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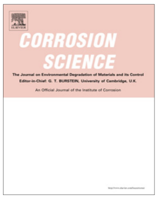

Preparation and photocathodic protection performance of CdSe/reduced graphene oxide/TiO_2 composite

Hong Li [a,b], Xiutong Wang [a,*], Liang Zhang [c], Baorong Hou [a,*]

[a] *Marine Corrosion and Protection Centre, Institute of Oceanology, Chinese Academy of Sciences, No. 7 Nanhai Road, Qingdao 266071, China*
[b] *University of Chinese Academy of Sciences, 19 (Jia) Yuquan Road, Beijing 100049, China*
[c] *University of Qingdao Technological University, No. 11 Fushun Road, Qingdao 266071, China*

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ABSTRACT

CdSe/reduced graphene oxide/TiO_2 films that served as photoanodes for cathodic protection application were prepared by electrochemical deposition. Under visible-light illumination, the open-circuit potential of the composite films coupled with 304 stainless steel could shift to a more negative value and offer an effective photocathodic protection for stainless steel. Moreover, the composite also exhibited stronger photocurrents and greater absorption of solar energy compared to that of pure TiO_2 films. The composite can also offer a sufficient cathodic protection even in the dark. In summary, the reduced graphene oxide/CdSe could greatly improve the photocathodic protection properties of TiO_2 films.

1. Introduction

The preparation of TiO_2 films and their photoelectrochemical properties have attracted significant attention in the field of corrosion and protection of metals [1–5]. Electrons generated in TiO_2 film under illumination can transfer to the metal coupled with the film; thus, the potential of the metal shifts toward a more negative value than its corrosion potential. Consequently, corrosion of the metal is prevented, which is the basic principle of the photocathodic protection of TiO_2 film for metals [6–9]. Compared with conventional cathodic protection, this method does not need supplied current or sacrificial anodes. However, given the wide band gap of TiO_2 (3.2 eV), this material can only absorb light with the wavelength less than 380 nm, which limits its practical application. In addition, maintaining cathodic protection in the dark is difficult because of the fast recombination of photo-generated electron–hole (e^-–h^+) pairs. To overcome these obstacles, many efforts have been made to modify TiO_2 and its composite films.

Coupling with narrow band gap semiconductors, such as CdSe [10–12], CdS [13,14] and CdTe [15,16], is one of the most effective method to improve the visible light response of TiO_2. CdSe, with a band gap of 1.6–1.8 eV can accept visible light, and the generated electrons in CdSe are transferred to the conduction band of TiO_2. Robel et al. [17] employed CdSe/TiO_2 composite as a photoanode in a photoelectrochemical cell, which showed 12% generation efficiency of the photon-to-charge carrier.

Graphene has attracted particular attention because of its electron transfer and charge separation ability [18–22]. Graphene is an ideal conductor with zero band gap, supplying the charge carriers with high mobility within the graphene film. In addition, the monolayer structure of graphene endows electron acceptors because of its large surface area. Herein, graphene is used to improve the photocathodic protection properties of TiO_2 [23–25]. Guo et al. [26] proved that introducing graphene to TiO_2 films can reduce recombination of photo-generated (e^-–h^+) pairs and improve the protection effect for 304 stainless steel (304SS) under UV illumination. Ghosh et al. [27] prepared CdSe–graphene–TiO_2 particles and found that graphene can capture electrons, which are transferred to the CB of CdSe and, in the same way, to TiO_2.

So far, electrochemical reduction of graphene oxide (GO) to graphene has drawn great attention due to its fast and green nature [28–31]. In this study, the composite was constructed via two steps: firstly, graphene films were prepared on TiO_2 nanotubes (NTs), which were fabricated via electrochemical anodization, directly from GO dispersions by one-step electrodeposition technique. And then CdSe nanoparticles were prepared on the reduced graphene oxide (RGO)/TiO_2 by electrodeposition method. The photocathodic protection properties of the CdSe/RGO/TiO_2 composite for 304SS were investigated by three-electrode system under visible light.

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* Corresponding authors. Tel.: +86 532 82898731.
E-mail addresses: lhqdio1987@163.com (H. Li), xiutongwang@gmail.com (X. Wang), zzll20081988@126.com (L. Zhang), brhou@qdio.ac.cn (B. Hou).

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2. Experimental

2.1. Preparation of graphene oxide (GO)

Graphene oxide (GO) was synthesized from natural graphite via the modified Hummers method. In a typical procedure, 23 mL of H_2SO_4 was added into a 200 mL flask filled with 1 g of graphite at room temperature. The flask was then cooled to 0 °C in ice bath, followed by slow addition of 3 g of $KMnO_4$. The suspension was stirred continuously for 2 h, cooled in ice bath and then diluted with 350 mL of deionised water. H_2O_2 (30%) was added until gas evolution ceased. The resulting suspension was filtered, washed with 0.5% HCl for three times and dried at 60 °C for 24 h. The as-obtained powder was exfoliated in 0.1 M phosphate buffer solution (PBS, pH 9.18) by ultrasonication for 30 min to form a homogeneous brown GO colloidal dispersion (0.5 mg mL^{-1}).

2.2. Preparation of RGO/TiO_2 and CdSe/RGO/TiO_2

Titanium foil (99.7%, 0.1 mm thick) was anodised in 0.5 wt% HF solution with a Pt counter electrode at 30 V (vs. SCE) for 30 min. After annealing at 450 °C for 2 h in air, the TiO_2 NTs were obtained. The procedures for the preparation of CdSe/RGO/TiO_2 are illustrated in Fig. 1. Cyclic voltammetric deposition of RGO on TiO_2 NTs was performed in the GO dispersion with the use of a three-electrode system [the annealed TiO_2 NTs/Ti sheet as the working electrode, Pt foil as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode] on a CHI 660D electrochemical workstation (CH Instruments, Shanghai, China). The scan was performed from −1500 mV to 1000 mV (vs. SCE) at 50 mV s^{-1}. After deposition of 25 RGO cycles, the working electrode was washed with deionised water and then dried at room temperature. Then, RGO/TiO_2 composite was obtained. For comparison, RGO was prepared by the same procedure on the Ti substrate.

CdSe was deposited by cyclic voltammetric reduction in 0.014 M SeO_2 and 0.25 M $CdSO_4$ solution mixed with 0.25 M H_2SO_4 solution using a three-electrode system (the as-prepared RGO/TiO_2 NTs/Ti sheet as the working electrode, Pt foil as the counter electrode and an SCE as the reference electrode) on a CHI 660D electrochemical workstation (CH Instruments). The scan was performed from −350 mV to −850 mV (vs. SCE) at 50 mV s^{-1}. After deposition of 25 CdSe cycles, the working electrode was washed with deionised water and annealed at 400 °C for 1 h under nitrogen atmosphere. Finally, the CdSe/RGO/TiO_2 composite was obtained.

Table 1
Composition of 304SS.

	C	Si	P	S	Cr	Ni	Mn	Fe
Composition (wt%)	0.08	0.72	0.035	0.029	18.25	8.5	1.86	Rest

304SS was purchased from Shanghai Baosteel (Shanghai, China). The composition of 304SS is shown in Table 1. The 304SS electrode was made by embedding a square 304SS specimen in epoxy resin and the exposed area for testing was 10 mm × 10 mm. This electrode was ground with 2400 grit wet SiC paper and then ultrasonically cleaned in analytical grade ethanol for 5 min. After air drying, the 304SS electrode was stored in a desiccator for 24 h.

2.3. Characterization

The crystalline structures of the as-obtained samples were determined by X-ray diffraction (XRD, Bruker AXS D8 ADVANCE X-ray diffractometer, Germany) using Cu Kα radiation (λ = 0.154 nm) and scanning at 2θ from 10° to 70°. The morphologies and microstructures of the samples were observed using a scanning electron microscope (SEM, Hitachi S-4800, Japan) operated at 25 kV. The chemical composition of the samples was analyzed by energy-dispersive X-ray spectroscopy (EDX, Hitachi S-4800). The optical absorption property of the samples was measured on a UV–visible spectrophotometer (Cary 5000, Varian, Australia). A two-phase lock-in amplifier (EG&G) was used in connection with a mechanical chopper (frequency: 13 Hz) in order to separate the photocurrent from the total current circulating in the cell. Photocurrent spectra were corrected for the photon emission of the light source at each wavelength.

2.4. Electrochemical measurements

Each electrochemical measurement was performed at room temperature on a PARSTAT 2273 Potentiostat/Galvanostat (Advanced Measurement Technology, USA). The schematic illustra-

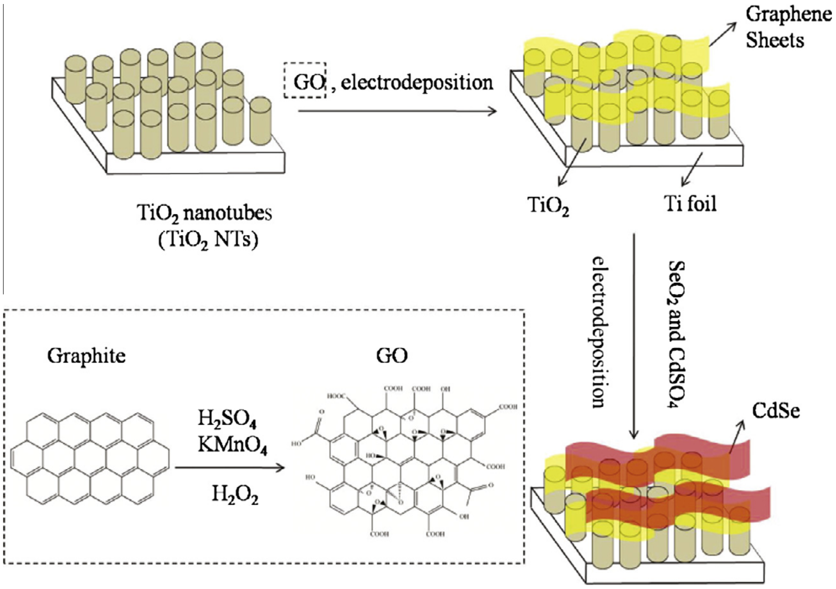

Fig. 1. Schematic diagram of procedures for preparing the CdSe/RGO/TiO_2 composites.