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Full Length Article

Preparation of PbS and CdS cosensitized graphene/TiO_2 nanosheets for photoelectrochemical protection of 304 stainless steels

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ABSTRACT

TiO_2 nanosheets with highly reactive {0 0 1} facet exposed were prepared and modified with graphene and PbS/CdS quantum dots (GT/PbS/CdS) by a facile two-step hydrothermal method and a sonication-assisted successive ionic layer adsorption and reaction (S-SILAR) process. The GT/PbS/CdS composites exhibit superior photoelectrochemical performance for the enhanced photocurrent density, corrosion potential and corrosion morphology of the connected 304 stainless steel. The light harvesting feature of the composites is improved for the narrow band gap quantum dots deposition and the interband transition of the photoexcited electrons in the heterostructure. The p-n junction electric field formed in the TiO_2/PbS interface and the CdS/PbS interface promotes the separation of electrons and holes in the hybrid semiconductor. The increased inner electric field intensity in the semiconductor/electrolyte interface and the Schottky barrier in the semiconductor/metal interface boost the photogenerated electron transfer from the semiconductor to the connected metal, leading to enhancement of the photoelectrochemical protection performance. Furthermore, the electrochemical oxidation and reduction of the PbS is expected to prolong the protection in dark.

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1. Introduction

Corrosion causes enormous economic loss, environmental damage and even catastrophic accidents across the globe [1]. 304 stainless steel (304 SS) is widely used for its excellent comprehensive properties and reliability. However, the pitting corrosion was easily found on the surface of 304 SS when exposed in seawater or chloride-containing environment [2,3]. There are some strategies to prevent metal form corrosion, such as coatings [4,5], cathodic protection [6,7] and corrosion inhibitors [8]. Using the photoelectrochemical property of n-type semiconductor to protect metal from corrosion has attracted much attention in recent decades as a promising and green technology [9–13]. TiO_2 has been widely investigated as a photoanode for the photoelectrochemical protection with the advantage of chemical stability, low cost and nontoxicity [14–17]. When 304 SS is connected with TiO_2 semiconductor, electrons in the conduction bond (CB) of the semiconductor will be excited under certain light and transferred to the coupled metal. Thus the oxygen depolarization in the electrolyte will consume the photo-excited electrons that prevent the 304 SS anodic from dissolution [18–20].

However, recombination of the photoexcited electrons and holes lowers the photo-quantum efficiency of TiO_2. Furthermore, the wide band gap of TiO_2 limits the photo-response in near ultraviolet region (3–5% power of sunlight) [21,22]. CdS [23] and PbS [24] quantum dots (QDs) with narrow band gap have been studied as effective sensitizers to broaden the optical absorption range of TiO_2, especially one-dimensional (1D) TiO_2 nanostructures including nanofibers [25], nanotubes [26] and nanorods [27]. One- and two-dimensional TiO_2 nanomaterials exhibit higher photo-quantum efficiency compared to nanoparticles [28,29]. However, insufficient surface area of the 1D nanostructure leads to deficiency in QDs loading [30]. TiO_2 nanosheets (NSs) with high reactive facets exposed will provide favorable terms for QDs deposition [31]. {1 0 1}, {0 0 1} and {0 1 0} facets are the three fundamental low-index facets in anatase. The {0 0 1} facets has been demonstrated to be extremely reactive compared with the generally dominated {1 0 1} facets [32,33]. Since Yang et al. [34] have synthesized anatase with 47% {0 0 1} facets exposed, tremendous efforts [35] have been concentrated on the exploration and synthesis of {0 0 1} facet-dominate anatase. The intriguing surface and electronic properties of anatase with dominant {0 0 1} facets are

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convinced to play a substantial effect on the photoelectrochemical performance [36].

Graphene has attracted great attention for its high electron mobility and large surface area [37,38]. We have studied the photoelectrochemical performance of graphene doped TiO_2 in our previous work that promotes the electron-hole separation greatly [39].

PbS and CdS QDs deposition on graphene doped TiO_2 NSs with {0 0 1} facets oriented is expected to exhibit an optimal coverage of solar spectrum and high photo-quantum efficiency. We prepared graphene doped TiO_2 NSs with highly reactive {0 0 1} facet by a two-step hydrothermal method in this paper. Furthermore, deposition of PbS and CdS QDs on graphene/TiO_2 NSs surface were achieved by a sonication-assisted successive ionic layer adsorption and reaction (S-SILAR) method. The configurations (GT/PbS/CdS) show enhanced photoelectrochemical performance for improved light harvest and electron-hole separation, leading to optimal photogenerated cathodic protection of 304 SS.

2. Materials and methods

2.1. Preparation of TiO_2 NSs

Anatase NSs with {0 0 1} facets exposed were prepared by a hydrothermal method according to Ref. [33]. Tetrabutyl titanate [$Ti(OC_4H_9)_4$, 98%,] was employed as the TiO_2 precursor and hydrofluoric acid (HF, 40%) as capping agent. In a typical synthesis procedure, 25 mL of $Ti(OC_4H_9)_4$ and 6 mL of HF were added to a 100 mL Teflon-lined stainless steel autoclave and subsequently heated at 180 °C for 24 h. The collected product was centrifuged and washed with absolute ethanol and deionized water, and then with NaOH aqueous solution (0.1 M) to remove the adsorbed fluorine ions.

2.2. Preparation of graphene/TiO_2 NSs composites

The dosage of graphene was 4% weight ratio according to our previous work [39]. 16 mL aqueous solution of graphene oxide (2 mg/mL, Tanfeng Graphene Techonogy (Suzhou) Co. Ltd) was mixed with 40 mL deionized water and 20 mL ethanol by ultrasonic treatment for 0.5 h. Then 0.8 g TiO_2 NSs was dispersed in this solution under sustaining stirring for 1 h, followed by hydrothermal treatment at 130 °C for 3 h. The collected product was centrifuged and washed by deionized water to obtain graphene/TiO_2 NSs composites that named GT.

2.3. Deposition of PbS and CdS QDs

The PbS and CdS QDs were assembled onto GT composites by a S-SILAR method. Briefly, the as-prepared GT composites were dipped into 0.02 M methanolic solution of $Pb(NO_3)_2$ to introduce Pb^{2+} ions. Similarly, Cd^{2+} ions was deposited from a 0.5 M ethanolic solution of $Cd(NO_3)_2{\cdot}4H_2O$. The sulfide source was 0.02 and 0.5 M $Na_2S{\cdot}9H_2O$ solutions in the mix solvent of methanol and deionized water (1/1 in volume) for Pb^{2+} and Cd^{2+} ions separately. Firstly, the sample was immersed into a precursor solution containing Pb^{2+} or Cd^{2+} ions for 5 min, and then dipped another 5 min into Na_2S aqueous solution. After each precursor impregnation, the sample was subjected to ultrasonic treatment and washed with deionized water to remove excess precursors. And the sample should be dried before the next dipping, which completes a single S-SILAR cycle. Previous reports have shown that 5 S-SILAR cycles of PbS and CdS deposition have favorable photoelectrochemical performance [40]. The graphene/TiO_2 NSs composites with 5 cycles of PbS, 5 cycles of CdS and 5 cycles of both PbS and CdS were synthesized and named as GT/PbS, GT/CdS and GT/PbS/CdS respectively.

2.4. Characterization

The morphology and EDS elemental mapping of the composites were observed by a field emission scanning electron microscopy (FESEM, NanoSEM450), a transmission electron microscopy (TEM, JEM-1200EX), and a high resolution transmission electron microscopy (HRTEM, Tecnai G2 F20). The crystalline phase of the samples were characterized by X-ray diffraction (XRD, D/max-RB, Japan) using Cu Kα radiation (λ = 1.5406 Å) with the operational current and voltage maintained at 40 mA and 40 kV. X-ray photoelectron spectroscopy (XPS) was performed by ESCALAB 250Xi electron spectrometer (Thermo Fisher Scientific, USA) with Al Kα X-ray source. UV–Vis absorption spectra were recorded in diffuse reflectance mode using an UV–Vis spectrometer (UV, uv-3101pc, Japan) with $BaSO_4$ as a reference.

2.5. Electrode preparation

The as-prepared powders were mixed with ethanol under ultrasonic vibration. The obtained homogeneous turbid liquid was evenly spread on the conductive side of the indium-tin oxide (ITO) glass with an effective area of $3 \times 3\ cm^2$. Then it was dried and attached to a platinum electrode clamp. The 304 SS electrodes were made by a polished square 304 SS inlaid in epoxy resin with the working area of $10 \times 10\ mm^2$ exposed.

2.6. Measurements of photoelectrochemical performance

The photoelectrochemical characterization were performed on a CHI660E electrochemical workstation (CH Instruments, Inc. USA) with a three-electrode system, of which saturated calomel electrode (SCE) and platinum late were reference electrode and counter electrode respectively. The photoelectricity cell with the photoelectrode and corrosion cell with the 304 SS electrode are connected by a salt bridge. The electrolyte in the photoelectricity cell was the mixed solution Na_2SO_4 and 0.2 M NaOH, while in the corrosion cell was 3.5 wt% NaCl. The photoelectrode and the 304 SS electrode were connected outside by copper wire. The light source was a 300 W xenon lamp (the power energy density = 1 W/cm^2, CEL-HXF300, Beijing Zhongjiaojinyuan Techonogy Co. Ltd., China). The photoinduced current density with time (I-t) curves and the open circuit potential (OCP) curves were tested at a 0 V bias potential. Electrochemical impedance spectroscopy (EIS) was obtained by applying a 5 mV alternating current (AC) signal in the frequency range from 100 kHz to 0.1 Hz. The potentiodynamic polarization curves were plotted in a potential range of −1 to 1 V with 10 mV/s scan rate. Mott-Schottky plots were tested at the frequency of 1000 Hz by 10 mV alternating current (AC) amplitude.

3. Results and discussion

3.1. Structures and morphology

Fig. 1 illustrated the XRD patterns of the synthesized composites, that of the TiO_2 nanoparticles (TiO_2 NPs) was provided by our previous work for comparison [41]. All samples show strong diffraction peaks of anatase (JCPDS No. 21-1272). The TiO_2 NSs show an intensive (2 0 0) diffraction peak compared with TiO_2 NPs, indicating considerable {0 0 1} facets exposed. As the {0 0 1} facets of anatase are highly reactive [32], F ions were adsorbed on the {0 0 1} facets in the hydrothermal process to reduce the

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