.

The macroscopic morphology of the exposed rutile TiO$_2$ thin film is uniform and smooth with blue luster. As shown in Fig. 3b, a honeycomb-like compact surface micromorphology of rutile TiO$_2$ was obtained, this is due to slight implantation of nanotube arrays in anodic oxidation. Fig. 3d gives the cross section morphology, the rutile thin film can be clearly seen and has a thickness of around 2 μm.

UV-Vis absorption.—The energy band gaps of conventional anatase nanotubes and rutile TiO$_2$ films are 3.2 eV and 3.0 eV, respectively, which correspond to the absorption peaks at 387 nm and 413 nm. It shows that both two crystalline of TiO$_2$ have almost only ultraviolet light absorption.

Performance of photoelectrochemical cathodic protection.—The corrosion potential of 304 stainless steel in 3.5 wt% NaCl solution is $-0.17$ V measured in the potentiodynamic polarization curve. The minimum protective current density required for cathodic protection of 304 stainless steel is 15 μA/cm$^2$. Accordingly, for cathodic protection of 304 stainless steel the photogenerated electrode potential should be $< -0.17$ V, and the photocurrent density should reach 15 μA/cm$^2$ under illumination.

Unmodified TiO$_2$ shows photoelectrochemical activity and can protect 304 stainless steel to some degree theoretically. To examine it, photogenerated potential changes (setup as in Fig. 1a) of anatase and rutile in the dark and under illumination over time were measured (see Fig. 5), and the dotted line represents the corrosion potential of 304 stainless steel ($-0.17$ V).

The results show that the potential generated with pristine anatase TiO$_2$ nanotubes is $< -0.30$ V, which is much lower than the corrosion potential of 304 stainless steel. This demonstrates that the 304 stainless steel electrochemical protection can be achieved by anatase TiO$_2$ nanotubes. The first potential drop in the presence of illumination quickly reaches $-0.35$ V for 300 s, indicating that the formation and transfer of photogenerated charges happen instantaneously. At this
moment the photogenerated holes haven’t yet reacted with OH\(^-\) and H\(_2\)O in the solution. Subsequently the potential reaches a stable value of \(-0.30\) V at 900 s after a cycle, with transfer and further reaction of photogenerated charge carriers achieving a dynamic balance. After further illumination cycles the potential still drops somewhat reliably, realizing photoelectrochemical protection of 304 stainless steel stably.

The first potential drop with unmodified rutile TiO\(_2\) film under illumination reaches only \(-0.16\) V at 300s, therefore the 304 stainless steel cannot be protected. The potential decreases slightly to \(-0.17\) V at 1500 s with further illumination cycles, barely reaching the corrosion potential of 304 stainless steel. Consequently, electrochemical protection for the 304 stainless steel cannot be achieved with plain rutile TiO\(_2\) film without modification. The non-modified TiO\(_2\) has a limited protection performance for metal.

Electrochemical performance results of Co(OH)\(_2\) particles on the surface of TiO\(_2\) films to protect 304 stainless steel (setup in Fig. 1a) have been studied as shown in Fig. 6. In this test, a long time illumination cycling experiment was run measuring photogenerated potentials for 12 h to analyze the photoinduced potential changes. At the beginning of the illumination, the potentials of modified anatase nanotubes and rutile TiO\(_2\) films decrease to \(-0.35\) V and \(-0.25\) V, respectively. With prolonged illumination time, potentials of both TiO\(_2\) films increase slightly, which may be caused by the accumulation of photogenerated holes. The potentials of both modified anatase nanotubes and rutile TiO\(_2\) films still remain at \(-0.30\) V and \(-0.18\) V stably after 12 h immersion time under illumination, indicating that the modified TiO\(_2\) films can protect 304 stainless steel for 12 hours.
The photoelectrochemical performance of Co(OH)₂-modified TiO₂ has been measured using the illumination cycle shown in Fig. 7 without any additional potential (connected as Fig. 1b) before and after 40 days' immersion in 3.5 wt% NaCl solution. The dotted line in Fig. 7a represents the corrosion potential of 304 stainless steel, and in Fig. 7b it is the minimum protective current density required for 304 stainless steel cathodic protection.

As shown in Fig. 7a, potentials reach to −0.42 V (anatase nanotubes) and −0.25 V (rutile film) at the beginning of the illumination, signifying that both modified TiO₂ films are able to achieve electrochemical protection. However, after immersion in 3.5 wt% NaCl solution for 40 days, the potentials increase to −0.15 V (anatase nanotubes) and −0.10 V (rutile film), respectively. Both potentials are positive to the corrosion potential of 304 stainless steel so that TiO₂ films fail to protect metal.

The corresponding current densities are 38 μA·cm⁻² (anatase nanotubes) and 16 μA·cm⁻² (rutile film) at the beginning as shown in Fig. 7b, indicating that both modified anatase nanotubes and rutile TiO₂ films can produce a protective current for 304 stainless steel. After 40 days' immersion in 3.5 wt% NaCl solution, the current density of modified anatase nanotubes and rutile TiO₂ films decrease to 8 μA and 0.3 μA, respectively, both of which are lower than the minimum protective current density for stainless steel. So the metal cannot be protected due to the decreased protective current.

The above results show that the appropriate Co(OH)₂ loading can significantly improve the photocatalytic activity and photoelectrocatalytic activity of the semiconductor, and thus greatly enhance the photoelectrochemical cathodic protection performance.
of TiO₂. The deposition of Co(OH)₂ on its surface significantly restrained the recombination rate of the interfacial charge carriers by providing the oxidative half reaction sites (as illustration below). It is seen that the surface modification of the catalyst is an effective way to improve the photocatalytic reaction rate in solution (from OH⁻ to O₂ proposed in Fig. 9). The EIS results demonstrate that the modified TiO₂ films could provide more electrons and show accelerated charge transfer, and thus provide effective photocathodic protection for 304 stainless steel.

Fig. 9 schematically illustrates the proposed mechanism of the enhanced photoelectrochemical cathodic protection performance of Co(OH)₂-modified TiO₂ films on 304 stainless steel under illumination. Upon irradiation, electrons from the valence band are excited to the conduction band while holes are left in the valence band. These electrons migrate into 304 stainless steel, leading to the suppression of the anodic dissolution of 304 stainless steel. Consequently, 304 stainless steel is cathodically protected by TiO₂ under illumination. The photogenerated holes are transferred to Co(OH)₂ particles where they oxidize Co²⁺ into Co³⁺. Co³⁺ ions easily oxidize water to O₂. In the oxygen evolution reaction Co³⁺ is reduced to Co²⁺ waiting for the next photogenerated holes to be oxidized again. This cyclic process works without consumption of Co(OH)₂, which is a mediator function. This valence transitions between Co⁵⁺ and Co³⁺ may accelerate the charge carrier distribution, separation, and migration rate of electrons. Co(OH)₂ particles can collect photogenerated holes from the TiO₂ surface as a hole-collecting contact. Therefore, it significantly restrains the recombination rate of the interfacial charge carriers, and the holes are consumed consequently to promote the production of electron hole pairs, which reduces the reverse reaction and accelerates the oxygen evolution kinetics. Moreover, it can also provide photogenerated charge trapping sites and restrain the recombination of charge carrier, thus improving the photo-stability of the catalyst and the efficiency of photoinduced electrons and holes. Meanwhile, Co(OH)₂ particles provide more active sites or reaction sites to promote redox reaction and lower the overpotential. Thus, an improved photoelectrochemical performance could be obtained due to enhanced charge separation of the photogenerated carriers, which means that the Co(OH)₂ modified TiO₂ films could provide better photogenerated cathodic protection for 304 stainless steel (as shown in Fig. 6).

Mechanism analysis.—EIS is a useful technique for the investigation of electrode surface properties and reaction mechanisms as well as kinetics. In order to explore the role of Co(OH)₂ on the surface of TiO₂ films, AC impedance measurements were performed at open circuit potential in 3.5 wt% NaCl solution. The diameter of impedance arc of Co(OH)₂ modified anatase TiO₂ nanotubes (Fig. 8b) decreases markedly compared with that of unmodified anatase TiO₂ nanotubes (Fig. 8a), the equivalent circuits used to fit the EIS data are shown as insets. Rₑ, Qₑ, Rₛ and Zₑ represent electrolyte resistance, a constant phase element, charge transfer resistance and Warburg impedance, respectively. According to the fitting results, the Rₛ value of the unmodified anatase TiO₂ nanotubes was 7734 Ω·cm², whereas the Rₛ value of Co(OH)₂-modified anatase TiO₂ nanotubes was 452 Ω·cm². The smaller Rₛ value indicates the faster charge transfer at the interface between the electrode and the solution, which increased the photogenerated current density. The presence of the Warburg element (0.004449 S·cm⁻⁰·⁵) can be deduced from the slope of value −1/2 in the low frequency region of Co(OH)₂-modified anatase TiO₂ nanotubes. This process depends on diffusion, which may illustrate that the production rate of electron-hole pairs is much higher than the reaction rate in solution (from OH⁻ to O₂ proposed in Fig. 9).

Characterization of TiO₂ after long-term immersion.—In order to explore the reasons for the performance loss of the TiO₂ materials, the characteristics of TiO₂ after long-time immersion have been studied.

Micromorphologies.—After 40 days’ immersion in 3.5 wt% NaCl solution, anatase TiO₂ nanotubes partly peel off from the surface of Ti matrix, as shown in Fig. 10a. The cross-section morphologies in Fig. 10c show the same phenomenon, the nanotube layer is partially damaged, indicating that adhesion to the support is weak between the anatase TiO₂ nanotubes and the Ti matrix. The damage of nanotubes directly influences the electrochemical protection performance for stainless steel, leading to a reduced current and an increased potential (Fig. 7).
No visible changes are observed on the surface of rutile TiO$_2$ film after 40 days’ immersion in 3.5 wt% NaCl solution, as shown in Fig. 10b. However, the cross section morphology in Fig. 10d also exhibits a very slight peeling-off from the surface, which also decreases the protection performance.

Chemical composition analysis.—The crystal structure changes of TiO$_2$ films after immersion were characterized by XRD patterns as shown in Fig. 11a. The diffraction peaks of the anatase TiO$_2$ nanotubes are obviously weaker after 40 days’ immersion in 3.5 wt% NaCl solution. The result shows that the immersion decreases the degree of crystallinity in anatase TiO$_2$ nanotubes, which may be associated with the peeling-off of anatase nanotubes.

Fig. 11b shows the rutile TiO$_2$ film pattern after 40 days’ immersion, with a very small decrease of rutile peak heights, indicating that the crystal structure is still rutile TiO$_2$ without any major changes. Since the surface modification with Co(OH)$_2$ is physisorption on TiO$_2$ thin film only and the content is very low, it exists only on the surface of the film, resulting in the absence of Co(OH)$_2$ diffraction peaks.

Therefore, XPS was further used to investigate the compositions of TiO$_2$ thin films, especially the changes of Co(OH)$_2$ content. Fig. 12 shows high-resolution XPS spectra for the complete survey spectrum, Ti 2p, Co 2p, and Cl 2p region in anatase TiO$_2$ nanotubes. The atomic percentages of the main elements before and after immersion are indicated. The initial Ti 2p peak (Fig. 12b) is assigned to the typical peak of anatase TiO$_2$; the peaks at 458.5 eV and 464.2 eV are caused by the Ti$^{4+}$ in anatase TiO$_2$ nanotube crystals. There are no obvious changes in Ti 2p spectrum after 40 days’ immersion (Fig. 12c), which means the composition of anatase TiO$_2$ nanotubes is stable. However, the Co 2p spectrum shows changes. In Fig. 12d, the initial Co 2p can be deconvoluted into two pairs of individual peaks at 781.1 eV and 797.0 eV.
Figure 12. XPS spectra of Co(OH)$_2$-modified anatase TiO$_2$ nanotubes before and after immersion in 3.5 wt% NaCl for 40 days: (a) survey spectrum, (b) Ti 2p peak before immersion, (c) Ti 2p peak after immersion, (d) Co 2p peak before immersion, (e) Co 2p peak after immersion, (f) Cl 2p peak after immersion.

eV, respectively, which are identified as the major binding energies of Co$^{2+}$ in Co(OH)$_2$. After 40 days’ immersion, the Co peaks disappear completely (Figs. 12a and 12e). Evidently Co(OH)$_2$ has disappeared from the surface of anatase TiO$_2$ nanotubes, resulting in the reduction of TiO$_2$ photoelectrochemical performance. In addition, the Cl 2p spectra (Fig. 12f) present no discernible peak. This result reveals that with 40 days’ immersion the anatase TiO$_2$ nanotubes are not corroded by Cl$^-$ in NaCl solution.

Fig. 13 shows spectral changes for the same elements in rutile TiO$_2$ film before and after immersion. The changes of Ti 2p and Co 2p spectra of rutile TiO$_2$ film are similar to those of anatase TiO$_2$ nanotubes. Compared with the initial peaks of Ti 2p (Fig. 13b) and Co 2p (Fig. 13d), the Ti 2p spectrum (Fig. 13c) shows no clear changes while the Co 2p peaks (Fig. 13a and 13e) disappear after immersion. The loss of Co(OH)$_2$ leads to the decreased photoelectrochemical performance of rutile TiO$_2$ film. Also, the rutile TiO$_2$ film is not corroded by Cl$^-$ in NaCl solution after 40 days’ immersion as implied by the absence of a discernible peak in Fig. 13f.

UV-Vis absorption.—The UV-vis diffuse reflectance spectra were recorded again to observe changes after 40 days’ immersion, results are shown in Fig. 14. The maximum absorption wavelengths of the
anatase and rutile TiO₂ change a little toward 440 nm and 408 nm, respectively, corresponding to band gaps of $\Delta E_g = 2.82$ eV and 3.04 eV. The absence of Co(OH)₂ causes the blueshift of the light absorption threshold, thus affects the protection performance.

Summary

In this work, the long-term photoelectrochemical cathodic protection behavior of Co(OH)₂-surface modified TiO₂ films has been studied in 3.5 wt% NaCl solution. The results indicate that the photo-generated electrode potential of both Co(OH)₂-modified anatase TiO₂ nanotubes and rutile TiO₂ films could decrease to $-0.35$ V and $-0.25$ V under illumination, respectively. Both modified TiO₂ films could realize a long period of 12 h protection for 304 stainless steel. In other words, Co(OH)₂-modification improves the photoelectrochemical ability of both TiO₂ films in 3.5 wt% NaCl solution for a long time. Anatase TiO₂ nanotubes always exhibit a better protection performance than the rutile TiO₂ film. However, the loss of Co(OH)₂ and the peeling-off of anatase TiO₂ nanotubes after prolonged immersion cause the reduced electrochemical protective efficiency.

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Figure 14. UV-Vis absorption spectra of Co(OH)2-modified anatase nanotubes and rutile TiO2 film after immersion in 3.5 wt% NaCl for 40 days.

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References
1. S. Li and J. Fu, Corros. Sci., 68, 101 (2013).
2. C.-X. Lei, Z.-D. Feng, and H. Zhou, Electrochim. Acta, 68, 134 (2012).
3. Y. Chen, S. Zhao, M. Chen, W. Zhang, J. Mao, Y. Zhao, M. F. Maitz, N. Huang, and G. Wan, Corros. Sci., 96, 67 (2015).
4. J. Yuan and S. Tsujikawa, Zaiyiro-to-Kankyo, 44, 534 (1995).
5. T. Tatsuma, S. Saitoh, Y. Ohko, and A. Fujishima, Chem. Mater., 13, 2838 (2001).
6. M. Sun, Z. Chen, Y. Bu, J. Yu, and B. Hou, Corros. Sci., 82, 77 (2014).
7. S. Song and Z. Chen, J. Electrochem. Soc., 161, C288 (2014).
8. R. Hasanov, S. Bilge, S. Bilgic, G. Gece, and Z. Kılıc, Angewandte Chemie, 99, 6191 (2010).
9. N. Wei, Y. Liu, T. Zhang, J. Liang, and D. Wang, Mater. Lett., 185, 81 (2016).
10. X.-t. Wang, Q.-y. Wei, L. Zhang, H.-j. Sun, H. Li, and Q.-x. Zhang, Mater. Sci. Eng., B, 208, 22 (2016).
11. X.-t. Wang, Q.-y. Wei, J.-r. Li, H. Li, X.-z. Zhang, and S.-s. Ge, Mater. Lett., 185, 443 (2016).
12. J. Ren, B. Qian, J. Li, Z. Song, L. Hao, and J. Shi, Corros. Sci., 111, 596 (2016).
13. Q. Liu, J. Hu, Y. Liang, Z.-C. Guan, H. Zhang, H.-P. Wang, and R.-G. Du, J. Electrochem. Soc., 163, C539 (2016).
14. Z.-Q. Lin, Y.-K. Lai, R.-G. Hu, J. Li, R.-G. Du, and C.-J. Lin, Electrochim. Acta, 55, 8710 (2010).
15. J. Hu, Y.-F. Zhu, Q. Liu, Y.-B. Gao, R.-G. Du, and C.-J. Lin, J. Electrochem. Soc., 162, C161 (2015).
16. J. Yang, H. Yan, X. Wang, F. Wen, Z. Wang, D. Fan, J. Shi, and C. Li, J. Catal., 290, 151 (2012).
17. U. G. Alkan and B. H. Hameed, Appl. Catal., A: Gen., 375, 1 (2010).
18. N. Kumar and L. G. Devi, J Phys Chem A, 115, 13211 (2011).
19. C. Pablos, J. Marugan, R. van Grieken, C. Adan, A. Riquelme, and J. Palma, Electrochim. Acta, 130, 261 (2014).
20. G. Riegel and J. R. Bolton, J. Phys. Chem., 99, 4215 (1995).
21. J. M. Herrmann, Sci. Chem., 53, 1831 (2010).
22. J. Li, C.-Y. Lin, Y.-K. Lai, and R.-G. Du, Surf. Coat. Technol., 205, 557 (2010).
23. M. Sun, Z. Chen, and Y. Bu, Surf. Coat. Technol., 266, 79 (2015).
24. M. Sun, Z. Chen, and Y. Bu, J. Alloys Compd., 618, 734 (2015).
25. Y. Bu, Z. Chen, W. Li, and J. Yu, ACS Appl Mater Interfaces, 5, 5097 (2013).
26. G. Liu, H. G. Yang, J. Pan, Y. Q. Yang, G. Q. Lu, and H. M. Cheng, Chemical reviews, 114, 9559 (2014).
27. J. Pan, G. Liu, G. Q. Lu, and H. M. Cheng, Angewandte Chemie, 50, 2313 (2011).
28. Y. F. Xie, Z. B. Yu, G. Liu, X. Li, Ma, and H.-M. Cheng, Energy, Environ. Sci., 7, 1895 (2014).
29. G. Liu, L. Wang, H. G. Yang, H.-M. Cheng, and G. Q. Lu, J. Mater. Chem., 20, 831 (2010).
30. P. Niu, L. C. Yin, Y. Q. Yang, G. Liu, and H. M. Cheng, Adv. Mater., 26, 8046 (2014).
31. R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, and Y. Taka, Sci., 293, 269 (2001).
32. G. Zhang, S. Zhang, and X. Wang, ACS CATAL., 5, 941 (2015).
33. O. Rosseler, M. V. Shankar, M. K.-L. Du, L. Schmidlin, N. Keller, and V. Keller, J. Catal., 269, 179 (2010).
34. M. Ziu, P. Chen, and M. Liu, Langmuir, 29, 9259 (2013).
35. G. Jacobs, U. Graham, E. Chenu, P. Patterson, A. Dozier, and B. Davis, J. Catal., 229, 499 (2005).
36. M. Liu, W. You, Z. Lei, G. Zhou, J. Yang, G. Wu, G. Ma, G. Luan, T. Takata, M. Hara, K. Domen, and C. Li, Chem. Commun., 2192 (2004).
37. L. Wang, F. Dionisii, N. T. Nguyen, R. Kirchgeorg, M. Gilech, S. Grigorescu, S. Prasser, and S. Schumki, Chem. Mater., 27, 2360 (2015).
38. G. S. Hutchings, Y. Zhang, J. Li, B. T. Yonemoto, X. Zhou, K. Zhu, and F. Jiao, J. Amer. Chem. Soc., 137, 4223 (2015).
39. A. Ishad and N. Munchandraiah, Phys Chem Chem Phys, 16, 5412 (2014).
40. M. Qorbani, N. Naseri, and A. Z. Moshfigh, ACS Appl. Mater. Interfaces, 7, 11172 (2015).
41. W. Grüner, A. Brückner, H. Hofmeister, and P. Claus, J. Phys. Chem. B, 108, 5709 (2004).
42. C.-H. Lin, J.-H. Chao, C.-H. Liu, and F.-C. Wang, Langmuir, 24, 9907 (2008).
43. F. Tao, Y. Shen, Y. Liang, and H. Li, J. Solid State Electrochem., 11, 853 (2006).
44. C. Zhen, L. Wang, L. Liu, G. Liu, G. Q. Lu, and H. M. Cheng, Chem. Commun., 49, 6191 (2013).
45. M. Liu, W. You, Z. Lei, G. Zhou, J. Yang, G. Wu, G. Ma, G. Luan, T. Takata, M. Hara, K. Domen, and C. Li, Chem. Commun., 2192 (2004).
46. D. P. Dubal, G. S. Gund, C. D. Lokhande, and R. Holze, ACS Appl Mater Interfaces, 5, 2446 (2013).
47. C. Zhen, L. Wang, G. Liu, G. Q. Lu, and H. M. Cheng, Chem. Commun., 49, 3019 (2013).
48. T. Miyagi, M. Kamei, T. Mitsuhashi, T. Ishigaki, and A. Yamazaki, Chem. Phys. Lett., 390, 399 (2004).
49. H. Nakajima, T. Mori, Q. Shen, and T. Toyoda, Chem. Phys. Lett., 409, 81 (2005).
50. L. Kavan, M. Gratzel, S. E. Gilbert, C. Klemenz, and H. J. Scheel, J. Am. Chem. Soc., 118, 6716 (1996).
51. T. Kawahara, Y. Konishi, H. Tada, N. Tohg, J. Nishi, and S. Bo, Angew. Chem., 114, 2935 (2002).
52. M. R. Nellist, F. A. L. Laskowski, J. Qiu, H. Hajibabaei, K. Sivula, T. W. Hamann, and S. W. Boettcher, Nature Energy, 3, 46 (2017).
53. J. Hou, Z. Wang, C. Yang, H. Cheng, S. Jiao, and H. Zhu, Energy, Environ. Sci., 6, 3322 (2013).
54. J. Yang, D. Wang, H. Han, and C. Li, Acc. Chem. Res., 46, 1900 (2013).