High-efficiency photoelectrochemical cathodic protection performance of the iron-nitrogen-sulfur-doped TiO₂ nanotube as new efficient photoanodes

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Abstract
Novel iron-nitrogen-sulfur-tridoped titanium dioxide nanotubes (Fe-N-S-TiO₂ NTs) have been synthesized via single step anodization of titanium using potassium ferricyanide, as a suitable additive, in dimethyl sulfoxide (DMSO) electrolyte and applied as photoanodes in the photocathodic protection of stainless steel 403 (SS403). Photocurrent density, open circuit potential and Tafel polarization curves have been used to study the photocathodic protection effect of the samples prepared. Upon the addition of potassium ferricyanide to the anodizing electrolyte and titanium dioxide nanotube doping, the light absorption of the Fe-N-S-TiO₂ NTs were increased to the visible region, comparable with pure TiO₂ NTs, according to the results obtained. Enhanced photoelectro-response activity and photocathodic protection performance for 403 stainless steel are exhibited by Fe-N-S-TiO₂ NTs under light illumination. In addition, the optimal sample electrode (FT4) potentials shifted negatively to −683 mV under illumination.

1. Introduction
Corrosion of stainless steel is a serious problem in the industry, which limits its application. One of the most extensively used methods for prevention of stainless steel corrosion is cathodic protection. Despite such advantages as long life and wide range of protection, the method requires impressed current or sacrificial anodes [1]. Therefore, it is essential to develop a new strategy to prevent metal corrosion without any loss of energy or materials. A novel, environmentally benign and clean method for metal protection, known as photoelectrochemical (PEC) cathodic protection, has recently attracted great interest given its outstanding advantages. Notably, the semiconductors used in this process must be of n-type and photo generated holes ought to be trapped by hole-trapping agents [2–5].

An n-type semiconductor, titanium dioxide (TiO₂) has been widely studied in different areas of photoelectrochemistry due to its excellent properties including non-toxicity, high stability, high photocorrosion resistance, remarkable photosensitivity and cheap price. Nevertheless, photogenerated electron excitation can be induced by the wide band gap (3.2 eV for anatase) of titanium dioxide only under UV light. Furthermore, the low quantum efficiency of titanium dioxide in photocatalytic reactions and its poor performance under visible light irradiation due to high recombination of photogenerated electron-hole pairs limit its application in photocathodic protection [3]. Different strategies such as metal and non-metal doping and semiconductor coupling have been developed to overcome these obstacles [6–10].

Iron-nitrogen-sulfur-tri doped titanium dioxide nanotubes (Fe-N-S-TiO₂ NTs) have been synthesized by one-step anodization of titanium in dimethyl sulfoxide (DMSO) electrolyte containing potassium ferricyanide...
in this work. To the best of the authors’ knowledge, the in situ iron-nitrogen-sulfur-tri-doping of titanium dioxide nanotubes by titanium anodization in this new electrolyte has not yet been reported. The photocathodic protection behavior of the samples prepared for 403 stainless steel under xenon light illumination has also been studied. Fe-N-S-TiO₂ NT photoanodes show remarkable photoelectrochemical performance in the protection of 403SS from corrosion, based on the results obtained.

2. Experimental

2.1. Synthesis of materials

All chemicals used in this work were of analytical grade and used as received. The pre-treated titanium plates (99.99% purity, 1 mm thick) were immersed into the anodization electrolyte, which consisted of HF (2 ml), DMSO (98 ml) and potassium ferricyanide. Different concentrations of K₃[Fe(CN)₆] (0, 0.006, 0.012, 0.018 and 0.024 mol l⁻¹) were used for a given electrolyte solution (table 1). Electrochemical anodization was performed in a two electrode system with platinum plate functioning as a counter electrode. Nanotube films were directly grown on the titanium plates at 40 V (DC power supply source; ADAK, PS405) for 8 h. Following anodization, the samples were washed several times with distilled water, air dried and annealed in an oxygen atmosphere at 450 °C for 1 h (2 °C min⁻¹).

2.2. Characterization

A Hitachi FE-SEM S-4160 field emission scanning electron microscope (SEM) was used to characterize the sample morphologies. X-ray diffraction (XRD, Philips XPert) for Cu Kα radiation was used to identify the crystalline phases. UV–vis diffuse reflectance spectrophotometry (JASCO V–570 Japan) was used to identify the UV–vis DRS of the composite.

A three-electrode photoelectrochemical cell consisting of Ag/AgCl and Pt foils as reference and counter electrodes, respectively, was used to measure transient photocurrents. Pure TiO₂ and Fe-N-S-TiO₂ NTs served as the working electrode, which was intermittently irradiated by a 35 W Xe lamp. A mixture of 0.1 M Na₂S and 0.1 M NaOH solutions was used as the electrolyte in the cell. An Origaflex electrochemical working station (OGF500 potentiostat/galvanostat, France) was used to carry out the measurements. The photocathodic protection efficiency of the samples prepared was evaluated using 403 stainless steel (403SS) as the specimen (exposed area of 1 cm²). This was carried out by examining the potential changes of 403SS coupled with the films. The experimental setup and methods have been described in detail in our previous work [2]. The setup consisted of a photoelectrochemical cell containing a mixture of 0.1 M Na₂S and 0.1 M NaOH solutions and a corrosion cell holding a 0.5 M NaCl aqueous solution. The samples prepared served as the photoanode in the photoelectrochemical cell. A 403SS specimen (working electrode), a platinum sheet counter electrode and a Ag/AgCl were located in the corrosion cell. The two cells were connected through a salt bridge and the 403SS specimen was electrically connected by a Cu wire to the prepared film intermittently irradiated by light.

3. Results and discussion

The SEM images of the top surface and cross section of Fe-N-S-TiO₂ NTs are shown in figure 1. As observed, the nanotubes are uniformly shaped and well-aligned, vertically grown from a Ti substrate and more nanotube mouths are open. The average inner diameter and wall thickness of sample FT4 are around 130 and 60 nm, respectively, and the average nanotube length is about 1.1 μm. Maintaining the tubular structure of the samples, even following the addition of suitable quantities of potassium ferricyanide to anodizing electrolyte, is necessary. According to the SEM images, titanium dioxide nanotube doping is performed without the destruction of the tubular nature of the nanotubes. There is no metal layer at the top of the nanotubes, suggesting that doping has occurred into the nanotubular walls. When K₃[Fe(CN)₆] concentration in solution is increased to 0.018 M, the
nanostructures formed become very non-uniform. Porous films are formed rather than nanotubes. Therefore, an appropriate potassium ferricyanide concentration is significant for the structure of nanotube arrays.

The XRD patterns of TiO₂ and Fe-N-S-TiO₂ NTs (sample FT4) are shown in figure 2(a). The presence of anatase crystal structure is confirmed by XRD patterns of pure and doped samples. Rutile phase is not formed because the annealing temperature (i.e. 450 °C for 1 h) is not sufficient for the transformation of the crystal phase from anatase to rutile. The absence of additional peaks corresponding to iron oxides or metallic iron suggests an amount of iron under the detection limit or complete Fe(III) integration of in the crystal lattice of titanium dioxide. Sample FT4 is analyzed using energy dispersive x-ray spectroscopy (EDX) (figure 3). The Ti, O, N, C and Fe peaks clearly observed in the spectra confirm the formation of Fe-N-S-TiO₂ NTs. It must be pointed out that EDX results only show the presence of elements, but do not provide detailed information on the valence state and composition. The surface chemical compositions of the Fe-N-S-TiO₂ NTs samples were further investigated using XPS surface analysis. The presence of Ti, O, Fe, S, N and C is observed in the XPS spectrum of sample FT4 (figure 2(b)). The Fe 2p₃/2 and Fe 2p₁/₂ binding energy of Fe⁴⁺ are verified by the peaks at 711 and 724 eV (figure 2(c)), respectively. The small shakeup satellite structure, which is located between two main peaks, is the fingerprint of Fe⁴⁺ electronic structures. The peak centered at 169.1 eV (figure 2(d)) is due to sulfate, mainly originating from dimethyl sulfoxide. The O 1s spectra are shown in figure 2(e). As observed, the O1s XPS spectra are wide and asymmetric. Thus, there are at least two types of chemical states according to the binding energy, ranging from 529 to 533 eV. This includes crystal lattice oxygen and hydroxyl groups. It must be indicated that photocatalytic activity is enhanced by increasing the quantity of hydroxyl groups on the sample.

Figure 1. Top-view, side-view, and cross-sectional SEM images of Fe-N-S-TiO₂ NTs (sample FT4) with different magnification.
surfaces. The binding energies of Ti 2p\textsubscript{3/2} and Ti 2p\textsubscript{1/2} peaks are observed at 459.1 and 464.8 eV, respectively, in the high resolution XPS spectrum of Ti in the 2p region (figure 2). These are typical values for Ti\textsuperscript{4+} in titanium dioxide. Therefore, there are no observable changes in the chemical environment of titanium. The N 1s peak is shown in figure 2. The peak centered at 400.8 eV is ascribed to the N species oxidized (NO) to form Ti-O-N linkage.

UV–vis DRS spectra are used to measure the light absorption properties of different samples, as shown in figure 4(a). The spectrum of pure titanium dioxide nanotubes shows that it initially absorbs ultraviolet light with a wavelength below 400 nm, associated with the intrinsic band gap absorption of TiO\textsubscript{2}. Strong and weak absorptions are observed in the UV and visible light regions, the absorption edge being about 390 nm. The absorption edges of Fe-N-S-TiO\textsubscript{2} NT samples are shifted to higher wavelength regions in comparison with pure TiO\textsubscript{2} NTs.
TiO$_2$ NTs. The visible light response region increases from sample TNT to sample FT4, and slowly decreases for sample FT4 to sample FT8. The high visible light activity of Fe-N-S-TiO$_2$ NTs makes them applicable in solar light-induced photocatalysts and enhance their photoelectric protection properties for 403 stainless steel.

Figure 3. EDX spectra of Fe-N-S-TiO$_2$ NTs sample (FT4).

Figure 4. (a) UV–vis absorbance spectra of different samples; (b) Photocurrent density-time curves of different samples under intermittent illumination. (c) Potential Variations of 403SS in a 0.5 M NaCl solution when it coupled to the different samples under intermittent Xe light irradiation and (d) Tafel polarization curves of 304SS, and 304SS coupled with different samples in a 0.5 M NaCl solution under illumination.
Transient photogenerated current density is a major parameter factor in the evaluation of the photoelectrochemical performance and electron transfer capability of a semiconductor under the illumination of on/off cycles. The transient photocurrent densities of the pure titanium dioxide nanotubes and Fe-N-S-TiO$_2$ NTs under 3 on/off cycles of light illumination are shown in figure 3(b). The photocurrent densities of these samples are almost zero in the dark. The photocurrent density of pure TiO$_2$ NTs becomes negligible upon turning on light irradiation whereas the photocurrent density of Fe-N-S-TiO$_2$ NTs is almost 100 $\mu$A cm$^{-2}$. This suggests the great enhancement of photon-to-current conversion property of Fe-N-S-TiO$_2$ NTs. In other words, more photoelectrons are formed in the Fe-N-S-TiO$_2$ NTs in comparison with pure TiO$_2$ NTs under the same irradiation conditions because of the narrowed band gap, broad range and strong capability of adsorption. Thus, it can be stated that these novel samples may provide more efficient photocathodic protection for metals compared with pure TiO$_2$ NTs. In addition, the photocurrent responses of Fe-N-S-TiO$_2$ NTs are reproducible during three on-off cycles of the irradiation, which indicates the remarkable stability of these novel samples in this mixed solution under the intermittent light irradiation.

Upon illumination, the new photoanodes must be able to provide photogenerated electrons to the stainless steel surface, leading to the steel surface polarization and potential changes. Thus, the photocathodic protection performance was evaluated by monitoring the potential variation of the metal coupled with these photoanodes as an effective parameter. The OCP variations of 403SS coupled with various photoanodes under the illumination of on/off cycles of xenon lamp light are shown in figure 4(c). As observed, the potential values of all coupled electrodes are more negative than that of 403SS electrode, which indicates that 403SS is cathodically polarized on coupling with these photoanodes. Photoelectrons are produced and transferred to the coupled 403SS through the external circuit (copper wire) when these photoanodes are irradiated by light. The potential of the 403SS is subsequently decreased, indicating the photocathodic protection of the steel by the photoanodes. Under the irradiation, the potentials (mV versus Ag/AgCl) can be ranked in decreasing order as follows:

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\text{FT4 (665)} > \text{FT6 (646)} > \text{FT2 (639)} > \text{FT8 (530)} > \text{TNT (484)}
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The higher photoelectrochemical activity of sample FT4 compared to the other samples could be attributed to the following reasons:

- Smaller band gap energy of FT4 sample compared to other samples cause more light absorption of this sample. According to the DRS results, doping enables the visible absorption of the Fe-N-S-TiO$_2$ NTs sample, so that under xenon lamp light irradiation, it is possible to generate higher amount of electron–hole pairs.
- The effect of surface morphology of the synthesized sample on their photoelectrochemical activity. Sample FT4 has regular arrays of oriented nanotubes on titanium substrate. These nanotube arrays provide direct conduction pathways, minimizing recombination of photogenerated charge carriers. Also, high surface area of nanotubes is benefit for the photoelectrochemical performance and the solar power conversion efficiency.

The photocathodic protection effects of the samples prepared were also shown by the Tafel polarization curves of 403SS in the 0.5 M NaCl solution. As observed in the polarization curves (figure 4(d)), the potential of 403SS shows a clear decreasing trend upon coupling to these photoanodes under irradiation. The corrosion potential ($E_{corr}$) of 403SS was almost $-0.270$ V (versus Ag/AgCl) prior to coupling. A remarkable negative shift of $-0.481$ V, $-0.578$ V, $-0.654$ V, $-0.656$ V and $-0.683$ V is shown under xenon light by the corrosion potential of 403SS coupled with pure titanium dioxide nanotubes and different Fe-N-S-TiO$_2$ NT samples. Furthermore, a higher corrosion current is shown by 403SS coupled with sample FT4 compared with 403SS, due to the formation of photogenerated charge under light illumination. The results show the successful protection of 403SS from corrosion by connecting it with these novel electrodes. In addition, the current density of 403SS coupled with the photoanodes under light irradiation was found to be higher than that of the uncoupled 403SS at the corrosion potential, indicating the transfer of a large number of photoexcited electrons from the photoanodes to 403SS and acceleration of the cathodic reaction on the steel surface, which cathodically protects 403SS from corrosion. The results also show the more effective photocathodic protection effect of sample FT4. Therefore, 403SS can be successfully protected from corrosion by connecting with the Fe-N-S-TiO$_2$ NT electrodes. Figure 5 schematically illustrated a mechanistic model for photoelectrochemical cathodic protection of SS403 using Fe-N-S-TiO$_2$ NTs. The light is absorbed by prepared photoanodes, generating hole-electron pairs. The holes are consumed by oxidation of S$^{2-}$ into S. Since the photoinduced holes are scavenged by S$^{2-}$, the photoelectrons can transfer to the 403 stainless steel, and are consumed by cathodic reaction (e.g., the reduction of dissolved oxygen). As a result, the SS403 is cathodically protected from corrosion.
4. Conclusions

To sum up, Fe-N-S-TiO₂ NTs have been successfully prepared via one-step electrochemical anodizing method. The samples prepared have been systematically characterized by XRD, FE-SEM, EDX, XPS and UV–vis. The photocathodic protection effect of the samples prepared was evaluated by measurement of photoinduced open circuit potential and Tafel curves. Based on the analysis of the optical property of titanium dioxide, the light absorbance edge was greatly enhanced by tri-doping with Fe, N, and S elements and higher photogenerated current density was shown by Fe-N-S-TiO₂ NTs compared with pure TiO₂ NTs. When 403SS was coupled to the Fe-N-S-TiO₂ NT in a 0.5 M NaCl solution under light irradiation, its potential decreased by 400 mV (relative to its corrosion potential), which indicated the more efficient photocathodic protection of 403SS by these novel samples in comparison with pure TiO₂ nanotubes.

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