Preparation of Graphene Sponge Coated Iron Electrode for the Electrolytic Decoloration of Methylene Blue

Xiaoliang Zhang, Jingru Xie, Sheng-Tao Yang, Fumin Xue

Abstract—**Electrolysis is a widely adopted technology in water treatment, while the major challenge focuses on developing better electrode materials. In this study, we reported that the hydrothermal coating of graphene sponge (GS) on Fe electrode (GS-Fe electrode) could significantly improve the decoloration performance of Fe electrode. The decoloration kinetics constant of GS-Fe electrode was five times of that of Fe electrode at the same current density. Mechanistically, the electrolytic oxidation of MB was via indirect pathway, where Cl^- was oxidized into ClO^- for the oxidation of other substances. Moreover, the performance of GS-Fe electrode remained nearly unchanged in the recycling evaluations. The implication to the applications of GS-Fe electrode in water treatment is discussed.**

Index Terms—**graphene sponge; hydrothermal synthesis; electrolysis; water treatment**

I. INTRODUCTION

Water pollution has been recognized as serious environmental problem nowadays [1, 2]. There are many technologies for water treatment, such as active sludge method, electrolysis, advanced oxidation process and adsorption [3, 4]. Among these methods, electrolysis is widely adopted in water treatment, because the relative low cost and general applicability [5-8]. Electrolysis can remediate those not suitable for active sludge method, including antibiotics, heterocyclic compounds, heavy metals, and so on. The major challenge in the electrolytic remediation is to develop high-performance electrode materials [9, 10].

Graphene is newly developed nanomaterial, which has found its applications in various areas [11]. Of particular interest and importance is that graphene has extraordinary electrical properties [12, 13]. Graphene modified electrodes have been used for the detection of pollutants with high sensitivity [14, 15] and the high-performance electrolysis of pollutants [16-18]. However, during the modification of graphene, the graphene sheets might stack and lose the large

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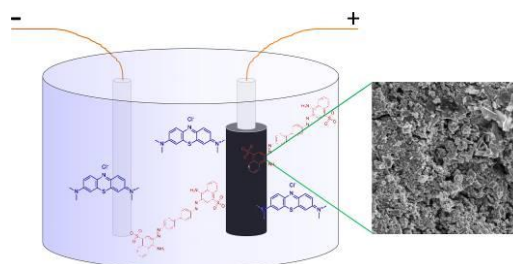
Scheme 1. GS-Fe electrode for the decoloration of dyes

surface area. Recently, graphene sponge (3D-strucutred porous graphene) attracts great interest, which largely retains the high surface area of graphene [19-21].

Herein, we reported that the hydrothermal coating of graphene sponge (GS) on Fe electrode (GS-Fe electrode) could significantly improve the decoloration performance of Fe electrode (Scheme 1). The decoloration performance was compared between GS-Fe electrode and Fe electrode at the same current density. The mechanism of the electrolytic oxidation was preliminarily investigated. Moreover, the performance of GS-Fe electrode in the recycling evaluations was determined. The implication to the applications of GS-Fe electrode in water treatment is discussed.

II. EXPERIMENTAL

A. Materials

Graphite, glucose and MB were obtained from Sinopharm Chemical Reagent Co. Ltd., China. Fe wire (diameter of 1 mm) was purchased from local market. The rest were of analytical grade. All reagents were used without purification.

B. Preparation of GS-Fe

Graphene oxide (GO) was prepared by the modified Hummers method following our previous reports [22, 23] GO (12 mg/mL) was well dispersed in the aqueous solution of glucose (60 mL, 6 mg/mL) under sonication. The homogeneous dispersion was transferred into a Teflon tube. The Fe wire (with the length of 130 mm) was sandpapered, twisted into spiral structure and put into the same Teflon tube. The hydrothermal treatment was performed under 393 K for 3 h. After cooling to room temperature, the GS-Fe electrode was washed with deionized water and lyophilized.

GS-Fe electrode and Fe electrode were characterized by scanning electron microscopy (SEM, Quanta 200FEG, FEI, Netherland), infrared spectrometer (IR, Magna-IR 750, Nicolet, USA) and X-ray photoelectron spectroscopy (XPS,

Kratos, UK). For IR and XPS analyses, the GS coating was scraped and grinded.

C. Decoloration of MB

In the decoloration experiments, GS-Fe electrode was set as the anode and the Fe electrode was set as the cathode. The distance of the two electrodes was 1.5 cm. At 298 K, 100 mL of MB (pH 6, 50 mg/L) was added and electrolyzed at the current density of 40 mA/cm^2 in the presence of NaCl (0.09 mol/L). At designed intervals, the solution samples were collected to measure the absorbance at 664 nm. The absorbance spectra of solutions were recorded accordingly. The C/C_0 values were fitted following equation 1. For comparison, the electrolysis of MB by Fe electrode was performed following the same protocol by changing the anode to Fe electrode. In addition, GS-Fe electrode was soaked in 100 mL of MB (pH 6, 50 mg/L) without electrification for 12 h. And the remnant MB concentration was measured to calculate the adsorption percentage.

$$-\ln(C/C_0) = kt \qquad (1)$$

D. Recycling

The GS-Fe electrode was regenerated by simply washing with deionized water. The performance of GS-Fe electrode was measured up to the cycle of 4. The distance of electrodes was 1.5 cm. The pH was adjusted to 6. The concentration of NaCl was 0.09 mol/L. The current density was set as 40 mA/cm^2.

III. RESULTS AND DISCUSSION

A. Characterization of GS-Fe electrode

GS-Fe electrode was prepared by hydrothermal reduction of GO in the presence of glucose. Around 3 mm of GS was coated on Fe electrode. As shown in Fig. 1, the naked Fe electrode was generally smooth with very few of scars. After the coating of GS, the surface of electrode became very rough. There were flakes and other morphologies presented under SEM. To further characterize the GS coating, we scraped the GS off the electrode and analyzed the sample by IR and XPS. In the IR spectrum, a broad band at 3490 cm^{-1} was observed, which could be assigned to -COOH/-OH. The peak at 2300 cm^{-1} referred to C-H bonds, which might come from glucose residues. The peak at 1720 cm^{-1} indicated the presence of C=O groups. The reduction of GO was clearly reflected in the C1s XPS spectrum. The majority of C atoms were in the form of C-C bond (72.4%). The presence of C-O (15.0%), C=O (8.7%) and -COO- (3.9%) was confirmed, too. Comparing to GO (C-C only reached about 43%), the GS coating here was significantly reduced [22, 23].

B. Decoloration of MB

MB is a widely used dye in textile. MB is also a model pollutant in water treatment studies [24, 25]. The electrolytic decoloration of MB was performed with GS-Fe electrode as the anode. As the control, naked Fe electrode was also used as the anode separately. As shown in Fig. 2, the decoloration was much more efficient when Fe electrode was coated by GS. Correspondingly, the decoloration efficiency for GS-Fe
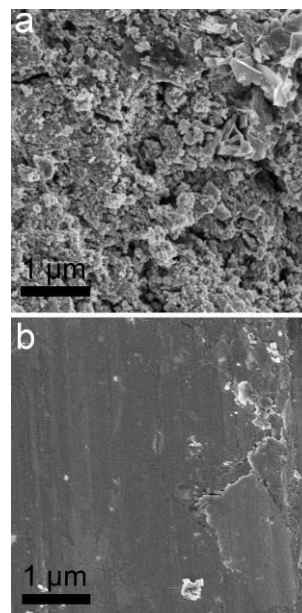

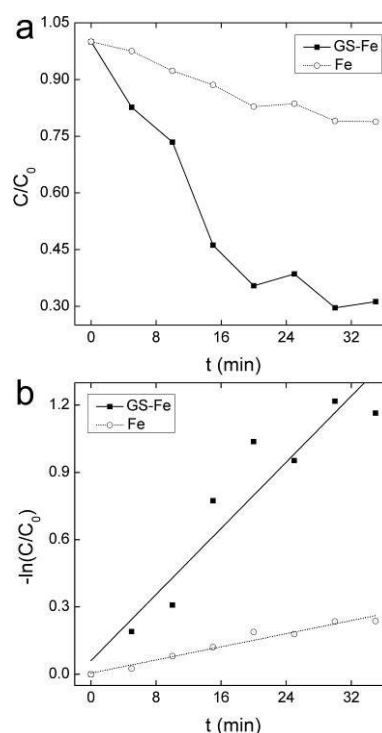Fig. 1. SEM images of GS-Fe electrode (a) and naked Fe electrode (b)

Fig. 2. Electrolytic decoloration of MB by GS-Fe electrode and naked Fe electrode. (a) decoloration as a function of time; (b) kinetics analyses

electrode was 69% after 35 min electrolysis, while the efficiency was 21% for Fe electrode. We calculated the kinetic constant of the decoloration [26]. The kinetic constant k for GS-Fe electrode was 0.0369 min^{-1} and the k for Fe electrode was 0.00733 min^{-1}. The decoloration speed for GS-Fe was four times higher than that for Fe electrode. This indicated that GS coating did improve the electrolysis capability of Fe electrode. The possible mechanism of enhanced performance should be related with the large surface and good conductivity of GS. Further investigations are highly encouraged. It should be noted that MB had low affinity to reduced graphene sheets. The adsorption of MB on
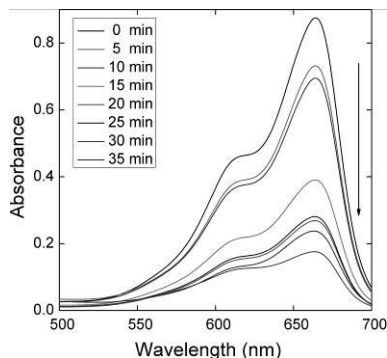
Fig. 3. Visible absorption spectra of MB solution during the electrolysis by GS-Fe electrode
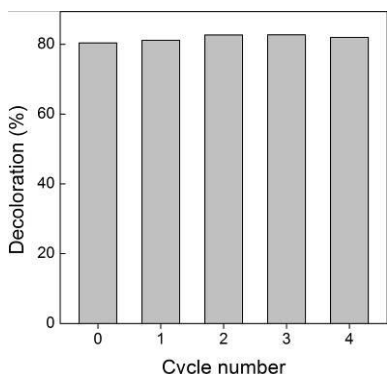

Fig. 4. Decoloration performance of GS-Fe electrode in recycling

GS-Fe electrode only contributed 3% of the decoloration.

We also recorded the visible absorption spectra of MB solution during the electrolysis (Fig. 3). The peak position of MB kept unchanged at 664 nm. The peak intensity decreased along with the decoloration. No new peak was observed, either.
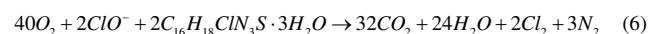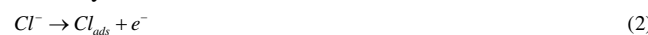
C. Recycling

Due to the coating of GS, Fe electrode was protected and the release of Fe ions into the solution was very low. Only 0.006% of Fe was detected upon 35 min electrolysis. Thus, GS-Fe electrode could be regenerated simply by washing with deionized water. It should be noted that ClO^- generated during the electrolysis could oxidize Fe from the potential perspective. However, ClO^- was generated on the surface of GS. The diffusion of ClO^- toward Fe might be slow due to the electrostatic repulsion, so ClO^- reacted with MB before reaching Fe. The GS-Fe electrode could be reused without obvious activity loss. As shown in Fig. 4, up to the cycle of 4, the decoloration efficiency with 35 min electrolysis remained nearly unchanged. The stable performance during the regeneration was important for the practical applications of GS-Fe electrode.

D. Mechanism of electrolytic decoloration

In our experiments, MB was decolorized by the electrolytic oxidation. It is well known that electrolytic oxidation has two major mechanisms, namely direct oxidation and indirect oxidation. According to our results, we speculated that the electrolytic oxidation of MB was via indirect pathway, where Cl^- was crucial. Cl^- was much better than NO_3^- and also SO_4^{2-} for the electrolysis in our pre-exploration. Cl^- was oxidized

into ClO^-, which was potent oxidant and could oxidize other organic pollutants. The possible reactions during the electrolytic oxidation are listed below.

$$Cl^- \rightarrow Cl_{ads} + e^- \tag{2}$$

$$Cl_{ads} + Cl^- \rightarrow Cl_2 + e^- \tag{3}$$

$$Cl_2 + H_2O \rightarrow HClO + H^+ + Cl^- \tag{4}$$

$$HClO \rightarrow H^+ + ClO^- \tag{5}$$

$$40O_2 + 2ClO^- + 2C_{16}H_{18}ClN_3S \cdot 3H_2O \rightarrow 32CO_2 + 24H_2O + 2Cl_2 + 3N_2 \tag{6}$$

IV. CONCLUSION

In summary, GS-Fe electrode could be used for the electrolytic decoloration of dyes, where the coating of GS was vital for the high performance. The electrolysis was regulated by pH, electrolyte and initial dye concentration. GS-Fe electrode could be washed to get regenerated. The electrolytic oxidation of MB was via indirect pathway, in which Cl- was oxidized into ClO-. It is hoped that our results would stimulate more interest on graphene-based environmental technologies.

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