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# Fabrication and corrosion resistance of a graphene-tin oxide composite film on aluminium alloy 6061

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## ABSTRACT

The synthesis of a graphene-tin oxide composite film prepared on aluminium alloy 6061 by self-assembly and hydrothermal methods is reported. The surface morphology of the film was investigated using field-emission scanning electron microscopy. The composition and microstructure were investigated using X-ray diffraction, Raman spectroscopy and X-ray photoelectron spectroscopy. The corrosion behaviour of the film was studied using an electrochemical method in a mixed acidic solution of 0.5 M H<sub>2</sub>SO<sub>4</sub> and 2 ppm HF. The resulting protection efficiency was up to 99.7%, illustrating that the film can immensely improve the corrosion of this alloy in a heavily acidic environment.

## 1. Introduction

To date, there has been significant research [1–6] to improve the performance of different metallic materials. Aluminium and its alloys [7] have been applied in many different kinds of fields. However, the poor corrosion resistance caused by the active chemical properties of aluminium and its alloys has greatly influenced their operation life and application. Therefore, current research is focused on improving the corrosion resistance of aluminium and its alloys, such as the preparation of superhydrophobic surface [8], metallic oxide film surface [9], alloying surface [10] and so on.

In addition, graphene [11,12] has drawn considerable interest because of its novel and excellent properties, such as good electrical and thermal conductivity, high strength and hardness. Moreover, the preparation of graphene on a large scale would be beneficial for more applications in the field of metal corrosion protection. For example, Sahu et al. [13–16] demonstrated that graphene nanosheets could be deposited on a copper substrate by an electrochemical method. Tin oxide (SnO<sub>2</sub>) is a typical *n*-type semiconductor material with a wide band gap [17,18]. In recent years, researchers have applied SnO<sub>2</sub> for corrosion protection film due to its desirable chemical stability. Wang et al. [19] investigated the corrosion properties of fluorine-doped SnO<sub>2</sub> film coated on the surface of stainless steel bipolar plates in proton exchange membrane fuel cells. The literature shows that graphene and SnO<sub>2</sub> are useful for corrosion protection. However, pure graphene film or pure SnO<sub>2</sub> film are hard to improve corrosion resistance dramatically and cannot be applied in relatively harsh conditions. No studies have

reported the preparation of graphene-SnO<sub>2</sub> composite film in the field of corrosion protection. In addition, some preparation methods, such as chemical vapour deposition [20] and heat treatment [21], are relatively high in cost and their preparation conditions are very rigorous. Therefore, combining graphene and SnO<sub>2</sub> to protect aluminium alloy 6061 (AA 6061) from corrosion with a simple and low-cost method can achieve good results, including a high protection efficiency of 99.7% in a heavily acidic solution of 0.5 M H<sub>2</sub>SO<sub>4</sub> and 2 ppm HF.

In this study, a graphene-SnO<sub>2</sub> composite film is successfully fabricated to improve the corrosion of AA 6061 in a heavily acidic environment. The sample is firstly etched to attain hydroxyl groups on the surface of AA 6061 [22], and is then immersed alternately in the positive charge of Poly (diallyl dimethyl ammonium chloride) (PDDA) aqueous solution and the negative charge of graphene oxide (GO) aqueous solution, respectively, to attain a (PDDA-GO)<sub>10</sub>-modified substrate by a self-assembly method [23]. The pH of tin dichloride dihydrate solution is adjusted to 10 in order to attain tin hydroxide. It can be easily combined with the hydroxyl and carboxyl groups of graphene oxide. The SnO<sub>2</sub> film is finally synthesised on the modified substrate by a hydrothermal method. This composite film shows good corrosion resistance in a mixed acidic solution of 0.5 M H<sub>2</sub>SO<sub>4</sub> and 2 ppm HF.

## 2. Experimental

### 2.1. Materials

The AA 6061 was purchased from Guanjie Water Treatment

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**Table 1**  
Chemical compositions of the AA 6061.

Element	Mg	Si	Fe	Cu	Mn	Cr	Zn	Ti	Al
Content (wt.%)	0.96	0.71	0.35	0.19	0.15	0.08	0.04	0.03	Balance

Technology Co., LTD., HangZhou, China, which was used as the substrate in this paper. The chemical compositions of the AA 6061 were listed in Table 1. GO was prepared from graphite by the Hummers' method. Tin dichloride dihydrate ( $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ ) and PDDA (MW 100000–200000  $\text{g mol}^{-1}$ , 20 wt.% aqueous solution of low molecular weight) were purchased from Aldrich. All of the chemicals were of analytical grade and were used without further purification.

## 2.2. Preparation of GO

First, graphite oxide was prepared from natural graphite powder. In a three-necked, round-bottomed flask provided with a mechanical stirrer was placed 3 g of graphite, and 120 mL concentrated sulfuric acid was slowly added with rapid stirring for 15 min. Then, 3 g of phosphoric anhydride and 2.5 g of potassium persulfate were dissolved into the above solution successively. After stirring homogeneously, it was heated up to 80 °C and kept for 5 h. After cooling naturally, it was transferred to an ice bath under magnetic stirring. The oxidation product was collected using a filtration method and rinsed with deionised water and dried under a vacuum (80 °C, 6 h) after the solution was cooled down to room temperature. Second, the dried product was then added to a three-necked, round-bottomed flask with a mechanical stirrer. Then, another 120 mL of concentrated sulfuric acid was slowly added with rapid stirring for 30 min. After that, 15 g of potassium permanganate was introduced along with an ice bath. In a typical procedure, the ice bath was removed and the solution was slowly stirred at room temperature for 30 min. Subsequently, it was heated to 35 °C and maintained for 2 h. After the reaction finished, the solution turned golden after 20 mL of hydrogen peroxide was added. The product was collected by centrifugation and rinsed with diluted hydrochloric acid and deionised water several times. The final product was dried under a vacuum (60 °C, 12 h).

## 2.3. Alkaline treatment

The substrate had dimensions of 10 mm × 50 mm × 2 mm. It was pre-treated by grinding with silicon carbide papers from 600 to 2000 meshes. Then, it was further ground by metallographic abrasive papers with the size of W 3.5. Next, it was ultrasonically washed with deionised water for 15 min and anhydrous ethanol for 15 min, respectively. The substrate was further dried with a nitrogen flow. The polished substrate was immersed in a 1 M NaOH solution for 30 s at 60 °C. Then, it was ultrasonically cleaned with deionised water and anhydrous ethanol for 5 min, respectively, and then dried for 15 min at 60 °C.

## 2.4. Film fabrication

### 2.4.1. Self-assembly method

The process of fabricating graphene- $\text{SnO}_2$  composite film on the AA 6061 substrate is clearly illustrated by the two-step method in Fig. 1. By using the self-assembly deposition method, PDDA and GO were first fabricated on the substrate. The surface of the aluminium substrate was negatively charged after alkaline treatment because of the hydroxyl ( $-\text{OH}$ ) groups produced. As PDDA has positive charge and GO has negative charge, they could be alternately deposited on the substrate. Then, the substrate was immersed in a 1% (v/v) aqueous PDDA solution for 10 min. Subsequently, after being rinsed with deionised water, it was dried with high purity nitrogen flow. Following that, it was submerged in a 1 wt.% aqueous GO solution for another 10 min, before

being rinsed with deionised water and dried with a high purity nitrogen flow in the same way. In total, ten deposition cycles were processed to gain the  $(\text{PDDA-GO})_{10}$ -modified substrate.

### 2.4.2. Hydrothermal method

By using a hydrothermal method, the tin oxide film ( $\text{SnO}_2$ ) could be finally prepared on the  $(\text{PDDA-GO})_{10}$ -modified substrate. The hydrothermal precursor solution was also prepared by adding 0.5 g of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  into a 40 mL basic mixture solution of anhydrous ethanol and water (1/3, v/v), which was adjusted for weak alkaline ( $\text{pH} \approx 10$ ) by 1 M aqueous sodium hydroxide. The  $(\text{PDDA-GO})_{10}$ -modified substrate was transferred into a Teflon-lined stainless steel autoclave. After, the precursor solution was also added into the autoclave. Subsequently, the autoclave was kept in a furnace at 120 °C for 6 h. Afterwards, the autoclave cooled naturally down to room temperature. Finally, the substrate was washed with deionised water and dried in the air for 6 h at 60 °C. During this procedure, GO could be reduced to graphene oxide, while the tin ions were converted to  $\text{SnO}_2$ .

Moreover, the samples of bare AA 6061, pure graphene film on AA 6061 and pure  $\text{SnO}_2$  film on AA 6061 were prepared for comparison. To obtain pure graphene film on AA 6061, the  $(\text{PDDA-GO})_{10}$ -modified surface was firstly prepared via the self-assembly method on the substrate, and then it was further processed with a mixture of anhydrous ethanol and water (1/3, v/v) ( $\text{pH} \approx 10$ ) by the hydrothermal method at 120 °C for 6 h to turn graphene oxide into reduced graphene oxide. The pure  $\text{SnO}_2$  film was prepared by the hydrothermal method at 120 °C for 6 h.

## 2.5. Characterisation

The morphology of the film was characterised by field-emission scanning electron microscopy (FE-SEM, JSM-7800F operated at 15 kV) and its composition was determined by an affiliated energy dispersive spectrometer (EDS). The crystal structure of the film was investigated by X-ray diffraction (XRD, Cu  $K\alpha$  radiation, Bruker, D8 Advance, Germany). Raman spectroscopy was carried out using a Thermo ESCALAB 250 system with a LabRAM HR Evolution (633 nm). The chemical bonding of the film was studied by X-ray photoelectron spectroscopy (XPS) analysis on a Thermo SCIENTIFIC ESCALAB 250Xi X-ray photoelectron spectrometer.

## 2.6. Corrosion resistance testing

All the samples were tested by the traditional three-electrode system. The corrosion protection behaviour of the film was studied by the measurements of Tafel polarisation curves and electrochemical impedance spectroscopy (EIS) on a CHI600E electrochemical workstation (Shanghai Chen Hua Instrument Co., China). The test was carried out in a mixed acidic solution of 0.5 M  $\text{H}_2\text{SO}_4$  and 2 ppm HF, which was used as the electrolyte. The exposed surface area of 10 mm × 10 mm on the samples was used as the working electrode, while a platinum auxiliary electrode and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. The composite film samples were immersed in the acidic solution for 2400 s to attain the stable open circuit potential (OCP) and the others were also immersed in the acidic solution for 2400 s. The Tafel polarisation curves were measured between  $-0.2$  and  $0.2$  V (vs. OCP) at a scanning rate of 1 mV/s, while the EIS was tested in a frequency range from 0.01 Hz to 100 kHz at OCP with the amplitude of voltage of 5 mV. The EIS results were simulated into the equivalent circuit via the ZSimDemo software.

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