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Cross-linked $ZnIn_2S_4$/rGO composite photocatalyst for sunlight-driven photocatalytic degradation of 4-nitrophenol

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ABSTRACT

A chemically cross-linked $ZnIn_2S_4$/reduced graphene oxide (ZIS/rGO) composite photocatalyst was synthesized as a stable sunlight photocatalyst for the degradation of 4-nitrophenol. The experimental results revealed that although the pure $ZnIn_2S_4$ exhibited reasonable visible light photocatalytic activity toward the degradation of 4-nitrophenol, it was suffered from severe photocorrosion under sunlight irradiation. In strong contrast, the chemically cross-linked ZIS/rGO possessed not only an enhanced visible light photocatalytic activity but also a dramatically improved sunlight stability. The characterization data suggested that $ZnIn_2S_4$ nanosheet was chemically interacted with rGO sheet through Zn—O—C covalent bonds, leading to a tunable band structure and enhanced photocatalytic activity. More importantly, such covalent bondings between $ZnIn_2S_4$ and rGO could improve the composite's structural stability, capable of dramatically enhancing the photocorrosion resistance under sunlight irradiation. The findings of this work would provide a new means for design of visible light active and sunlight stable photocatalysts for environmental remediation applications.

1. Introduction

As a green technology, heterogeneous photocatalysis has demonstrated a great potential for environmental remediation applications [1,2]. However, the most reported semiconductor photocatalysts to date are active only under UV light illumination, greatly limited their practical applications. Extensive efforts have therefore been devoted to develop visible light active photocatalysts, resulting in a large number of visible light active photocatalysts being synthesized [3–5]. However, a key issue remains unresolved, that is, most of reported visible light active photocatalysts are unstable under sunlight irradiation due to the severe photocorrosion caused by the UV component of the sunlight [6–9]. In order to practically utilize sunlight-driven photocatalysis, a photocatalyst must be not only visible light active but also stable under sunlight irradiation.

$ZnIn_2S_4$, a ternary semiconductor chalcogenide with a narrow bandgap (2.34–2.48 eV), well corresponding to the visible light region, has attracted great interest for visible light-driven photocatalytic degradation of organic pollutants and water splitting to produce hydrogen [10–14]. However, as a photocatalyst, the $ZnIn_2S_4$ suffers a critical drawback of high photocorrosion under sunlight irradiation, which in fact is a general issue for most of narrow bandgap semiconductors [15]. For example, the metal sulfide semiconductors with narrow bandgaps such as CdS possess high activity, reasonable stability and photocorrosion resistance under visible light irradiation. However, they become unstable when subjected to sunlight irradiation [16].

Recently, graphene has received considerable attention due to its unique optical, electronic and mechanical properties, promising for a wide range of applications [17,18]. More recently, a number of reports have indicated that the photocatalytic performance of semiconductor materials can be significantly improved when composited with graphene [19–23]. Importantly, some wide bandgap semiconductors (*e.g.,* TiO_2) could exhibit visible light activity after composited with graphene [18,19,24,25]. This is attributed to the advantageous properties of graphene such as visible light absorptivity, superior electron transport ability within the

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photocatalysts, and suppressed charge recombination and tuned band structure can be induced into the semiconductor/graphene composites [18,19,26,27]. More importantly, the narrow bandgap semconductor/graphene composite photocatalysts have shown an increased photocorrosion resistance with enhanced photostability [6]. For example, several groups have demonstrated that the reduced graphene oxide (rGO)–$ZnIn_2S_4$ composites possess the enhanced visible light photocatalytic activity and stability for the solar hydrogen production [28,29], and pollutants degradation [30]. However, to the best of our knowledge, fabricating narrow bandgap semiconductor/rGO composite photocatalysts with chemically cross-linked semiconductor and graphitic carbon bonding to improve the sunlight stability has not been previously reported.

Herein, $ZnIn_2S_4$/rGO (ZIS/rGO) composites with Zn—O—C cross-linked bonds were synthesized to improve the visible light photocatalytic activity and the sunlight stability. The enhanced photocatalytic performance was due largely to the existence of the cross-linked covalent bonds between inorganic component and rGO, which was differing remarkably from the reported approaches for which the composite was formed via non-covalent bonding. The readily tunable optical property and band structure of the resulting composite *via* simple control of the amount of GO enabled the control synthesis of the composite with high photocatalytic activity and excellent solar stability. The photocatalytic performance of the resultant ZIS/rGO composite photocatalysts was systematically investigated using 4-nitrophenol (4-NP) as a model contaminant under both visible light and simulated sunlight irradiations. The selection of 4-NP as the model contaminant was because of its environmental importance. As well known, 4-NP was a highly toxic compound which was widely used as intermediates for synthesis of pesticides, insecticides, herbicides and dyes [31]. The widespread use and high solubility made 4-NP often present in industrial and environmental waters, potentially causing severe chronic poisoning even at very low concentrations.

2. Experimental

2.1. Synthesis

Graphene oxide (GO) was synthesized by modified Hummers method through the oxidation of graphite powder, as reported in our previous report [18]. For synthesis of ZIS/rGO composite, a certain amount of GO was dispersed into a 10 mL of distilled water by ultrasonication for 30 min. Then, 0.147 g $InCl_3{\cdot}4H_2O$, 0.072 g $ZnSO_4{\cdot}7H_2O$ and 0.150 g C_2H_5NS was added into the above solution under stirring. The formed mixture was then stirred for another 30 min. Finally, the obtained solution was transferred into a 15 mL Teflon-lined stainless steel autoclave, and heated to 180 °C for 12 h. After the hydrothermal reaction, the as-synthesized products were obtained by centrifuged, rinsed adequately with distilled water and then dried at 60 °C for 12 h in a vacuum oven. The obtained composite was denoted as ZIS/rGO-X%, where X% is the initial weight ratio of GO. For comparison, $ZnIn_2S_4$ and rGO were also fabricated with the same method.

2.2. Characterization

X-ray diffraction (XRD, Shimadzu XRD-6000 diffractometer, equipped with a graphite monochromator) was employed to characterize the crystal structure. Raman spectra were recorded on a Renishaw inVia Raman microscope with a laser excitation wavelength of 520 nm. Morphology and microstructures of the samples were observed by the scanning electron microscopy (SEM, JEOL JSM-6300F) and transmission electron microscopy (TEM, Philips F20), and the elemental mapping was characterized by JEOL 7001 scanning electron microscopy. The specific surface areas of the materials were calculated using the Brunauer–Emmett–Teller method. UV–visible (UV–vis) diffuse reflectance spectra of the samples were recorded on a UV–vis-NIR spectrophotometer (Varian Cary 300). Chemical compositions of the prepared composites were analysed by X-ray photoelectron spectroscopy (XPS, Kratos Axis ULTRA incorporating a 165 mm hemispherical electron energy analyser). Fourier transform infrared spectroscopy (FT-IR, PerkinElmer spectrum 1000) analysis of the composite was performed using FT-IR spectrophotometer (KBr as the reference sample). Photoluminescence spectra (PL, Hitachi F-7000, excitation wavelength: 330 nm, scanning rate: 1200 nm min^{-1}, PMT voltage: 500 V, widths of the excitation slit and emission slit: 20 nm) of the composites were obtained using a fluorescence spectrometer at 293 K.

2.3. Photocatalytic activity and stability measurement

The visible light (VL) photocatalytic activity was evaluated in a XPAII photoreactor (Nanjing Xujiang Machineelectronic Plant, China). 100 mg of photocatalyst was put into 60 mL of quartz test tube containing 50 mL of 10 mg L^{-1} 4-NP, and then stirred in dark for 30 min to achieve adsorption equilibrium before light irradiation. After that, a 1000 W Xe lamp was used as the VL source (the UV light was cut off by 2.0 M sodium nitrite [18]) to perform the photocatalytic experiment at 25 °C. Under simulated sunlight (SSL) irradiation, a 500 W Xe lamp (Trusttech Co., Beijing) with an AM 1.5 G filter (Sciencetech, Canada) was used as the light source. The incident visible-light and solar-light intensity were 82 and 100 mW cm^{-2}, respectively. The remaining concentration of 4-NP in reaction solution was determined using the UV–vis spectrophotometer (UV-1800, Shimadu). To determine the extent of mineralization, total organic carbon (TOC) contents of solution were measured with a Shimadzu $TOC_{VCPH/CPN}$ analyzer. To evaluate the photostability, the photocatalyst after the first run of 360 min for VL irradiation (or 180 min for SSL irradiation) was separated by centrifuged from the suspension, washed with water, and dried at 60 °C, and then, the recovered photocatalyst was reused for the next run of the photocatalytic degradation under the same conditions.

3. Results and discussion

3.1. Structural characteristics

XRD patterns of the prepared composites are shown in Figs. 1A and S1. As can be seen, $ZnIn_2S_4$ and ZIS/rGO composites show the same diffraction peaks of (0 0 6), (1 0 2), (1 0 4), (1 0 8), (1 1 0), (1 1 6) and (2 0 0) crystal planes at $2\theta = 21.6°$, 27.7°, 30.4°, 39.8°, 47.2°, 52.4° and 55.0°, respectively, which can be indexed to a hexagonal phase of $ZnIn_2S_4$ (JCPDS NO. 65-2023), indicating that low content of GO added ($\leq$wt. 3.0% in our case) has no significant influence on the crystal phase of $ZnIn_2S_4$ in composite. The presence of rGO in composite can be confirmed by Raman spectra, and two typical peaks are found to be located at 1340 and 1590 cm^{-1}, corresponding to D and G bands, respectively (Fig. 1B). For ZIS/rGO–1.5%, besides these two peaks, two new characteristic peaks at around 250 and 355 cm^{-1} attributed to the typical stretching modes of $ZnIn_2S_4$ can also be observed [28], confirming the existence of both $ZnIn_2S_4$ and GO in the composite. Furthermore, an increased D/G intensity ratio ($I_D/I_G = 1.16$) for ZIS/rGO–1.5% is also obtained in comparison with that of GO ($I_D/I_G = 0.88$), indicating that the GO has been, to some extent, reduced to rGO during the hydrothermal process.