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Photo-ultrasonic assisted in-situ synthesis of RGO/ Ag_2CrO_4 photocatalyst with high photocatalytic activity and stability under visible light

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ABSTRACT

Visible-light-active reduced graphene oxide/ Ag_2CrO_4 (RGO/ Ag_2CrO_4) composites were prepared by a novel photo-ultrasonic assisted reduction process. Compared to single Ag_2CrO_4 photocatalyst, as-prepared RGO/ Ag_2CrO_4 composites had displayed dramatically enhanced photocatalytic activity toward the degradation of methylene blue (MB) and tetracycline (TC) under visible light illumination ($\lambda > 420$ nm). And when the mass ratio of RGO to Ag_2CrO_4 was 0.5%, sample showed the most superior photocatalytic activity,with degrading 97.68% and 80.03% of MB and TC in 60 min, respectively, which was about 0.9 times and 2 times higher than that of pure Ag_2CrO_4.

The excellent photocatalytic activity was majorly due to the coupling of nano-sized Ag_2CrO_4 (6–9 nm) with high electron-conductive RGO, which had boosted charge separation and transfer. Improved photocatalytic stability was mainly ascribed to the fast transferring of photogenerated electrons from Ag_2CrO_4 to RGO before the reduction of Ag ions to metallic Ag. This work can provide a more economical and effective method for the exploration of efficient RGO-based photocatalysts.

1. Introduction

As a promising solution for mitigating pollution and hydrogen evolution, semiconductor photocatalysis has received incessant public interest with its low-cost, excellent reusability and environmental friendliness [1–6]. As one of the Ag-based semiconductor photocatalysts, Ag_2CrO_4 has a unique electronic and crystal sturcture, which are favorable for visible light utilization [7,8]. Therefore, it has been widely applied as a visible light responsive photocatalyst [9,10]. Unfortunately, like other Ag-based photocatalysts [11], Ag_2CrO_4 is viable to photocorrosion upon the visible light irradiation, which will seriously damage its sturcture and deteriorate photocatalytic activity [12,13]. Besides, small band gap (1.75 eV) of Ag_2CrO_4 is the another drawback of Ag_2CrO_4 photocatalysts, which impairs photocatalytic properties due to fast recombination of photoexited charge carriers [14]. Literatures suggested that Ag_2CrO_4 could maintain its stability and improve its photocatalytic activity by coupling Ag_2CrO_4 with other acceptor materials, by which photoinduced electrons on the surface of Ag-based compounds could rapidly transfer to the surface of acceptor materials before Ag ions were reduced to metallic Ag [15–18].

Carbon-based materials such as graphene (GO), carbon-nitride, carbon nanotubes, and graphene oxide(RGO) are desirable candidates for Ag-based semiconductors to form composites [8,19–22]. As one of the carbon-based materials, RGO has high specific surface area and unique electron conductivity, which are favorable for the photocatalytic properties of RGO-based photocatalysts [23]. Recently, Xu et al. [5]. developed a Z-scheme Ag_2CrO_4-GO photocatalysts with enhanced photocatalytic activity and stability by a facile precipitation method, confirming that GO in Ag_2CrO_4-GO composite can act as an electron acceptor to hinder the recombination of e^-/h^+, which prevented the photocorrosion of Ag_2CrO_4. Nevertheless, with the existence of lots of structure defects and poor electronic conductivity, GO is far from becoming a functional photocatalytic material. By contrast, RGO is a thin two-dimensional material with better electronic conductivity than GO, which is beneficial for electron separation and transmission in photocatalytic materials [18,24,25]. Methods of reducting reducing GO into RGO includes chemical vapor deposition (CVD) reduction [26,27], chemical reduction [28,29] and hydrothermal reduction [30,31]. However, above methods have some intrinsic drawbacks such as complex procedure, secondary pollution and the need for special instrument, which hamper their practical application. Therefore, it is imperative to develop a green way to produce RGO. Recently, new green ways of photo-assisted [32] and ultrasonic-assisted [33] reduction methods have been reported. Photo-assisted reduction is an economical

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and efficient method to obtain RGO from GO [34]. And ultrasonic cavitation of an ultrasonic method could provide high temperature, high pressure and fast cooling rate, which are beneficial for the preparation of samples with smaller-size, more exposed active sites and porous structure, as well as the generation of hydrogen radicals(·H) and H_2O_2 from H_2O [35]. Therefore, it is a possible insight to combine the advantages of aforementioned two methods to reduce GO into RGO, and coupling Ag_2CrO_4 with RGO to construct RGO/ Ag_2CrO_4 composites with improved photocatalytic activities and stabilities. However, to the best of our knowledge, no researches on the fabrication of smaller nanosized RGO/ Ag_2CrO_4 composites by a photo-ultrasonic assisted method has been reported previously.

Herein, RGO/ Ag_2CrO_4 was prepared via a green and facile photo-ultrasonic assisted strategy. Photocatalytic properties of the composites were investigated by the decomposition of methylene blue (MB) and tetracycline (TC), and resultant composites exhibited a remarkably enhanced photoctalytic activity than pure Ag_2CrO_4. Besides, the photocorrosion of Ag_2CrO_4 has also been inhibited effectively upon the coupling of RGO. The mechanism for the improved photocatalytic activity and stability of RGO/ Ag_2CrO_4 was also explored.

2. Experimental

2.1. Materials

All the chemicals involved were of analytical grade and supplied by Tianjin Yong Sheng Chemical Factory of China without any purification. Distilled water was employed in the experiments.

2.2. Synthesis of Ag_2CrO_4 and GO/ Ag_2CrO_4

GO was fabricated by chemical exfoliation of graphite powder by a modified Hummers' method [28].

The GO/ Ag_2CrO_4 samples were prepared by a self-assembly precipitation process under the dark conditions. Briefly, 50 mg GO was dissolved into 100 mL of distilled water, sonicated for 1 h to get a GO aqueous suspension with a concentration of 0.5 mg/mL. Subsequently, 16 mL cyclohexane, 5 mL Triton X-100 and 3 mL n-hexanol were mixed via magnetic stirring. At the same time, an appropriate amount of GO aqueous suspension was poured into above solution to obtain a mixture. 1.25 mL K_2CrO_4 solution (0.1 M) was mixed to the suspension and stirred for 1 h to make the $CrO_4{}^{2-}$-contained water droplets adsorbed on the surface of hydrophilic GO. 1.25 mL $AgNO_3$ solution (0.2 M) was added dropwise into the above mixture with vigorous stirring for 1 h at room temperature. The resultant suspension was aged for 24 h. Then, yielded brick-red sediment was collected by centrifugation at 12,000 rpm for 10 min, washed with ethanol and distilled water for several times in turn, then dried at 60 °C for 12 h.

Ag_2CrO_4 samples were fabricated by the same route without GO.

2.3. Synthesis of RGO/ Ag_2CrO_4

RGO/ Ag_2CrO_4 was synthesized by a photo-ultrasonic assisted reduction process from GO/ Ag_2CrO_4 precursor. In brief, 0.3 g GO/ Ag_2CrO_4 was dispersed into 100 mL ethanol solution and irradiated by visible-light (300 W Xe lamp with a 420 nm cut-off filter, CEL-S500, China) and ultrasonic irradiation (Xin zhi Co, China, JY92-2D, 10 mm diameter, Ti-horn, 20 kHz, 60 W cm^{-2}) for 30 min. The yielded precipitate was separated by centrifugation at 12,000 rpm for 10 min, washed with distilled water and ethanol for several times, and then dried at 60 °C for 12 h. To optimize RGO loading amount, a series of composites with different theoretical mass ratios of RGO to Ag_2CrO_4 (0.25, 0.5, 1 wt%) were obtained. And corresponding samples were labeled as S-0.25, S-0.5 and S-1, respectively.

2.4. Characterization

The phase of the RGO/ Ag_2CrO_4 samples was investigated by powder X-ray diffractometer (Shimadzu XRD-6000) equipped with a Cu-Kα radiation at a scanning rate of 5°/min in 2θ range of 10–80°. The overall morphology, structure and particle size of the sample were analysed by field emission scanning electron microscopy (SEM, SU-8010, Hitachi, Japan) Transmission electron microscopy (TEM) images were performed by a JEM-2100 microscope. Chemical composition of the samples was examined by energy dispersive X-ray spectroscopy EDS. Fourier transform infrared (FT-IR) spectra were performed by using a Nicolet Avatar 370 spectrometer. X-ray photoelectron spectra (XPS) were recorded on a Kratos Axis Ultra system (Kratos Analytical Ltd, Manchester, UK). The UV–vis diffuse reflectance spectra (UV-DRS) were recorded on a UV–vis spectrophotometer (U-3010, Hitachi, Japan) with $BaSO_4$ used as a reference.

2.5. Photocatalytic activity measurement

The photocatalytic activities of the samples were evaluated by the degradation of MB and TC under visible light irradation. The visible light was supplied by a 300 W Xe lamp (CEL-S500, China) with a 420 nm cut-off filter. In each experiment, 20 mg sample was added into 100 mL MB (TC) aqueous solution (10 mg L^{-1}). Prior to visible light irradiation, suspensions were agitated for 0.5 h in dark to ensure that MB (TC) could achieve absorption–desorption equilibrium on the surface of photocatalyst. Then, the mixture was stirred continuously under simulated visible light illumination. The concentrations of MB and TC were investigated by UV–vis spectrophotometer (PG, TU-1901) in every 10 min at a wavelength about 663 nm and 357 nm, respectively. Active species trapping experiments were performed under similar procedure, except that different scavengers were added.

2.6. Photoelectrochemical measurements

The photoelectrochemical characterization was carried on CHI 660E (China) with a three electrodes electrochemical system. Indium tin oxide (ITO) glass deposited with samples had served as working electrode, Ag/AgCl and Pt wire were used as reference and counter electrode, respectively. The electrolyte was 0.5 M Na_2SO_4 aqueous solution. And the light source was an 300 W Xeon lamp. Working electrodes were prepared as follows: 5 mg sample was dispersed in 5 mL ethanol with 10 μL 5% Nafion solution. Then, a certain amount of suspension was dropped on the ITO (1 cm × 1.5 cm) glass. Subsequently, the ITO glasses coated with photocatalysts were annealed for 10 h in air at 100 °C.

3. Results and discussion

3.1. Characterization of as prepared samples

Fig. 1 shows the XRD patterns of GO, RGO, Ag_2CrO_4, S-0.25, S-0.5 and S-1. A characteristic peak at $2\theta = 10.6°$ was found, which was assigned to pure GO. For bare RGO, the characteristic peak of GO at 10.6° had disappeared and was replaced by a weak and broad peak at 25.1°, suggesting that RGO was successfully prepared [5]. All the samples other than pure RGO and GO had demonstrated similar XRD patterns and all the diffraction peaks were in good consistence with the standard data of orthorhombic phase of Ag_2CrO_4 (JCPDS No. 26-0952). No peaks of any impurities was observed in Ag_2CrO_4/ RGO composites, indicating the coupling of RGO hadn't influenced crystallite structure of Ag_2CrO_4. Besides, no characteristic peaks of RGO was observed in the XRD patterns of Ag_2CrO_4/ RGO composites, which could be ascribed to the low coupling amount of RGO [36].

Fig. 2 presents the EDS and XPS spectra of the S-0.5 composite. As depicted in Fig. 2**a**, C was contributed to RCO, and Ag, Cr, O were