



Facile fabrication of RGO-WO₃ composites for effective visible light photocatalytic degradation of sulfamethoxazole



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ABSTRACT

The presence of various antibiotics in the aquatic systems has become one of the emerging environmental issues. Sulfonamides group is one of the most commonly used antibiotics which cannot be effectively removed by conventional treatment methods. This study aims to explore the degradation feasibility of sulfonamides by applying novel photocatalysts powered by visible light. Sulfamethoxazole (SMX), one of the most widely used sulfonamide class antibiotics was chosen as target pollutant to evaluate the photocatalytic degradation performance. Three types of reduced graphene oxide-WO₃ (RGO-WO₃) composites (RW-100, RW-200 and RW-400) as visible light driven photocatalysts were prepared via a facile one step hydrothermal method. Without pH adjustment, more than 98% removal of SMX was achieved within 3 hours by both RW-200 and RW-100 under visible light irradiation. The good photocatalytic activity of RGO-WO₃ composites demonstrates that they can be utilized as effective photocatalysts to degrade sulfonamide class of antibiotics. In addition, the photocatalytic intermediates of SMX were analyzed and the photodegradation pathway was proposed. RW-200 can be used for real application due to its high photocatalytic efficiency and excellent recyclability.

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1. Introduction

Recently, the emergence of antibiotics and their residues in various aquatic systems has drawn wide attention due to their potential threat to both human health and aquatic ecosystems. As emerging persistent pollutants, though the concentration of antibiotics and their residues in the aquatic environment is usually low, they are believed to be able to raise antibiotic resistance in microorganisms in the long term [1]. Sulfonamides are one of the most extensively used antibiotics in human and veterinary medicine and large amount of sulfonamides finds their way into the environment every year [2–4].

Though sulfonamides are biodegradable, the biodegradation process is generally slow and not effective, therefore, conventional wastewater treatment plants (WWTPs) have limited removal ability towards sulfonamides [5,6]. Hence, it is necessary to develop more efficient treatment technologies to eliminate sulfonamides as well as other antibiotics. Many researchers are now turning their

attention to application of advanced oxidation processes (AOPs) to remove trace micropollutants including antibiotics. Particularly, AOPs can be employed as complementary methods to conventional water treatment or as alternative strategies for industrial wastewater treatment. Among various AOPs, heterogenous photocatalysis driven by solar energy is demonstrated to be efficient, cost effective and environmental friendly, which make it a promising approach to remove trace micropollutants [5,7,8].

In comparison to widely studied TiO₂ with a wide band gap (around 3.2 eV) [9,10], n-type semiconductor Tungsten trioxide (WO₃) has a much narrower band gap of 2.4–2.8 eV which presents strong absorption of the solar spectrum [11]. Together with its other specific properties like nontoxicity, stable physicochemical properties, and good resistance to photocorrosion, WO₃ has been proposed to be an effective photocatalyst in degrading organic compound [11–15]. Nevertheless, the photocatalytic efficiency of pure WO₃ is limited by the slow charge transfer and the rapid recombination of photogenerated electron-hole pairs. To improve its photocatalytic performance, different methods such as morphology control, doping and synthesis of heterogeneous composites have been developed [15].

Graphene (GR) has unique two-dimensional (2D) structure, large surface area, excellent electronic and physicochemical properties [12,13,16–18]. GR and/or reduced graphene oxide (RGO)

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are thereby regarded as excellent co-catalysts in constructing high performance heterogeneous photocatalysts [18–20]. They can work not only as superior supporting matrixes for bonding functional components but also excellent electron mediators to adjust electron transfer, and thus restrain the recombination of photogenerated charges and subsequently improve the electron-hole separation [10,18,21]. Together with the increased adsorption capacity for reactants, extended photoresponding range and enhanced visible light absorption intensity, graphene-based heterogeneous photocatalysts have shown improved photocatalytic activity.

To date, several researchers have reported the synthesis of WO_3 -RGO composites as gas sensor [15,22–24], UV photodetector [25], photocatalysts [13–15,26,27] and oxygen evolution catalysts in PEC system [10,11,28–30]. However, it is still a challenge to synthesize uniform scattered WO_3 with good crystallinity, controlled morphology and particle sizes on RGO sheets [31]. Moreover, there has been no attempt to apply RGO- WO_3 composites to remove emerging pollutants like sulfonamides. Though several studies reported the use WO_3 as photocatalyst to degrade antibiotics, the addition of inorganic oxidants was usually required [32,33].

In this study, we report a facile one-step hydrothermal method to construct RGO- WO_3 composites with good crystallinity and small size 2D monoclinic- WO_3 (m- WO_3) nanoplates. It is supposed that compared to bare WO_3 , the RGO- WO_3 composites would possess better photocatalytic performance as a result of the introduction of RGO sheets. In order to evaluate the photocatalytic activity of the as prepared composites, sulfamethoxazole (SMX), one of the commonly used sulfonamides antibiotics was chosen as target pollutant. According to the US Geological Survey, SMX is listed in the 30 most frequently detected wastewater contaminants with a long half-life of 85 to more than 100 days [34–36]. Since current WWTPs are insufficient at degrading SMX as well as other trace micropollutants, it is necessary to explore the possibility to apply photocatalytic process as an alternative strategy. Therefore, a systematic study has been conducted to investigate the photocatalytic properties of WO_3 -RGO composites under visible light illumination towards SMX degradation without other additives.

2. Materials and methods

2.1. Materials

Natural graphite powder (LBG8010) was purchased from Superior Graphite (USA). Sulfuric acid (H_2SO_4 , 95–98%), hydrochloric acid (HCl, 35%), potassium permanganate (KMnO_4), ethanol, sodium tungstate dihydrate ($\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$), sodium nitrate (NaNO_3), isopropanol (IPA), benzoquinone (BQ) and sodium oxalate (SO) and sulfamethoxazole (SMX) were purchased from Sigma-Aldrich. Hydrogen peroxide (H_2O_2 , 30%) was supplied by VWR. All chemicals were used as received and no further purification was needed.

2.2. Preparation of graphene oxide (GO)

GO was synthesized based on the modified Hummer's method [37,38]. In brief, 2.5 g natural graphite powders and 2.5 g NaNO_3 were firstly mixed by 120 mL concentrated H_2SO_4 in an ice bath. Then, 15 g KMnO_4 was divided into five equal parts and was slowly added into above slurry under continuous stirring. The mixture was then allowed to react at 35 °C for 6 h and after that 150 mL deionized water was carefully added to avoid boiling. The diluted solution was then kept at around 95 °C for 15 min and subsequently the suspension was poured into a beaker with 700 mL DI water. To purify the product, 60 mL H_2O_2 (30%) was added, and the obtained yellow

low solution was then washed by diluted HCl (10 wt%), dialyzed for one week and centrifuged with DI water until the pH of the supernatant was close to 7. Finally, the obtained GO was dried at 80 °C and grinded into powders for further usage.

2.3. Synthesis of reduce graphene oxide-tungstate trioxide composites (RGO- WO_3)

For the preparation of RGO- WO_3 composites, one-step hydrothermal method was developed. First, the as prepared graphene oxide was dispersed in DI water with the assistance of ultrasonicator forming a stable suspension with a concentration of 0.5 mg mL⁻¹. Then preset amount of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (100 mg, 200 mg and 400 mg, respectively) were dissolved in 10 mL above GO suspension. 5 mL 35% HCl was then slowly added in the 10 mL mixture with continuous stirring. The suspension was transferred to a 45 mL Teflon-lined stainless steel autoclave to undergo a heating process for 8 h at 140 °C. After cooling down naturally, the sample was collected and washed with ethanol and DI water for several times before being dried by vacuum freeze drier. Pure WO_3 sample was prepared with the same method where $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ was dissolved by DI water rather than GO suspension. The samples obtained were annealed at 300 °C for 30 min to further reduce the GO sheets. With different $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ dosages, the three samples were named RW-100, RW-200, and RW-400 respectively.

2.4. Materials characterization

The crystal phases of the obtained products were characterized by X-ray powder diffraction (XRD) using a D8-Advance Bruker-AXS diffractometer with Cu K α irradiation operated at 40 kV and 30 mA. The morphologies and structures of the samples were observed by a field-emission scanning electron microscope (FESEM, JEOL 6340) and transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) using a JEOL 2010 microscope operated at 200 kV. X-ray photoelectron spectra (XPS) were measured by a Kratos Axis Ultra Spectrometer with a monochromic Al K α source at 1486.7 eV, a voltage of 15 kV and an emission current of 10 mA. UV-vis Spectra were obtained with a Scan UV-vis spectrophotometer (UV-vis Spectrometer 2501PC, Shimadzu). Photoluminescence (PL) emission spectra were recorded on a PerkinElmer LS 55 Fluorescence spectrometer at 325 nm. Raman Spectra were tested by a Renishaw inVia Raman microscope with the excitation wavelength of 514.5 nm.

2.5. Photocatalytic activity test for SMX degradation

Photocatalytic activity of pure WO_3 nanoplates and its WA composites was evaluated by degradation of SMX (10 mg L⁻¹) using a 1.5 AM solar simulator (NEWPORT, USA) with a 200 W Xe arc lamp. Dichroic mirrors were utilized to control wavebands in specific ranges 420–630 nm (visible light). To remove the UV residual, a polycarbonate filter was utilized. In a typical experimental procedure, 100 mg sample was firstly dispersed into 50 mL of DI water in the reaction vessel of 250 mL, and then mixed with 50 mL of 20 mg L⁻¹ SMX solution and the final concentration was 10 mg L⁻¹. After that, the vessel was continuously stirred for 1 h in the dark to reach the adsorption equilibrium. The photocatalytic test was initiated by switching on the solar simulator. Sampling was carried out at various time intervals by drawing 3.0 mL of the aliquot from the reaction vessel. The samples were immediately filtered with 0.45 μm cellulose acetate syringe membrane filters. Filtered samples were analyzed by high performance liquid chromatography (HPLC) to determine the SMX concentration. Operating conditions of HPLC can be found in Supplementary Information. The total organic carbon (TOC) remaining in the solution was measured with

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