



Highly efficient polypyrrole sensitized TiO₂ nanotube films for photocathodic protection of Q235 carbon steel



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ABSTRACT

Polypyrrole (PPy) sensitized TiO₂ nanotube arrays (PPy/TNAs) are fabricated via anodic oxidation and electropolymerisation method. The crystallinity, morphology, optical property and photocathodic protection performance of PPy/TNAs composites can be readily controlled by varying the electropolymerisation time. PPy acts as a photosensitizer and a “pool” to gather photoexcited electrons, and an appropriate quantity of PPy contributes to the photosensitization, heterojunction formation and electron pool effect. The PPy/TNAs film acquired at 15 min exhibits excellent visible-light response and favourable photocathodic protection for the coupled Q235 carbon steel under white-light irradiation.

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1. Introduction

Compared with organic coatings and cathodic protection, the photocathodic protection of metals using TiO₂ coatings is an environment-friendly and sustainable anticorrosion technology that has attracted increasing attention over the past two decades. However, the practical application of this technology remains restricted by low photocurrent, wide band gap of TiO₂ (3.2 eV) and poor efficiency in the dark [1–3]. In response to the aforementioned limitations, TiO₂ nanotube arrays (TNAs) film was developed. TNAs film can promote the generation and transfer of photogenerated electron-hole (e⁻-h⁺) pairs because it has a larger specific area than traditional nanoparticle film. Great efforts are also under way to tune the band gap response of TNAs to the visible region [4–6]. Coupling with noble metals [7–9], doping with narrow band semiconductor quantum dots [10–14], compositing with carbon materials (e.g. GO [15], rGO [16,17]) and polymer [18] and sensitizing with organic dyes [19–21] are considered feasible ways to modify TNAs. Nevertheless, some of the main challenges also exist in the instability and short life of sensitizers during light irradiation [22,23] and the toxicity of the organic dyes. A candidate that has

most recently emerged to replace the aforementioned sensitizers is polypyrrole (PPy), a polymer with high conductivity and excellent mobility of charge carriers [24]. The narrow band gap of PPy (2.2 eV) allows it to absorb visible light and inject the photoexcited electrons to the conduct band of TiO₂, an effect that is favourable for separating photogenerated e⁻-h⁺ pairs, as well as to enhance photoconversion efficiency [25]. Given its excellent stability and easy preparation, PPy has become an important precursor for fabricating or modifying composite materials, including TNAs-based films [26,27]. PPy may also serve as an electron pool in the hybrid system and help provide metals good protection from corrosion in the dark. Thus far, the research is mainly focused on the preparation of PPy/TNAs hybrids and their photocatalytic performance. To the best of our knowledge, a report related to PPy/TNAs for the photocathodic protection of carbon steel, which has a more negative self-corrosion potential than stainless steel, is lacking.

In this work, PPy/TNAs hybrid films were fabricated by polymerising pyrrole onto the outer/inner surface of TNAs and then applied for the photocathodic protection of Q235 carbon steel in 3.5 wt% NaCl solution. These procedures were not shown in previous publications. The resultant film exhibited good photoelectrochemical performance and effective photocathodic protection of Q235 carbon steel both under illumination and dark conditions, a result that might be applicable in practice. The mechanism of the

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visible-light-induced protection of the as-prepared films was also proposed.

2. Experimental

2.1. Fabrication of TNAs and PPy/TNAs thin-film photoelectrodes

TNAs were firstly prepared via an anodic oxidation method in a two-electrode electrochemical cell, Ti foil ($1.0 \times 2.0 \times 0.02$ cm) and graphite flake ($15 \times 2 \times 0.1$ cm) were used respectively as working electrode (WE) and counter electrode (CE). Prior to anodising, the Ti foils were preprocessed as follows: (1) cleaned in the hydrofluoric acid solution, (2) abraded with 3000 mesh sandpaper to remove scratches and the oxide film, and (3) ultrasonically cleaned in acetone and ethanol and then dried with nitrogen flow. The anodising process continued in ethylene glycol (EG) electrolyte containing 0.3 wt% NH_4F and 5 vol% deionised water at 60 V for 2 h. After anodisation, the sample was annealed at 450°C for 2 h in air with a heating rate of $5^\circ\text{C}/\text{min}$, and then naturally cooled down to room temperature. The prepared TNAs were then sealed using epoxy resin to achieve an exposed electrode area of 1×1 cm.

The PPy/TNAs hybrids were assembled via electrochemical polymerisation in a three-electrode system at room temperature, with the annealed TNAs as WE and the Pt foil as CE. A silver/silver chloride (Ag/AgCl) electrode immersed in saturated KCl solution ($E = 0.1981$ V vs. NHE) was used as the reference electrode (RE). The electrolyte was composed of acetone solution containing 0.1 M LiClO_4 and 0.2 M pyrrole monomer. Electropolymerisation was conducted with a CHI 660D electrochemical workstation (CHI, Co., Shanghai, China) at 0.8 V for different time (5, 10, 15 and 20 min), and the obtained films were named as 5-PPy/TNAs, 10-PPy/TNAs, 15-PPy/TNAs and 20-PPy/TNAs, respectively.

2.2. Characterisation

The crystalline structures of the films were identified with X-ray diffraction (XRD, Bruker AXS D8 ADVANCE) using Ni filtered $\text{Cu K}\alpha$ radiation at 40 kV and 40 mA. Fourier transform infrared (FTIR) spectra were recorded using an FTIR (Nicolet IR200) spectrophotometer. The morphologies were characterised via scanning electron microscopy (SEM, JEOL 7500F) and transmission electron microscopy (TEM, Hitachi H-7000). The optical properties of the samples were characterised using a UV-vis spectrophotometer (Hitachi U-3900) equipped with an integration sphere. The chem-

ical composition of the as-prepared film was detected via X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250XI).

2.3. Photoelectrochemical measurements

The photoinduced current density and open circuit potential (OCP) of the as-prepared samples were investigated using a CHI660D electrochemical workstation. The schematic illustrations are shown in Figs. 1a and 1b. The experimental setup was composed of two couple cells connected by a salt bridge; one was the corrosion cell containing 3.5 wt% NaCl, while the other was the photoelectricity quartz cell filled with 0.1 M Na_2S and 0.2 M NaOH, in which Na_2S served as a hole scavenger and NaOH was used to inhibit the hydrolysis of S^{2-} . The Q235 carbon steel and the PPy/TNAs film were separately immersed into the NaCl solution and the Na_2S -NaOH solution, both having an active area of 1 cm^2 (1×1 cm). Before electrochemical signal collection, both the carbon steel and the PPy/TNAs photoanode were immersed into the solution for approximately 20 min to achieve the potential and environmental stabilization. Then, the measurements were performed under intermittent white light ($87 \text{ mW}/\text{cm}^2$) supplied by a 300 W Xe lamp (PLS-SXE 300, Beijing Bofeilai Co., Beijing, China). This arrangement was convenient for the measurement of the variations in current density and OCP [28].

Fig. 1a shows the setup for the measurement of the photoinduced current density. The Q235 carbon steel and the PPy/TNAs film were connected to the ground wire (GW) interface and WE interface of the workstation respectively. The CE and RE of the workstation were connected by short circuit. Thus, the workstation worked as a zero-resistance ammeter, and the photocurrent flowing between the film and the carbon steel could be measured without polarisation [29]. Fig. 1b illustrates the setup for the OCP measurement. To measure the OCP variations, the as-prepared film and Q235 carbon steel were connected using Cu wire and then used as the WE. A saturated calomel electrode (SCE, $E = 0.2415$ V vs. NHE) and a Pt foil were used as RE and CE respectively.

The electrochemical impedance spectra (EIS) had ever been measured using the setup similar to Fig. 1b [30,31]. In this study, the EIS measurements were performed using a conventional three-electrode system [32] in a quartz cell with PPy/TNAs films, Pt foil and SCE as the WE, CE, and RE, respectively. It was accurate to acquire the photo-induced charge transfer properties of PPy/TNAs films. The electrolyte was composed of 0.1 M Na_2S and 0.2 M NaOH. After the OCP of the photoanode remained fairly constant over time, the EIS was measured at the OCP over a frequency range of 10^5 – 10^{-2} Hz with an AC signal of 10 mV and a data density of five

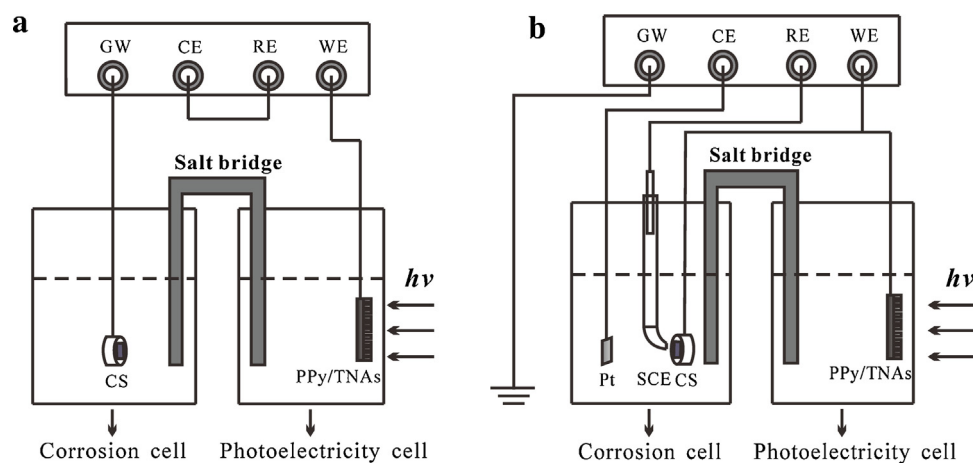


Fig. 1. Schematic illustrations of the experimental setup for (a) photoinduced current density and (b) photoinduced open circuit potential. The abbreviations of GW, CE, RE and WE are defined as the ground wire, the counter electrode, the reference electrode and the working electrode, respectively.

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