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Electro-catalytic degradation of sulfisoxazole by using graphene anode

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ABSTRACT

Graphite and graphene electrodes were prepared by using pure graphite as precursor. The electrode materials were characterized by a scanning electron microscope (SEM), X-ray diffraction (XRD) and cyclic voltammetry (CV) measurements. The electro-catalytic activity for degradation of sulfisoxazole (SIZ) was investigated by using prepared graphene or graphite anode. The results showed that the degradation of SIZ was much more rapid on the graphene than that on the graphite electrode. Moreover, the graphene electrode exhibited good stability and recyclability. The analysis on the intermediate products and the measurement of active species during the SIZ degradation demonstrated that indirect oxidation is the dominant mechanism, involving the electro-catalytic generation of $^{\cdot}OH$ and $O_2^{\cdot-}$ as the main active oxygen species. This study implies that graphene is a promising potential electrode material for long-term application to electro-catalytic degradation of organic pollutants.

Introduction

Because of its unique structure and properties, graphene, a single layer of graphite, has been receiving increasing attention in the catalytic, optical, electrical, and magnetic fields (Geim, 2009; Wang et al., 2009; Henrik and Peter, 2010; Guo et al., 2009). This makes graphene sheets a highly promising electro-catalyst or catalyst support (Bong et al., 2010). As electrode material, the performance of graphene is usually superior to the conventional carbon materials like graphite and active carbon because of its enriched surface sites, high specific surface area, high electrical conductivity, and chemical stability (Yan et al., 2010; Liu et al., 2013a, 2013b). Although the electro-catalytic activity of graphene-based electrodes has been extensively studied for processes such as oxygen reduction and H_2 production (Benson et al., 2014), little attention has been given to its application in the electro-catalytic degradation of organic pollutants.

In addition, the residues of sulfa antibiotics have raised serious environmental problems because of their extensive use in a variety of human and veterinary applications and resistance to biodegradation. In our previous study, it was demonstrated that residues of antibiotics like tetracycline can be degraded by electro-catalytic methods (Liu et al., 2013a), and a graphite composite electrode exhibited excellent potential for removing persistent organic pollutants (POPs) in wastewater (Liu et al., 2013b). In the present work, our aim was to investigate the electro-catalytic reactivity for oxidative degradation of sulfa antibiotic pollutants using sulfisoxazole (SIZ) as a model. The mechanistic study suggested that the hydroxyl radical is responsible for the degradation of SIZ on the graphene electrode. The present

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work highlights the promising potential of graphene in the application of environmental remediation.

1. Experimental

1.1. Reagents

SIZ solution (30 mg/L) and horseradish peroxidase (POD) solution (0.10%) were prepared and stored in the dark at low temperature (<4°C). A 0.30% H_2O_2 solution was calibrated using $KMnO_4$. N,N-diethyl-p-phenylenediamine (DPD) aqueous solution (1.0%) was prepared just before its use. Other chemicals were analytical grade. Distilled water was used throughout the experiments.

1.2. Instrumentation

The graphene was prepared by a two-step method: graphite oxide (GO) was obtained first and then was reduced to graphene by using hydrazine hydrate (Raj and John, 2013). Then 1.2 g graphite or graphene, 200 μL emulsifier OP-10 (OP) emulsifier, 0.4 mL ethanol and 0.7 mL polytetrafluoroethylene emulsion were added sequentially to a 50 mL beaker. The subsequent ultrasonic treatment dispersed the mixture into a condensed paste. The paste was rolled into 2 mm membranes and attached to a stainless steel net. Under a pressure of 20 MPa, it was compressed into electrodes, followed by washing with ethanol and distilled water to neutrality and then dried in an infrared box for 2 hr at 80°C. Electrochemical analysis of electrodes was performed using a three-electrode system with an AUTOLAB analyzer to measure the I–V loop curve, at a scanning speed of 50 mV/s.

SIZ was chosen as a target contaminant and samples were collected at specific time intervals for high-performance liquid chromatography (Agilent 1220, American) measurement after filtration. The chromatograph was equipped with a C18 reverse phase column (5 μm, 4.6 mm I.D. × 250 mm, Kromasil) as stationary phase. The mobile phase was 0.1% HCOOH and CH_3CN (V:V = 65:35) with a flow rate of 1 mL/min, column temperature at 30°C, 20 μL of sample volume, and at 275 nm wavelength. The solvent was removed with a rotary evaporator and the structure and morphology of the samples were analyzed by a Fourier transform infrared spectrometer (Nicolet, American).

The H_2O_2 concentration measurement was conducted with a UV–Vis spectrophotometer (Lambda-25, PerkinElmer, American) at 510 nm using a 10 mL colorimetric cuvette with plug, 10 min after addition of 150 μL 1.0% DPD, 1 mL pH 6.8 KH_2PO_4 buffer solution, 20 μL 0.1% POD into the 1 mL sample. The total volume was made up to 5 mL with addition of distilled water. Determination of $O_2^{\cdot-}$ was performed using 2.5×10^{-5} mol/L Nitrotetrazolium Blue chloride solution as trapping reagent. The sample was collected at specific time intervals for absorbance measurement at 259 nm using the UV–Vis spectrophotometer. Similar to $O_2^{\cdot-}$, the determination of $^{\cdot}OH$ used 5×10^{-4} mol/L terephthalic acid as trapping reagent for the relative fluorescence intensity measurement (Ex = 315 nm, Em = 425 nm, and slit widths 5 nm and 10 nm, respectively).

Liquid phase mass spectrometry equipped with a C18 reversed phase column as stationary phase (Poroshell 120 SB-C18, 150 × 4.6 mm, 2.7 μm) used 0.1% formic acid and acetonitrile (V:V = 80:20) as mobile phase at a flow rate of 4 mL/min. The other operational parameters were the same as mentioned above.

2. Results and discussion

2.1. Characterization of graphite and graphene powers

Scanning electron microscope (SEM) analysis of graphite and graphene is shown in Fig. 1. The graphite flake had a smooth surface with a size of several tens of micrometers and thickness of less than 5 μm. In contrast, graphene exhibited obvious fold morphology, and the regular layered structure of graphite disappeared. Such a structure would increase its plasticity, and should be the origin of the unique thermal, electrical, and mechanical properties of graphene (Yuan et al., 2013).

X-ray diffraction (XRD) patterns of graphite and graphene are shown in Fig. 2. For graphite, a sharp and strong peak at around 26.3° accorded with its standard XRD data (PDF41-1487). Calculated by prague formula, the graphite (002) crystal plane spacing was about 0.34 nm. Due to partial oxidation of the graphite surface (Han and Wang *et al.*, 2003), there was a small diffraction peak of GO at around 54.5°. Compared with graphite, the XRD peak of graphene showed a negative shift to around 24.8°, suggesting that the graphene layer spacing was slightly greater than that of graphite (0.34 nm). In addition, the diffraction peak of graphene became wider and weaker.

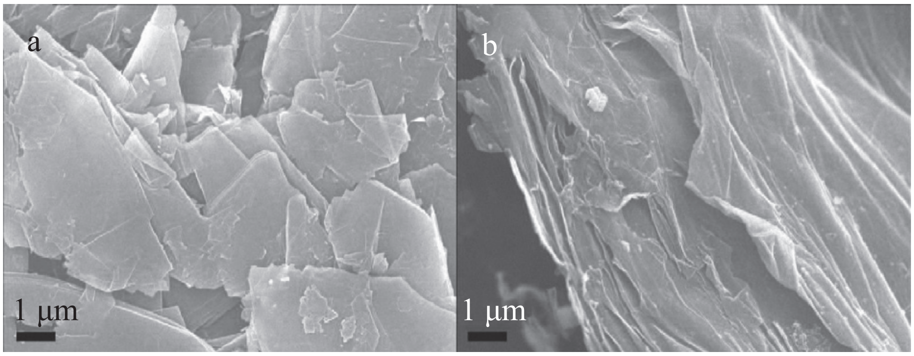

Fig. 1 – Scanning electron microscope (SEM) images of graphite (a) and graphene (b) powder.