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# Characteristics and anticorrosion performance of Fe-doped $TiO_2$ films by liquid phase deposition method

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ABSTRACT

Fe-doped $TiO_2$ thin films were fabricated by liquid phase deposition (LPD) method, using Fe(III) nitrate as both Fe element source and fluoride scavenger instead of commonly-used boric acid ($H_3BO_3$). Scanning electron microscopy (SEM), X-ray diffraction (XRD), and UV–vis spectrum were employed to examine the effects of Fe element on morphology, structure and optical characteristics of $TiO_2$ films. The as-prepared films were served as photoanode applied to photogenerated cathodic protection of SUS304 stainless steel (304SS). It was observed that the photoelectrochemical properties of the as-prepared films were enhanced with the addition of Fe element compared to the undoped $TiO_2$ film. The highest photoactivity was achieved for Ti13Fe (Fe/Ti = 3 molar ratio) film prepared in precursor bath containing 0.02 M $TiF_4$ + 0.06 M $Fe(NO_3)_3$ under white-light illumination. The effective anticorrosion behaviors can be attributed to the Fe element incorporation which decreases the probability of photogenerated charge-carrier recombination and extends the light response range of Fe-doped $TiO_2$ films appeared to visible-light region.

## 1. Introduction

The corrosion prevention of stainless steels has been deeply studied since it becomes a more serious issue. Conventional techniques [1–3] applied to corrosion protection have been limited by the shortage life-time of sacrificial anode or energy. Very recently, Yuan and Tsujikawa [4] reported the sol–gel $TiO_2$ films could offer a sustainable anticorrosion way for copper substrate under illumination and proposed the concept of photogenerated cathodic protection for the first time. Afterwards, Park et al. [5,6] have developed a new idea of using the $TiO_2$ photoanode coupled with the stainless steel for corrosion prevention. Since then, such novel approach has been widely studied by many researcher [7–16]. The basic principle of their investigations is to replace the conventional sacrificial anode with a $TiO_2$ photoanode that generates electrons upon band-gap illumination, and the photogenerated electrons can transfer into the stainless steel shifting the potential to a more negative value than corrosion potential. However, the large band-gap of $TiO_2$ (3.2 eV) limits the efficiency of photocathodic protection due to the low absorption capability for visible light and the high recombination rate of photogenerated electron-hole ($e^-$-$h^+$). Various strategies including doping with non-metal [17–19] or metal element [20–22] and narrow band-gap semiconductors [23,24] have been adopted to extend the photoresponse into visible spectral range and improve separation rate of $e^-$-$h^+$.

Among all reported available candidates, Fe element is considered as a suitable dopant of $TiO_2$ in terms of its low cost and easy preparation, especially its semi-full electronic configuration and ion radius close to $Ti^{4+}$. Many efforts have demonstrated that Fe-doped $TiO_2$ nanoparticle or nanotube films could enhance photocatalytic behavior, using sol–gel [25,26], hydrothermal method [27], and electrochemical anodization technique [28]. However, the above methods usually require special apparatus or a complicated process, e.g. post-treatment (anneal above 450 °C) to obtain the crystalline pure $TiO_2$ or Fe-doped $TiO_2$ films, which would largely limit for their industrial applications and lead to environmental problems.

Liquid phase deposition (LPD) is a soft wet-chemical technique based on the controlled hydrolysis of metallic fluoro-complexes and has got attractive attentions to fabricate $TiO_2$ films due to its advantages, such as low energy-cost equipment and partially crystalline products at ambient temperature [19,29–31]. In addition, deposition rate and crystal orientation can be easily controlled by alternative fluoride scavengers (e.g. metallic cations) compared with the commonly used scavenger $H_3BO_3$. Meanwhile, these metallic cations may draw into $TiO_2$ lattice forming metallic cation doped $TiO_2$ composite films [32]. It was found that the addition of ferric ions during the LPD process could improve the

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**Table 1**
Experimental bath conditions for preparation of the samples and their corresponding photoelectric properties.

| Sample | Fluoride scavenger | $[TiF_4]$ (mM) | $[Ti:Fe^{3+}]$ molar ratio | Photoactivity |
|---|---|---|---|---|
| Ti11Fe | $Fe^{3+}(Fe(NO_3)_3{\cdot}6H_2O)$ | 20 | 1:1 | Low |
| Ti12Fe | $Fe^{3+}(Fe(NO_3)_3{\cdot}6H_2O)$ | 20 | 1:2 | Medium |
| Ti13Fe[a] | $Fe^{3+}(Fe(NO_3)_3{\cdot}6H_2O)$ | 20 | 1:3 | High |
| Ti13B | $H_3BO_3$ | 20 | 1:3 | Low |

[a] It should be noted that when the Fe content exceeding 3 times of Ti source, it is not easy to obtain $TiO_2$ films on substrate rather than $TiO_2$ particles in suspension since the large nucleation rate.

photocatalytic activities of $TiO_2$ [33,34]. However, according to our best knowledge, few reports have mentioned the LPD Fe-doped $TiO_2$ composite films applied to the photogenerated cathodic protection of metals.

In this work, Fe-doped $TiO_2$ thin films were fabricated on fluorine doped tin oxide (FTO) substrate using different contents of Fe(III) nitrate ($Fe(NO_3)_3{\cdot}9H_2O$) as both fluoride scavenger and Fe element source by LPD technique. The effects of Fe element content on the structure and morphology characteristics of $TiO_2$ films was discussed in detail. The photogenerated cathodic protection properties of the Fe-doped $TiO_2$ films coupled SUS304 stainless steel (304SS) electrode were also investigated. The results indicate that the continuous Fe-doped $TiO_2$ films with dense morphology exhibit a more effective photocathodic protection for stainless steel either under light illumination or dark condition.

## 2. Experimental

### 2.1. Materials

The substrates used for the preparation of Fe-doped films were FTO conducting glass (30 mm × 10 mm × 1 mm). Before experiments, the FTO substrates were degreased with detergent, and then ultrasonically cleaned in isopropyl alcohol, acetone, ethanol and de-ionized water for 15 min, successively. Several precursor solution baths, i.e. containing different stoichiometric relations between titanium and scavenger were presented and summarized in Table 1. Each liquid phase bath composition has been labeled according to the nomenclature “Ti molar ratio scavenger” (first column in Table 1). That Fe/Ti = 0, 1, 2, and 3 molar ratio, which were designated as Ti13B, Ti11Fe, Ti12Fe, and Ti13Fe, respectively. The pretreated clean FTO substrates were then placed vertically into the bath solution with a natural pH value. Subsequently, the whole deposition system was kept at 80 °C for 2–4 h to get similar thickness specimens. After film deposition, the specimens were gently washed and naturally dried in the air.

The 304SS (10 mm × 30 mm × 1 mm) plates used in this work were mechanically polished to a mirror finish with $Al_2O_3$ suspension solution, and then ultrasonically cleaned in acetone, ethanol and de-ionized water, respectively.

### 2.2. Characterization

The surface and cross section morphologies of the prepared films were observed using a field emission scanning electron microscopy (FE-SEM, LEO1530). In addition, the chemical composition of the samples was analyzed by an energy dispersion spectroscopy (EDS, Oxford INCA300, England) attached to SEM. Phase structure of the samples was performed through an X-ray diffractometer with a Cu-$K_{\alpha 1}$ radiation ($\lambda = 0.154056$ nm) source (XRD, X'pert PRO, Panalytical, Netherlands) at 40 kV and 30 mA. In order to increase the sensitivity of the thin films signals, a grazing incident configuration was used (1.0°). The photoabsorption properties were measured with a diffuse reflectance UV–vis spectrometer (DRS, Varian, Cary 5000) at the wavelength range of 300–600 nm, using the bare FTO substrate as blank.

### 2.3. Photoelectrochemical measurements

The photoelectrochemical measurements were performed in a three-electrode system using a PARSTAT2273 Advanced Electrochemical System connected to an Omni-λ 300 grating spectrometer with an LSXS-500 Xe lamp as the illumination source. To investigate the photogenerated cathodic protection properties of the as-prepared photoanodes, the open circuit potential (OCP) changes and electrochemical impedance spectroscopy (EIS) of the 304SS electrode coupled with photoanode in the presence and absence of white-light illumination were measured. During EIS measurements, the frequencies were ranged between $10^5$ Hz and $10^{-2}$ Hz using a 10 mV sinusoidal potential modulation. The detailed description of experimental measurements were similar to the other work [14]. Briefly, the photoelectrochemical setup included two cells. A polytetrafluoroethene (PTFE) container with a quartz window to transmit the light was used as the photoelectrochemical cell. The $TiO_2$/FTO electrode with an active area of 1 $cm^2$ was used as a photoanode in the photoelectrochemical cell, while the coupled 304SS electrode also with exposed area of 1 $cm^2$ served as the working electrode in the corrosion cell. The two cells were connected by a salt bridge (1 M KCl in agar contained in a U-type glass tube), and a Cu wire was used to couple the two electrodes to complete the circuit. Moreover, the saturated calomel electrode (SCE) and a platinum foil served as the reference electrode and counter electrode, respectively. The electrolyte used in the photoelectrochemical cell was a 0.1 M sodium formate ($HCOONa{\cdot}2H_2O$) solution, while in the corrosion cell was a 0.5 M sodium chloride (NaCl) solution.

During the measurement of photocurrent spectra, a SR830 lock-in amplifier and SR540 chopper setup (with a chopper frequency of 34 Hz) were used and connected to the above electrochemical working station. Furthermore, the Tafel polarization curves of the as-prepared electrodes were also measured between −130 mV and +130 mV at the OCP with a scanning rate of 0.167 mV/s. Before the measurement of polarization, the samples were immersed into the electrolyte solution and the OCP of each sample was monitored until a constant value was reached.

## 3. Results and discussion

### 3.1. Structure and morphology

The morphologies of LPD samples under typical conditions (for details see Table 1) were examined by SEM. Fig. 1(a) and (b) shows the SEM images of Ti13B specimen prepared by LPD technique, i.e. the solution bath containing 0.02 M $TiF_4$ and 0.06 M $H_3BO_3$ as the fluoride scavenger. The sample gave irregular rod-like shapes and sizes ∼150 nm, as clearly shown in the high magnification SEM image (Fig. 1(b)). However, when Fe(III) was used as fluoride scavenger (Fig. 1(c) and (d)), Ti13Fe films revealed hemispherical features consisted of nanocrystals with a dense morphology. The similar morphology has been observed in previous reports [19,32],