Journal of Catalysis 299 (2013) 210–221

Contents lists available at SciVerse ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

A critical and benchmark comparison on graphene-, carbon nanotube-, and fullerene-semiconductor nanocomposites as visible light photocatalysts for selective oxidation

Nan Zhang [a,b], Yanhui Zhang [a,b], Min-Quan Yang [a,b], Zi-Rong Tang [b], Yi-Jun Xu [a,b,*]

[a] State Key Laboratory Breeding Base of Photocatalysis, College of Chemistry and Chemical Engineering, Fuzhou University, Fuzhou 350002, People's Republic of China
[b] College of Chemistry and Chemical Engineering, New Campus, Fuzhou University, Fuzhou 350108, People's Republic of China

ARTICLE INFO

Article history:
Received 23 September 2012
Revised 6 November 2012
Accepted 7 November 2012
Available online 20 January 2013

Keywords:
Carbon
Semiconductor CdS
Visible light photocatalyst
Critical study
Selective oxidation

ABSTRACT

A systematic comparison between graphene (GR)–semiconductor CdS and its analogs fullerene (C_{60}) and carbon nanotube (CNT)–semiconductor CdS composite photocatalysts for selective oxidation of alcohols has been carried out based on a reasonable benchmark framework. The results reveal that GR cannot manifest its unique advantage over its carbon allotropes in enhancing the photoactivity of semiconductor CdS. The primary roles of these carbon allotropes (C_{60}, CNT, and GR) are found to be quite similar in terms of structure–photoactivity correlation analysis. Overall, this work highlights that (i) the exponential increase in publications on GR–semiconductor photocatalysts has not been matched by increases in our knowledge regarding the similarity and difference of these carbon allotropes in relation to improving the photocatalytic performance of semiconductors; (ii) efforts should be more rationally focused on how to make the best use of remarkable properties of GR in designing more efficient GR-based semiconductor composite photocatalysts, thereby advancing the sufficient realization of GR's potential in constructing efficient GR–semiconductor photocatalysts for solar energy conversion.

1. Introduction

Carbon materials have attracted ever-increasing research attention since over 20 years ago, when zero-dimensional fullerene (C_{60}) and one-dimensional carbon nanotubes (CNTs) were discovered [1–10]. In 2004, the successful isolation of monolayer two-dimensional graphene (GR) ignited a profound worldwide revolution aiming to utilize the unique structural and electronic properties of GR to improve the performance of GR-based composite materials for target applications [11–21]. Among numerous utilizations of GR-based composites, the synthesis of GR–semiconductor photocatalysts for conversion of solar to chemical energy, such as, degradation of organic pollutants [13,17,22–25], synthesis of fine chemicals [13,26–31], or water splitting to hydrogen [13,32–36] has been attracting immense interest. Notably, research available in this respect often attributes the photoactivity enhancement of GR-semiconductor composites to the so-called excellent electron conductivity of GR for the effective separation of electron–hole pairs photogenerated from semiconductors [13,36–38]. This status is very similar to that of its forebears, C_{60}– or CNT–semiconductor photocatalysts [4,7,8]. However, these carbon-semiconductor photocatalysts are often studied separately; a necessary and systematic comparison *based on a reasonable benchmark framework* is scarce, which inevitably causes incomplete or exaggerated information on the contribution of GR to enhancing semiconductor photoactivity [29,39–42].

In a previous report, our group has demonstrated that TiO_2-reduced graphene oxide (RGO is also called GR in the literature [13,22–38,41]) nanocomposites obtained by a hard integration of solid P25 nanoparticles with RGO is in essence the same as its TiO_2–CNT counterpart with respect to photoactivity enhancement of TiO_2 [22]. Afterward, a more efficient RGO–TiO_2 photocatalyst was achieved by establishing intimate interfacial contact between RGO and TiO_2 [29], which exhibits significantly enhanced

---

Abbreviations: AO, ammonium oxalate; BQ, benzoquinone; BTF, benzotrifluoride; C_{60}, fullerene; C and Y, conversion and yield; CNT, carbon nanotube; D, dimensional; DI, deionized; DMF, *N,N*-dimethylformamide; DMPO, 5,5-dimethyl-l-pyrroline-*N*-oxide; DMSO, dimethyl sulfoxide; DRS, UV–vis diffuse reflectance spectroscopy; e^-, electron; ESR, electron spin resonance; FESEM, field emission scanning electron microscopy; GO, graphene oxide; GR, graphene; h^+, hole; NS, nanosheet; $O_2^{\cdot-}$, superoxide radicals; $^{\cdot}OH$, hydroxyl radicals; P25, Degussa commercial titanium oxide particles; PL, photoluminescence; PVP, polyvinylpyrrolidone; RGO, reduced graphene oxide; SEG, solvent exfoliated graphene; SWCNT, single-walled carbon nanotube; TBA, *tert*-butyl alcohol; TEM, transmission electron microscopy; XPS, X-ray photoelectron spectroscopy; XRD, X-ray diffractometer.

[*] Corresponding author at: State Key Laboratory Breeding Base of Photocatalysis, College of Chemistry and Chemical Engineering, Fuzhou University, Fuzhou 350002, People's Republic of China. Fax: +86 591 83779326.

E-mail address: yjxu@fzu.edu.cn (Y.-J. Xu).

0021-9517/$ - see front matter © 2012 Elsevier Inc. All rights reserved.
http://dx.doi.org/10.1016/j.jcat.2012.11.021

photoactivity over that of CNT–TiO_2 with poor interfacial contact. Thus, increasing interfacial contact between carbon and semiconductors is one promising way to improve the photoactivity of carbon-semiconductor composite photocatalysts. On the other hand, recent work has shown that the photocatalytic performance of TiO_2–GR can also be improved by minimizing the covalent defect density of the graphene matrix by using solvent exfoliated graphene (SEG) [26,31]. Hersam's group [28] reported that 2D–2D graphene–titania nanosheet composites with low carbon defect densities (SEG–TiNS) exhibit enhanced photoactivity toward selective reduction of CO_2 compared to 1D–2D carbon nanotube–titania nanosheet composites (SWCNT–TiNS), suggesting that carbon nanomaterial dimensionality is a key factor determining the spectral response and reaction specificity of carbon–titania nanosheet composite photocatalysts.

Although much progress has been made in recognizing the key importance of GR's advantageous properties to improving the photocatalytic performance of TiO_2–GR nanocomposites, the exponential increase in publications on GR-semiconductor photocatalysts has not been matched by expected increases in our knowledge regarding the similarity and difference of these carbon allotropes with regard to improving the photocatalytic performance of semiconductors [12,13,15–17,26,28,29,41,43]. It is worth noting that previous comparisons between GR-semiconductor and CNT-semiconductor were based on composite materials in which the degree of carbon-semiconductor interfacial contact is remarkably different [22,28,29,40,41,44]. In other words, a rational and systematic comparison among the carbon materials *on the basis of a reasonable benchmark framework*, in which all the carbon–semiconductor composites with close interfacial contact are realized, is still lacking. In such circumstances, it is insufficient for us to affirm that GR is able to manifest its truly unique and outstanding advantage over its forebears (C_{60} and CNT) in enhancing the photocatalytic performance of semiconductors.

Here, we have prepared a series of cadmium sulfide (CdS)–carbon (C_{60}, CNT, and GR) nanocomposites, all with intimate interfacial contact, via a simple solvothermal method, as illustrated in Scheme 1. For the purpose of sufficient comparison, the precursors of GR include both graphene oxide (GO) having higher defect density and solvent exfoliated graphene (SEG) having lower defect density. Based on such a desirable system, a comparison among these CdS–carbon nanocomposites featuring analogous and close interfacial contact has been conducted, which demonstrates that GR fails to manifest its unique and outstanding advantage over its forebears (C_{60} and CNT) in enhancing semiconductor photocatalytic performance in selective oxidation of alcohols under ambient conditions. On the contrary, the role of these different carbon allotropes in the nanocomposites of CdS–carbon is quite similar. Thus, this work represents a first systematic comparison study *in a reasonable benchmark framework* among semiconductor-carbon (C_{60}, CNT, RGO, and SEG) composite photocatalysts. Importantly, our critical comparison study highlights the mismatch between the exponential increase in publications on GR-semiconductor composite photocatalysts and our knowledge regarding the similarity and difference of these carbon allotropes in tuning the morphology and improving the photocatalytic performance of semiconductors [13,22,25–31,33,34,38,40,41,43–45]. Together with recalling the development history of C_{60}– and CNT–semiconductor composite photocatalysts [6–8], this work strongly indicates that ongoing efforts should be more rationally made to focus on how to make the best use of the remarkable properties of GR instead of on a graphene-based gold rush.

2. Experimental

2.1. Chemicals

Cadmium acetate ($Cd(CH_3COO)_2\cdot 2H_2O$), dimethyl sulfoxide ($C_2H_6OS_2$, DMSO), 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), ethanol (C_2H_6O), *N,N*-dimethylformamide (C_3H_7NO, DMF), ammonium oxalate ($(NH_4)_2C_2O_4\cdot H_2O$, AO), benzoquinone ($C_6H_4O_2$, BQ), silver nitrate ($AgNO_3$), and *tert*-butyl alcohol ($(CH_3)_3COH$, TBA) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Carbon nanotubes were obtained from Shenzhen Nanotech Port Co., Ltd. (China). High-purity C_{60} (99.9%) was supplied by Yongxin Chemical Reagent Company (Henan, China). All materials were used as received without further purification. Deionized (DI) water used in the preparation was from local sources.

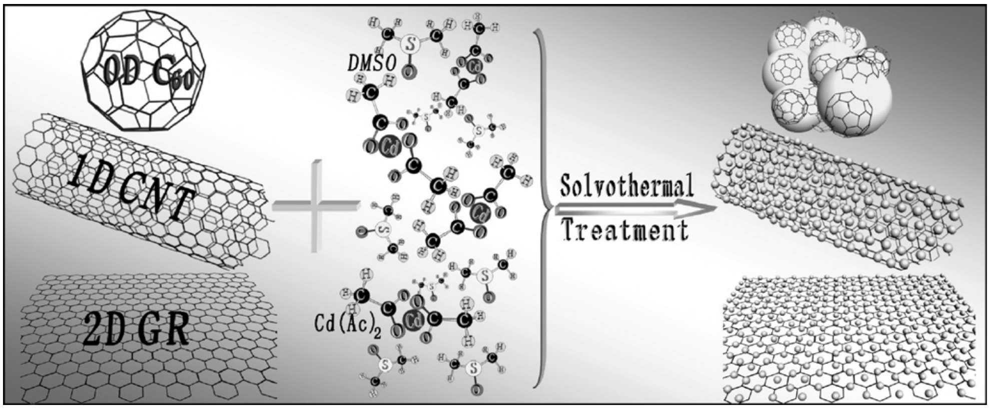
2.2. Photocatalysts preparation

2.2.1. Synthesis of graphene oxide

Graphene oxide (GO) was fabricated from natural graphite powder by a modified Hummers method that involves a strong oxidation process in solution [46]. The details of the typical process can be seen in our previous research work [22,30]. GO prepared in this way is widely used as a precursor of graphene (GR) to synthesize reduced graphene oxide (RGO)-semiconductor composite photocatalysts described in the literature [13,14,22,25,27,29,34].

2.2.2. Fabrication of solvent exfoliated graphene

SEG with lower defect density was synthesized from natural graphite powder via an exfoliation method in *N,N*-dimethylformamide



Scheme 1. The schematic flowchart for preparation of CdS–carbon (C_{60}, CNT, and GR) nanocomposites.