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Efficient synergy of photocatalysis and adsorption of hexavalent chromium and rhodamine B over Al_4SiC_4/rGO hybrid photocatalyst under visible-light irradiation

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ABSTRACT

A novel visible-light-driven Al_4SiC_4/rGO hybrid photocatalyst was fabricated using carbothermic reduction and hydrothermal methods. The as-prepared samples were characterized using various techniques and different factors during the photocatalytic reaction were well optimized. Compared with the commonly used photocatalysts, e.g. TiO_2 (P25), g-C_3N_4, etc. the Al_4SiC_4/rGO hybrid not only exhibits super photocatalytic activity in the mixed system containing Cr(VI) and rhodamine B (RhB) but also can degrade different kinds of dyes selectively by modifying surface charge. For the degradation mechanism, there are two stages. The first is the high adsorption capacity owing to surface positive charge on Al_4SiC_4. The second is the active species including photo-electron (e^-) and photo-hole (h^+), which can promote the photocatalytic removal of Cr(VI) and RhB, respectively. In addition, rGO can improve the whole photocatalytic performance via rapid separation and transportation of photoinduced carriers. Furthermore, the cyclic and long-term experiments indicate great reusability and stability of the Al_4SiC_4/rGO hybrid.

1. Introduction

With the rapid development of industry and agriculture, water pollution issues are becoming more and more serious owing to the excessive industrial and agricultural contaminations containing a complex range of toxic inorganic heavy metal ions and poisonous organic compounds [1–3]. These inorganic and organic pollutants, including but not limited to cadmium, lead, mercury, chromium, pesticides, fertilizers and organic dyes, are always highly toxic and do harm to the living beings [4,5]. For instance, hexavalent chromium (Cr(VI)) from industrial activities such as tanning, metal finishing, electroplating, steel production, etc. perceives the top priority on account of its higher toxicity and carcinogenicity even at very low concentration [6]. The permissible limit of Cr(VI) in drinking water is 0.05 mg/L [7]. Therefore, various researches have been carried out to remove Cr(VI) from wastewater. One of the most preferred methods is to convert Cr(VI) to Cr(III) [8] by photocatalysis because Cr(III) is much less toxic than Cr(VI).

Since organic pollutants usually coexist with Cr(VI) in wastewater, it is highly meaningful to reduce Cr(VI) and oxidize organic pollutants simultaneously. The simultaneous reduction of Cr(VI) and oxidation of dye or phenol have been carried out on TiO_2 and ZnO photocatalysts in the past years. Yu et al. [9] employed a TiO_2-boron doped diamond (TiO_2-BDD) heterojunction to simultaneously oxidize reactive yellow 15 (RY15) and reduce Cr(VI) under UV illumination. Wang et al. [10] investigated the synergistic photosensitized removal of Cr(VI) and RhB dye on amorphous TiO_2. Zhen et al. [11] synthesized porous ZnO nanoplates with a high photocatalytic activity toward the photoreduction of Cr(VI) in the presence of phenol. Nonetheless, TiO_2 and ZnO, etc. can only respond to the UV irradiation accounting for about 4% of the solar energy. Nowadays, significant attention has been given to develop semiconductor-based heterostructures and composite systems for visible-light-driven light harvesting systems [12].

It has been reported that Al_4SiC_4 as a new wide band gap (2.5 eV) semiconductor material [13,14] exhibits unique structures and properties such as outstanding electrical conductivities, electrical resistivity and physicochemical properties [15]. In our recent work, it has been adopted as a sensor for the effective determination of heavy metal ion

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(Cu^{2+}, Cd^{2+}, Pb^{2+}) [16,17]. To expand the application of Al_4SiC_4 as a new kind of photocatalyst, it is expected to combine with other materials such as electrons accepter or hole accepter to suppress the recombination rate of electron-hole pairs and improve the photocatalytic performance. Reducing graphene oxide (rGO), an excellent electrons accepter [18–21], has been considered as a promising method to improve photocatalytic performance due to its flexible layered feature, chemical inertness, excellent conductivity and high specific surface area [22].

In this work, Al_4SiC_4 in combination with rGO are applied as the photocatalyst for the first time in the simultaneous reduction of Cr(VI) and oxidation of rhodamine B (RhB). To further enhance the photocatalytic performance, surface modification is also adopted, which can remove different kinds of dyes selectively. Compared with the results reported in the literatures, Al_4SiC_4/rGO hybrid photocatalyst exhibits super photocatalytic activity.

2. Experiment section

2.1. Preparation of Al4SiC4 and Al4SiC4/rGO

In this work, all reagents, as analytical reagent grade, were purchased from Sinopharm Chemical Reagent Co., Ltd., Beijing China and used without further purification. Al_4SiC_4 was synthesized using commercial alumina (Al_2O_3, ≥98.1 mass%), silica (SiO_2, ≥98.8 mass%) and natural graphite (C, ≥99.0 mass%) as raw materials in a molar ratio of Al_2O_3: SiO_2: C of 2: 1: 12. The mixtures were ball milled for 24 h with ethanol and dried at 80 °C for 24 h. The obtained mixtures were then pressed into a cylinder under a pressure of 30 MPa and calcined at 1300 °C for 4 h in a tube furnace in flowing high purity argon. The yellow powder was obtained after the furnace was cooled to room temperature. Finally, the powder was ball-milled with ethanol for 4 h for further experiments.

The Al_4SiC_4/rGO hybrid was synthesized by a one-step hydrothermal method in an ethanol water solvent. A certain amount of dried graphene oxide (GO), i.e. 1.5, 4.5, 7.5 and 10.5 mg was dispersed in 60 mL deionized water and 20 mL ethanol under ultrasonication for 60 min. Then 300 mg Al_4SiC_4 powder was added in above GO suspension. The dispersion was sonicated for 30 min and further magnetically stirred for 30 min. This above operation was repeated twice to ensure the suspension to become more uniform. The suspension was then transferred into a 100 mL-Teflon-lined stainless-steel autoclave and heated at 120 °C for 180 min. During the hydrothermal process, GO was reduced to rGO by ethanol as the active agent and Al_4SiC_4 particles were dispersedly attached on the surface of rGO owing to its higher surface area. After being cooled to room temperature, the suspension was centrifugated and dried in an oven at 60 °C for 12 h. Finally, the Al_4SiC_4/rGO hybrids with different rGO contents i.e. 0.5 mass%, 1.5 mass%, 2.5 mass%, 3.5 mass% were obtain.

2.2. Characterization

The phase and structure of all samples were characterized using X-ray diffraction (XRD) analysis on a PW1710 in diffractometer with Cu Kα radiation under operation conditions of 40 KV and 20 mA. The morphology was examined by a field emission scanning electron microscopy (FE-SEM) on a JSM-6701F. Microstructure of Al_4SiC_4 was performed by transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) on a JEM-2010 HR. Surface electronic states of Al_4SiC_4 and Al_4SiC_4/rGO were determined by X-ray photoelectron spectra (XPS) using a Thermo Escalab 250Xi with a monochromatic Al Kα source. All blinding energies were referred to the C 1s peak at 284.80 eV of the surface adventitious carbon and revised. The absorption edges and band gaps of all samples were detected by a UV–vis spectrophotometer. Ultraviolet photoelectron spectroscopy (UPS) was performed with a monochromatic He I light source (21.2 eV) and a VG Scienta R4000 analyzer to obtain the position of valance band maximum (VBM). A sample bias of −5 V was applied to observe the secondary electron cutoff (SEC). The work function (ϕ) can be determined by the difference between the photon energy and the binding energy of the secondary cutoff edge. Zeta potentials were measured by “Malvern Zetasizer Nano ZS” to analyze the surface charge and dispersibility of samples. Photo-luminescence (PL) spectra of samples with an excitation wavelength at 365 nm were carried out to evaluate recombination of photoinduced charge carries.

2.3. Photoelectrochemical measurement

Indium tin oxide (ITO) glass was ultrasonic washed successively using acetone and ethanol for 10 min. It was then cleaned by deionized water and dried as the substrate. A suspension by mixing Al_4SiC_4/rGO power, polyvinylidene fluoride (PVDF) with the mass ratio of 8:2 in *N*-methyl-2-pyrrolidone (NMP) was coated on ITO glass with a thin coating of $10 \times 10\ mm^2$. Finally, the ITO glass was dried at 90 °C for 6 h to evaporate the solvent for the later photoelectrochemical detection as the working electrode.

Photoelectrochemical measurement was performed on the conventional three electrodes setup consisting of a platinum plate as the counter electrode, Ag/AgCl (saturated KCl solution) as the reference electrode, Al_4SiC_4/rGO-ITO as the working electrode and 0.2 $mol\ L^{-1}$ Na_2SO_4 solution as the electrolyte connected to a CHI 760E electrochemical workstation (Shanghai Chenhua Instrument Co., China). The experiments were carried out under visible light irradiation (≥ 400 nm, 100 $mW\ cm^{-2}$) using a 300 W Xe lamp (PLS-SXE300UV, Beijing Perfectlight Co., Ltd.). All working electrodes were backilluminated through the ITO glass. Linear sweep voltammetry (LSV) was measured both in the dark and under light illumination from −0.2 to 0.8 V. The photocurrent *vs.* irradiation time curve ($I-t$) was recorded at 0 V and 0.5 V under dark (20 s) and light (20 s) alternately. Electrochemical impedance spectroscope (EIS) was conducted by applying the AC voltage amplitude of 5 mV at 0 V within a frequency range of $0.001–10^5$ Hz. Long-time photocurrent decay curve was also recorded for 10,800 s to analyze the photoelectric stability.

2.4. Photocatalytic reduction of Cr(VI)

The photoreduction experiment was carried out using 100 mL solution of potassium dichromate (10 $mg\ L^{-1}$ Cr(VI), pH is about 3.0 controlled by HCl), which was mixed with 70 mg catalyst. According to the usual experimental procedure reported in the literatures, the mixture should be stirred in the dark to reach adsorption-desorption equilibrium before conducting the photocatalytic reaction. However, in this work, the Al_4SiC_4/rGO hybrid exhibits a strong adsorption capacity with about 98% removal of Cr(VI) after 120 min in the dark. Therefore, it is meaningless to study the photocatalytic performance after the adsorption-desorption equilibrium. In order to investigate the adsorption and photocatalytic performance separately, two parallel experiments were carried out at the same time to investigate the effective photocatalytic performance. In these two parallel experiments, the same suspensions were stirred simultaneously while one was under dark condition and the other was irradiated with visible light by a 300 W Xe lamp with 400 nm cutoff filter (Light intensity density = ca. 100 $mW\ cm^{-2}$). The former represents the adsorption performance and the latter represents the overall removal capacity. Furthermore, 3 mL suspension was sampled at each given time interval and centrifuged to get the clear solution. The Cr(VI) concentration was determined spectrophotometrically at 540 nm via 1,5-diphenylcarbazide method [23]. After the optimal rGO content is confirmed, a series of experiments were conducted to investigate the effect of such parameters as pH, catalytic dosage, initial concentration on the adsorption and photocatalysis. The photocatalyst stability was further evaluated by reusing