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CdS–graphene nanocomposites as visible light photocatalyst for redox reactions in water: A green route for selective transformation and environmental remediation

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ABSTRACT

A series of CdS–graphene (GR) nanocomposites with different weight addition ratios of GR have been fabricated via a facile one-step solvothermal approach. CdS–GR nanocomposites are proven to serve as selective visible light photocatalysts toward aerobic selective oxidation of alcohols and reduction of heavy ions Cr(VI), instead of being nonselective in water. Furthermore, we find that decreasing the defect density of GR by using the solvent-exfoliated graphene (SEG) instead of graphene oxide (GO) as the precursor of GR can efficiently enhance the photocatalytic activity of CdS–GR nanocomposites due to its improved electron conductivity as compared to reduced GO (RGO). In addition, the hybridization of CdS with GR (RGO, SEG) via an intimate interfacial interaction can also effectively inhibit the photocorrosion of CdS during the photocatalytic redox reaction. It is hoped that this work can draw attention to making better use of graphene to synthesize more efficient GR-based nanocomposite photocatalysts for solar energy conversion, especially in the field of diverse redox processes in water in the framework of green chemistry.

1. Introduction

Life, the most complex form of organic compounds on the Earth, enlightens us on the fact that water is a versatile and benign solvent for organic chemistry following nature's lead [1]. Water as a solvent is not only inexpensive and environmentally friendly, but also gives new reactivity [1,2]. Indeed, there have been reports on various chemical reactions occurring in water, including reactions of carbanion equivalent, reactions of carbocation equivalent, transition metal catalysis, reactions of radicals and carbenes, pericyclic reactions, oxidations–reductions, and synthesis of biological compounds from carbohydrates [1,3–8].

In addition to water as a green and abundant resource, solar light represents an affordable, renewable, and clean energy source, which holds great promise for diverse applications, especially for photocatalysis [9]. It has been recognized that semiconductor-based heterogeneous photocatalysis possesses prominent advantages in terms of green chemistry, because various redox reactions can be driven by photogenerated electron–hole pairs under mild conditions, where environmentally dangerous strong chemical oxidant or reducing agents and harsh reaction conditions are not required [9–11].

Based on the above statements, it is clear that heterogeneous photocatalysis in water is ingeniously characterized by the feature of green chemistry and the potential of advancing the reactions toward "sustainable chemistry" [9,11,12]. So far, the aqueous-phase photocatalysis has received broad research interest, mainly in the nonselective degradation of pollutants for environmental cleanup, such as dyes, pesticides, and fertilizers [12–14]. In recent years, with increasingly stringent environmental limitations on chemical processes, the applications of aqueous-phase photocatalysis have been driven to some other processes, including selective transformations for organic synthesis [10,11,15–19]. For example, Palmisano's group has carried out aqueous-phase photocatalytic selective oxidation of alcohols to the corresponding aldehydes over home-prepared TiO_2 under UV light irradiation [19–22]. The reported research works in this context substantiate the versatile capability of semiconductor-based photocatalysis to promote diverse selective redox reactions in water [10,11,15–22].

During the search for effective components to construct efficient photocatalysts, graphene (GR), because of its unique two-dimensional (2D) structure and excellent electron conductivity, has caught immense research attention to synthesizing various GR–semiconductor composites, aiming to improve the photocatalytic performance of semiconductors [23–27]. Nevertheless, most research works are focused on utilizing GR-based composite photocatalysts in the fields of nonselective oxidation and water splitting [23–27]. Our group has demonstrated that GR-based semiconductor (CdS or TiO_2) nanocomposites can serve as a type of effective photocatalysts to promote the selective oxidation of alcohols in the organic solvent benzotrifluoride (BTF) [28–33]. However, it remains unclear if GR-based semiconductor

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composites can still be a good selective photocatalyst for aerobic oxidation of alcohols in water, although it is challenging for the application of semiconductor-based photocatalysis to selective transformation in water because overoxidation in water often results in the difficulty of controlling selectivity [19–22]. In particular, the typical tenet of green chemistry promotes us to investigate the application of GR–semiconductor composite photocatalysts to selective transformation processes in water along with visible light irradiation.

Herein, we report effective photocatalytic selective oxidation of alcohols to corresponding aldehydes and acids in water, a green solvent in organic chemistry, over CdS–GR nanocomposites with different weight addition ratios of GR under visible light irradiation. Furthermore, the effect of defect density of graphene on its performance for improving the photocatalytic activity of CdS–GR nanocomposites toward selective oxidation of alcohols in water has also been investigated by using the solvent-exfoliated graphene (SEG) with lower defect density as the precursor of GR. The photocatalytic performance trend and rationale revealed by the results of aerobic selective oxidation of alcohols, and various characterizations have also been confirmed by reduction of heavy metal ions, Cr(VI), in water. Thus, it is expected that this work could open up new frontiers for advancing the utilizations of GR-based semiconductor nanocomposites as visible light photocatalysts in aqueous-phase selective transformation to synthesis of fine chemicals or reduction of heavy metal ions for environment remediation under the framework of green chemistry.

2. Experimental section

2.1. Chemicals

Cadmium acetate ($Cd(CH_3COO)_2{\cdot}2H_2O$), dimethyl sulfoxide ($C_2H_6OS_2$), graphite powder, sulfuric acid (H_2SO_4), nitric acid (HNO_3), hydrochloric acid (HCl), potassium persulfate ($K_2S_2O_8$), phosphorus pentoxide (P_2O_5), potassium permanganate ($KMnO_4$), hydrogen peroxide, 30% (H_2O_2), N,N-dimethylformamide (DMF), polyvinylpyrrolidone (PVP), acetone (C_3H_6O), and ethanol (C_2H_6O) were supplied by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All materials were used as received without further purification. Ultrapure water and deionized water used in the preparation were from local sources.

2.2. Catalyst preparation

2.2.1. Synthesis of graphene oxide

Graphene oxide (GO) was synthesized from natural graphite powder by a modified Hummers method that involves a strong oxidation and exfoliation process in solution [14,28,34]. GO prepared by this way is widely used as the precursor of graphene (GR) to synthesize the reduced graphene oxide (RGO)–semiconductor composite photocatalysts in the literature [14,23–33,35].

2.2.2. Preparation of solvent-exfoliated graphene

SEG, with lower defect density, was fabricated from natural graphite powder via an exfoliation method in N,N-dimethylformamide (DMF) with the assist of ultrasonication, as reported in the literature [29,32,36,37].

2.2.3. Fabrication of CdS–GR (RGO, SEG) nanocomposites

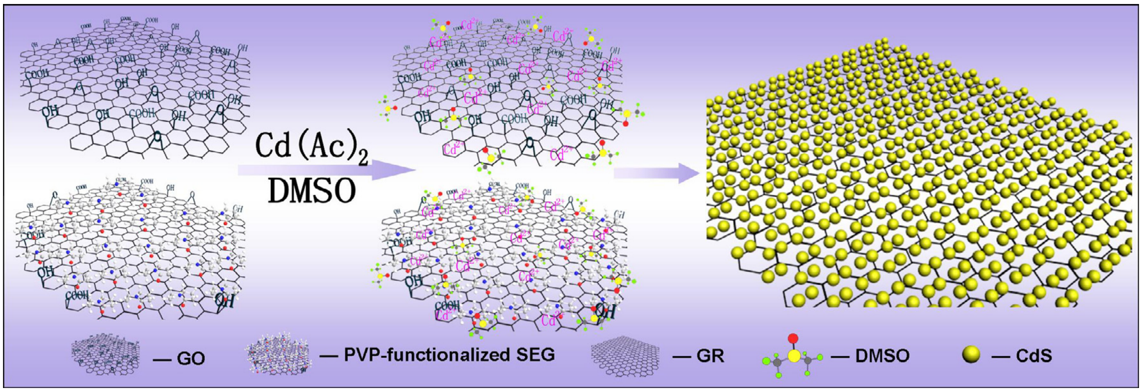
The synthesis procedures are based on a one-step solvothermal method [31,38,39]. The preparation process is illustrated in Scheme 1. The given amount of the as-prepared GO or PVP-functionalized SEG [29,32] was dispersed in 40 mL DMSO by ultrasonication to obtain a homogeneous GO/SEG–DMSO dispersion. Then, 0.106 g $Cd(CH_3COO)_2{\cdot}2H_2O$ was added to the solution. The mixture was stirred vigorously and then transferred to a 50-mL Teflon-lined stainless steel autoclave to conduct solvothermal treatment at 453 K for 12 h. After that, the cooled products were separated by centrifugation and then washed three times with acetone and one time with absolute ethanol. Followed by a dry process, a series of CdS–GR (RGO, SEG) nanocomposites with different weight addition ratios of GR (RGO, SEG) were obtained.

2.2.4. Synthesis of blank-CdS

Blank-CdS was prepared via the same procedure as that for CdS–GR nanocomposites except for the addition of the precursor of GR.

2.3. Catalyst characterization

The phase composition of the samples was analyzed using a Bruker D8 Advance X-ray diffractometer (XRD) using Ni-filtered Cu Kα radiation at 40 kV and 40 mA in the 2θ range from 10° to 80° with a scan rate of 0.02° per second. The optical properties of the samples were characterized by UV–vis diffuse reflectance spectroscopy (DRS) using a UV–vis spectrophotometer (Cary 500, Varian Co.), in which $BaSO_4$ was used as the internal reflectance standard. Field-emission scanning electron microscopy (FESEM) was employed to determine the morphology of the samples on a FEI Nova NANOSEM 230 spectrophotometer. Transmission electron microscopy (TEM) images, high-resolution TEM (HRTEM) images, and energy-dispersive X-ray spectroscopy (EDX) were obtained using a JEOL Model JEM 2010 EX instrument at an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) measurement was carried out on a Thermo Scientific ESCA Lab250



Scheme 1. The schematic illustration for fabrication of CdS–GR (RGO, SEG) nanocomposites based on a one-step solvothermal approach.