Abstract

Graphene (GR)-CdS nanocomposites with different weight addition ratios of GR have been assembled by a facile solvothermal treatment. The GR-CdS nanocomposite photocatalyst with an appropriate ratio of GR exhibits enhanced photoactivity for selective reduction of aromatic nitro compounds to the corresponding aromatic amines in water under visible light irradiation as compared with blank-CdS. The characterization of GR-CdS nanocomposite photocatalysts by a collection of techniques discloses that: i) GR can tune the microscopic morphology of CdS nanoparticles and improve light absorption intensity in the visible light region; ii) GR scaffolds act as an electron reservoir to trap and shuttle the electrons photogenerated from CdS semiconductor under the visible light illumination; iii) the introduction of GR enhances the adsorption capacity of GR-CdS nanocomposites toward the substrates, aromatic nitro compounds. The synergistic effect of these factors should account for the photoactivity advancement of GR-CdS nanocomposites toward the probe reactions. Furthermore, because the photogenerated holes in the system are trapped by the quenching agent ammonium oxalate, the as-obtained GR-CdS photocatalyst is stable during the photocatalytic reduction reactions. A reasonable model has also been proposed to illustrate the reaction mechanism.

Key words

graphene; CdS; photocatalytic selective reduction; nitro compounds; visible light; water

1. Introduction

Photocatalysis, as a green technology, has been widely utilized to various applications which are mainly focused on nonselective reactions for environmental harness and water splitting to clean hydrogen or oxygen [1–9]. Recent progress has demonstrated that semiconductor-based heterogeneous photocatalysis offers a promising alternative to conventional synthetic routes for the synthesis of fine chemicals in virtue of the appropriate assembly of semiconductor nanocomposites and fine control of reaction conditions [10–15]. For instance, Zhao’s group has investigated TiO2-based photocatalysts for photocatalytic aerobic oxidation of alcohols to the corresponding aldehydes. And they have carried out in-depth investigation on the reaction mechanism [16–18]. Palmisano and coworkers have prepared home-prepared TiO2 for photocatalytic selective oxidation of aromatic alcohols with high selectivity [19–21]. In this field, our group has reported a series of nanomaterials for effective photocatalytic selective oxidation of alcohols, alkenes and toluene under ambient conditions, including carbon (fullerene, carbon nanotube, graphene)-based nanocomposites, core@shell structured and one-dimensional nanocomposites [13–15, 22–34].

Besides selective oxidation processes, selective reduction of aromatic nitro compounds to the corresponding aromatic amines is a significant chemical transformation in synthetic organic chemistry because amino group can serve as a site for further derivatization towards final products, and aromatic amines are widely used as important intermediates in the preparation of a number of valuable chemicals, such as pharmaceuticals, agrochemicals, dyes and polymers [35–42]. Herein, we assemble graphene (GR)-CdS by a facile solvothermal treatment to photocatalyze selective reduction of aromatic nitro compounds to the corresponding aromatic amines in water with visible light irradiation under mild conditions. The GR-CdS nanocomposites exhibit improved photocatalytic performance for selective reduction of nitro...
compounds as compared with blank-CdS under visible light irradiation. The recycle tests indicate that GR-CdS photocatalyst is reusable. In view of the fact that the reports on GR-based nanocomposites for photocatalytic applications are often centered on the degradation of pollutants in liquid and gas phases, and water splitting for H₂ evolution [43–47], this work is anticipated to provide testimony to the capability of GR-based semiconductor photocatalysts for solar energy conversion in the field of selective organic transformations.

2. Experimental

2.1. Materials

Cadmium acetate (Cd(CH\(_3\)COO\(_2\)-2H\(_2\)O), dimethyl sulfoxide (C\(_2\)H\(_6\)OS\(_2\)), DMSO), graphite powder, sulfuric acid (H\(_2\)SO\(_4\)), nitric acid (HNO\(_3\)), hydrochloric acid (HCl), potassium persulfate (K\(_2\)S\(_2\)O\(_8\)), phosphorus pentoxide (P\(_2\)O\(_5\)), potassium permanganate (KMnO\(_4\)), hydrogen peroxide (H\(_2\)O\(_2\), 30%), acetone (C\(_3\)H\(_6\)O), ethanol (C\(_2\)H\(_5\)OH) and ammonium oxalate ((NH\(_4\))\(_2\)C\(_2\)O\(_4\)-H\(_2\)O) were supplied by Sinopharm chemical reagent Co., Ltd (Shanghai, China). All the materials were used as received without further treatment. Deionized water was obtained from local sources.

2.2. Catalyst preparation

(a) Fabrication of graphene oxide (GO). Graphene oxide (GO) was fabricated by a modified Hummers method that involves a strong oxidation and exfoliation process of natural graphite powder in solution [4,13,48]. GO prepared by this way, often called reduced graphene oxide (RGO), is widely adopted as the precursor of GR to synthesize the graphene-based composite photocatalysts in literatures [4,13−15,43−45,49,50]. (b) Synthesis of GR-CdS nanocomposites. The preparation process is vividly delineated in Scheme 1. The given amount of the as-prepared GO was dispersed in 40 mL DMSO by ultrasonication to obtain the homogeneous GO-DMSO dispersion into which 0.4 mmol Cd(CH\(_3\)COO\(_2\)-2H\(_2\)O was added. The above mixture was stirred vigorously and then transferred to 50 mL Teflon-lined stainless steel autoclave to undergo a solvothermal treatment at 453 K for 12 h [51]. Afterwards, the products were cooled to room temperature, separated by centrifugation and then washed with acetone three times and with absolute ethanol one time, respectively. After a drying process at 333 K in an electrical oven, a series of GR-CdS nanocomposites with different weight addition ratios of GR were obtained. (c) Preparation of blank-CdS. Blank-CdS was synthesized via the same procedure as that of GR-CdS nanocomposites except the addition of graphene oxide (GO).

2.3. Catalyst characterization

The phase composition of the samples was characterized using a Bruker D8 Advance X-ray diffractometer (XRD) with Ni-filtered Cu K\(_\alpha\) radiation (λ = 1.5418 Å) at 40 kV and 40 mA with a scan rate of 0.02° per second. UV-vis diffuse reflectance spectroscopy (DRS) on UV-vis spectrophotometer (Cary 500, Varian Co.) was used to measure the optical properties of the samples with BaSO\(_4\) as the internal reflectance standard. The morphology of the samples was analyzed by field-emission scanning electron microscopy (FESEM) on a FEI Nova NANOSEM 230 spectrophotometer and transmission electron microscopy (TEM) using a JEOL model JEM 2010 EX instrument at an accelerating voltage of 200 kV. The photoluminescence (PL) spectra for solid samples were obtained on an Edinburgh Analytical Instrument FLS 920 spectrophotometer with the excitation wavelength of 358 nm. The electrochemical analysis was carried out in a conventional three-electrode cell using a Pt plate and an Ag/AgCl electrode as the counter electrode and reference electrode, respectively. The electrolyte was 0.2 mol/L Na\(_2\)SO\(_4\) aqueous solution without additive (pH = 6.8). The working electrode was prepared on indium-tin oxide (ITO) glass that was cleaned by sonication in ethanol for 30 min and dried at 353 K. The boundary of ITO glass was protected using Scotch tape. 5 mg sample was dispersed in 0.5 mL N,N-dimethylformamide (DMF) by sonication to get slurry. The slurry was spread onto the pre-treated ITO glass. After air drying, working electrode was further dried at 393 K for 2 h to improve adhesion. Then, the Scotch tape was unstuck, and the uncoated part of the electrode was isolated with epoxy resin. The exposed area of working electrode was 0.25 cm\(^2\). The chopping photocurrent-voltage curves were measured on a BAS Epsilon workstation with applied potentials of 0 to +0.67 V. The electrochemical impedance spectroscopy (EIS) experiments were conducted on a Precision PARC workstation. Micromeritics ASAP2010 equipment was used to determine the nitrogen adsorption-desorption isotherms and the Brunauer-Emmett-Teller (BET) surface areas at 77 K. The sample was degassed at 413 K for 5 h and then analyzed at 77 K. The relative pressure (p/p\(_0\)) range used for calculation of BET surface area was from 0.05 to 0.35.

2.4. Catalyst activity

The photocatalytic selective reduction of aromatic nitro compounds to corresponding aromatic amines was performed in a self-designed photochemical reactor equipped with an electromagnetic stirrer. In a 100 mL glass flask equipped with a magnetic stir bar and a three-hole plug, 10 mg catalyst was dispersed in 30 mL of a 20 mg/L aqueous solution of aromatic nitro compounds with 20 mg ammonium oxalate as holes scavenger. The mixture was stirred in the dark for 1 h to ensure the establishment of adsorption-desorption equilibrium between sample and reactant. Then, the above suspension was irradiated with a 300 W Xe arc lamp (PLS-SXE 300, Beijing Perfect light Co., Ltd.) with a UV-CUT filter to cut off light of wavelength λ<420 nm. During the process of the reaction, 3 mL sample solution was taken from the reac-
tion system at a certain time interval. Then, the solid photocatalyst was immediately separated from the mixed phase by centrifugation and the remaining supernatant was analyzed on a Shimadzu high performance liquid chromatograph (HPLC-LC20AT equipped with a C18 column and SPD-M20A photo diode array detector). The whole experimental process was conducted under N₂ bubbling at a flow rate of 80 mL/min.

Scheme 1. Fabrication of GR-CdS nanocomposites

Figure 1. XRD patterns of (a) graphene, graphene oxide, (b) blank-CdS, GR-CdS nanocomposites with different weight ratios of GR, and the standard XRD pattern of cubic CdS (JCPDS No. 10-0454)

3. Results and discussion

As illustrated in Scheme 1, graphene oxide (GO), as the precursor of graphene (GR), is obtained from graphite through a strong oxidation and exfoliation process. GO prepared by this way, often called reduced graphene oxide (RGO), is widely adopted as the precursor of GR to synthesize the graphene-based composite photocatalysts in literatures [4,13−15,43−45,49,50]. GR-CdS nanocomposites are fabricated via a facile one-step process in a solution phase. The mixture of cadmium salt and GO-dimethyl sulfoxide (DMSO) suspension undergo a solvothermal treatment, during which DMSO solvent serves as the reducing agent to reduce GO and the source of sulfur to produce S²⁻ ions. Therefore, in this solvothermal process, the transformation of insulating GO to electron conducting GR, the production of CdS nanoparticles and the intimate interfacial contact of CdS with GR are all achieved simultaneously, which can be verified by a series of characterizations as discussed in the following part. Firstly, it can be observed from Figure 1(a) that GO shows a sharp diffraction peak at 2θ value of ca. 10.1°, which is derived from its ordered staking layered structure with ca. 0.87 nm interlayer spacing [4,13,14,52]. For GR obtained from the solvothermal reduction process, the diffraction peak at ca. 10.1° disappears and a very broad diffraction peak centered at 2θ value of ca. 25.6° appears, indicating that GO nanosheets have been effectively exfoliated from the graphite oxide and, after the solvothermal reduction treatment, almost all GO nanosheets have been reduced to GR with a random packing and significantly less functionalities [4,13,14,52]. The production of CdS is also reflected by XRD results. As shown in Figure 1(b), the as-prepared GR-CdS nanocomposites with different weight addition ratios of GR as well as blank-CdS all exhibit the diffraction peaks of cubic CdS phase (JCPDS No. 10-0454) and the lattice constant a equals to 5.818 Å. More specifically, the main characteristic peaks at 2θ values of 26.5°, 44.0° and 52.1° are corresponding to (111), (220) and (311) crystal planes of cubic CdS, respectively, as obtained by comparison of the samples patterns with the standard one (Figure 1b). However, there is no apparent diffraction peak for the separate GO with regard to GR-CdS nanocomposites, indicating the effective
reduction of GO by DMSO solvent. The relatively low diffraction intensity of GR at ca. 25.6° might be shielded by the main peak of cubic CdS at 26.5°, which can account for the absence of GR diffraction peak in XRD results [4,13,23,25,49]. A survey of the XRD patterns of GR-CdS nanocomposites with different weight addition ratios of GR leads us to find that the diffraction intensity of these samples is strengthened and the average crystallite size of CdS nanoparticles is increased with the increase of GR content. For each sample, the full width at half maximum (FWHM) for cubic CdS (220) facet diffraction peak is obtained by fitting to a Lorentzian function with high adjusted R-square. As summarized in Table 1, on the basis of Scherrer formula, the calculated average crystallite sizes of CdS particles are about 2.0, 2.4, 2.7, 2.9, 3.8 and 4.6 nm, corresponding to blank-CdS, 1%GR-CdS, 5%GR-CdS, 10%GR-CdS, 30%GR-CdS, 50%GR-CdS and 70%GR-CdS, respectively. The increases in CdS particle size and crystallinity could be attributed to the platform role of GR for the in-situ nucleation and growth of CdS nanoparticles [25,49].

<table>
<thead>
<tr>
<th>Samples</th>
<th>Average crystallite sizes (nm)</th>
<th>Full width at half maximum (FWHM)</th>
<th>Adjusted Square</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank-CdS</td>
<td>2.0</td>
<td>4.1881</td>
<td>0.9112</td>
</tr>
<tr>
<td>1% GR-CdS</td>
<td>2.4</td>
<td>3.5288</td>
<td>0.9167</td>
</tr>
<tr>
<td>5% GR-CdS</td>
<td>2.7</td>
<td>3.1818</td>
<td>0.9141</td>
</tr>
<tr>
<td>10% GR-CdS</td>
<td>2.7</td>
<td>3.1631</td>
<td>0.9166</td>
</tr>
<tr>
<td>30% GR-CdS</td>
<td>2.9</td>
<td>2.9147</td>
<td>0.9092</td>
</tr>
<tr>
<td>50% GR-CdS</td>
<td>3.8</td>
<td>2.2287</td>
<td>0.9175</td>
</tr>
<tr>
<td>70% GR-CdS</td>
<td>4.6</td>
<td>1.8411</td>
<td>0.9089</td>
</tr>
</tbody>
</table>

*Scherrer equation: \( D = \frac{K \lambda}{\beta \cos \theta} \) where \( D \) is the mean size of the ordered crystalline domains, \( K \) is the shape factor, \( \lambda \) is the X-ray wavelength, \( \beta \) is the line broadening at half the maximum intensity (FWHM) in radians, \( \theta \) is the Bragg angle. \(^b\) The FWHM and adjusted R-Square are obtained by the fitting results according to Lorentzian function

Figure 2 displays the UV-vis diffuse reflectance spectra (DRS) of GR-CdS nanocomposites and blank-CdS. It can be seen clearly that the introduction of GR results in an enhanced light absorption intensity in the visible light region of 500–800 nm, as compared with blank-CdS. This is consistent with the color change of the samples. It can be observed from the bottom panels of Figure 2 that the color generally becomes deeper with the increase of weight addition ratios of GR. Furthermore, a qualitative red-shift of the optical absorption band edge to higher wavelength is obviously revealed by DRS results. There is a band gap narrowing of semiconductor CdS due to the introduction of GR. The band gap values estimated from Kubelka-Munk functions are ca. 2.36, 2.31, 2.11, 2.04 and 1.99 eV, corresponding to blank-CdS, 1%GR-CdS, 5%GR-CdS, 10%GR-CdS and 30%GR-CdS, respectively. As for the nanocomposites with high weight addition ratios of GR, such as 50%GR-CdS and 70%GR-CdS, it is difficult to determine the value of such a red shift because of the strong background absorption induced by the incorporation of GR [4,13,22–24]. Evidently, the introduction of GR into the matrix of CdS is able to promote the visible light response of GR-CdS nanocomposites, which is attributed to the electronic interactions between GR and CdS instead of the C-doping into CdS crystal. This is further demonstrated by the comparison of Cd 3d XPS spectra of 5%GR-CdS and blank-CdS (Figure 3). Such an extended optical absorption has also been observed in previous research works regarding carbon (fullerene, carbon nanotube, graphene)-semiconductor photocatalysts [4,5,13, 14, 22–24].

Figure 2. UV-vis diffuse reflectance spectra (DRS) of blank-CdS and GR-CdS nanocomposites with different weight addition ratios of GR (top panel) and the sample pictures (bottom panels)

Considering the preparation procedure which involves an in-situ crystallization process, the morphology of the as-prepared GR-CdS is likely to be different from that of blank-CdS due to the introduction of planar two-dimensional (2D) graphene nanosheets. The field-emission scanning electron microscopy (FESEM) images faithfully validate this inference. As displayed in Figure 4(a), blank-CdS consists of spherical particles with the diameter ranging from 100 to 400 nm. However, when GR is incorporated into the matrix of semiconductor CdS, such as 5 wt% of GR, GR-CdS composite possesses distinct morphology. It is easy to see from Figure 4(c) that, as compared with blank-CdS, much smaller CdS nanoparticles spread uniformly on the surface of GR nanosheets and 2D structure of GR nanosheets with micrometers-long wrinkles can be clearly distinguished, suggesting the ability of GR to tune the microscopic structure of...
semiconductor CdS effectively and its own chemical stability. The transmission electron microscopy (TEM) images of 5%GR-CdS further corroborate its microscopic morphology. A nice dispersion of CdS nanoparticles on the surface of GR nanosheet support can be observed from Figure 4(d) and 4(e). Additionally, the size distribution of CdS particles in blank-CdS and 5%GR-CdS (Figure 4b and 4f) gives direct comparison of their particle sizes. The great influence of GR on the morphology of the samples is quite reasonable due to the fact that GR nanosheets as a 2D “mat” can function as a platform to facilitate the growth of CdS nanoparticles and hinder their aggregation concurrently, leading to a homogeneous distribution of CdS nanoparticles on the surface of GR nanosheets. In addition, the intimate interfacial contact between GR and CdS particles is also reflected by TEM images. The lattice fringe with 0.336 nm spacing marked in the high-resolution TEM (HRTEM) image (Figure 4g) is indexed to (111) crystal plane of cubic CdS. Three distinct diffraction rings as shown in the selected area electron action (SAED) pattern (the inset of Figure 4g) are corresponding to (111), (220) and (311) crystal planes of CdS, which is consistent with the polycrystalline structure reflected by XRD patterns of GR-CdS nanocomposites. Furthermore, the energy-dispersive X-ray (EDX) spectra confirm the elemental composition of GR-CdS nanocomposite. The EDX result of 5%GR-CdS (Figure 4h) contains the signals of C, Cd and S elements, in which the signal of C was mainly from GR nanosheets in the nanocomposite since the lacey support film without carbon coating is employed in TEM sampling.

**Figure 3.** XPS spectra of Cd 3d recorded on 5%GR-CdS and blank-CdS

**Figure 4.** Typical FESEM images of blank-CdS (a) and 5%GR-CdS (c); TEM (d,e), HRTEM (g) and EDX (h) results of 5%GR-CdS (the inset of HRTEM image is the corresponding SAED pattern); the size distribution of CdS particles in blank-CdS (b) and 5%GR-CdS (f)

It can be learned from a literature survey on reduction of nitro compounds to amines that one of the most common approaches to construct appropriate systems for this organic transformation is to couple the reducing agents with catalysts under selected reaction conditions [37,53−56]. For example, the combinations of hydrazine and metal (e.g., Raney nickel, Pd-C), NaBH₄ and metal (e.g., Au, Ag, Pd, Pt), H₂ and RuCl₂(PPh₃)₂, CO and Ru₃(CO)₁₂, 1,1'-dioctyl-4,4'-bipyridinium dibromide and samarium (0) have been used for this purpose [37,53−56]. However, the disadvantages of these reduction methods lie in the need of a closed high-pressure system, the addition of stoichiometric reducing agent, the relatively high costs for hydrazine hydrate and noble metal catalysts [57]. Two decades ago, Li and coworkers reported the photoinduced reduction of nitro compounds on semiconductor particles for the first time [58]. Since then, utilization of photocatalytic process for the reduction of aromatic nitro chemicals to aromatic amines has attracted increasing research attention [58]. In contrast to the conventional approaches, photocatalytic routes for this reduction reaction dismiss the re-
quirement of harsh reaction conditions and additional reducing agents, thus offering a green and facile approach for the reduction procedures, which is demonstrated by the following part.

Photocatalytic selective reduction of 4-nitroaniline (4-NA) to the corresponding amine, p-phenylenediamine (PPD), in water is initially selected as a model reaction to evaluate the photoactivity of GR-CdS nanocomposites under visible light irradiation with the addition of ammonium oxalate as quenching agent for photogenerated holes and N$_2$ purge under ambient conditions, i.e., room temperature and atmospheric pressure. Blank experiments in the absence of photocatalysts and/or visible light irradiation show no conversion of substrate reactants, indicating that the reaction is really driven by a photocatalytic process. As shown in Figure 5, obviously, the introduction of an appropriate amount of GR can improve the photoactivity of GR-CdS nanocomposites for the target reaction. For example, when 5 wt% GR is added, the apparent kinetic rate constant ($K_a$) is increased to 0.006 min$^{-1}$, being twice as high as that obtained over blank-CdS (0.00292 min$^{-1}$). However, when the weight addition ratio of GR is too high, such as 30%, 50% and 70%, the photocatalytic performance is deteriorated. Such phenomenon has also been reported in other GR-based nanocomposites for photocatalytic nonselective and selective processes [4,13,22,23,49,59,60]. This is reasonable because the relatively high weight ratio of GR in GR-CdS nanocomposites would unavoidably reduce the contact surface of semiconductor CdS nanoparticles with the light illumination and lower the light intensity through the depth of reaction solution, which results in a decreased photocatalytic activity [4]. The optimal weight addition ratio of GR in GR-CdS nanocomposites is found to be 5%. The results obtained on high performance liquid chromatograph (HPLC) confirm that the product is primarily dominated by PPD with a high selectivity of ca. 99%.

Subsequently, the visible light photoactivities of the optimum 5%GR-CdS nanocomposite and blank-CdS has been measured by selective reduction of other aromatic nitro compounds to the corresponding aromatic amino organics in aqueous phase, including 3-nitroaniline, 2-nitroaniline, 4-nitrophenol, 3-nitrophenol, 2-nitrophenol, 4-nitrotoluene, 4-nitroanisole, 1-bromo-4-nitrobenzene and 1-chloro-4-nitrobenzene, with the addition of ammonium oxalate as holes scavenger under anaerobic conditions. As for all the conducted reactions, the superiority of 5%GR-CdS nanocomposite over blank-CdS for photocatalytic reduction of various aromatic organics is observed from Table 2.

![Figure 5. Photocatalytic performance of blank-CdS and GR-CdS with different weight addition ratios of GR for selective reduction of 4-nitroaniline (4-NA) in aqueous phase under visible light irradiation ($\lambda>$420 nm) with the addition of holes scavenger, ammonium oxalate and N$_2$ purge: (a) time-online reduction curves with conversion of 4-NA versus irradiation time, and (b) apparent kinetic rate constant $K_a$ (the x-axis title represents the weight addition ratio of GR in the corresponding nanocomposite)](image)

It is well known that one of the primary roles of GR in GR-semiconductor nanocomposite photocatalysts is to capture and shuttle the photogenerated electrons, lengthen the fate of charge carriers and thus improving the photocatalytic performance of the nanocomposites [43–45,49,50,60–65]. In addition to the as-evidenced enhancement of the photoactivity of GR-CdS nanocomposites for selective reduction of aromatic nitro compounds, a collection of characterizations have been carried out to reveal the function of GR on enhancing the photocatalytic performance of GR-CdS nanocomposites. The photoluminescence (PL) spectra are often used to study surface processes involving the fate of charge carriers photoexcited from semiconductors [5,23,61–64]. When the electron-hole pairs in an excited photocatalyst upon irradiation recombine, photons are emitted in the form of photoluminescence [5,23]. As displayed in Figure 6, 5%GR-CdS nanocomposite shows diminished PL intensity as compared with that of blank-CdS, which suggests more efficient...
inhibition of charge carriers recombination in 5%GR-CdS nanocomposite and squares well with its higher photocatalytic performance for selective reduction of aromatic nitro chemicals. This result is further ascertained by the transient photocurrent responses of blank-CdS and 5%GR-CdS under intermittent visible light illumination with very wide wavelength range used in the photocatalytic reactions. It can be seen from Figure 7(a) that the addition of GR is able to enhance the photocurrent remarkably, signifying a more efficient separation of the photoexcited electron-hole pairs obtained in 5%GR-CdS nanocomposite in contrast to blank-CdS. Additionally, electrochemical impedance spectroscopy (EIS) Nyquist plots have also been analyzed. As shown in Figure 7(b), both the EIS Nyquist plots of blank-CdS and 5%GR-CdS electrode materials cycled in 0.2 mol/L Na₂SO₄ electrolyte solution give rise to semicycles at high frequencies, which corresponds to the charge transfer limiting process and is ascribed to the double-layer capacitance (C_{dl}) in parallel with the charge transfer resistance (R_{ct}) at the contact interface between electrode and electrolyte solution [25,66,67]. Clearly, the introduction of GR leads to a dramatic decrease of the semicycle arc as compared with blank-CdS, suggesting that GR can facilitate the interfacial charge transfer more effectively [68]. Therefore, the above results authenticate that the key role of GR in GR-semiconductor nanocomposite photocatalysts is to act as an electron reservoir to improve the lifetime and transfer of photoinduced charge carriers, thus contributing to photoactivity enhancement for selective reduction of aromatic nitro compounds under visible light illumination.

![Figure 6. Emission photoluminescence (PL) spectra of blank-CdS and 5%GR-CdS nanocomposite obtained with the excitation wavelength λ at 358 nm](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrates</th>
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<th>Time (min)</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
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<tr>
<td>1</td>
<td>H₂N—Ph—NO₂</td>
<td>H₂N—Ph—NH₂</td>
<td>60</td>
<td>67(52)</td>
<td>98(97)</td>
</tr>
<tr>
<td>2</td>
<td>H₂N—Ph—NO₂</td>
<td>H₂N—Ph—NH₂</td>
<td>60</td>
<td>77(49)</td>
<td>97(95)</td>
</tr>
<tr>
<td>3</td>
<td>HO—Ph—NO₂</td>
<td>HO—Ph—NH₂</td>
<td>60</td>
<td>63(48)</td>
<td>99(96)</td>
</tr>
<tr>
<td>4</td>
<td>HO—Ph—NO₂</td>
<td>HO—Ph—NH₂</td>
<td>60</td>
<td>45(31)</td>
<td>98(97)</td>
</tr>
<tr>
<td>5</td>
<td>H₃C—Ph—NO₂</td>
<td>H₃C—Ph—NH₂</td>
<td>40</td>
<td>89(58)</td>
<td>97(96)</td>
</tr>
<tr>
<td>6</td>
<td>H₃C—Ph—NO₂</td>
<td>H₃C—Ph—NH₂</td>
<td>40</td>
<td>84(72)</td>
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<td>H₃CO—Ph—NH₂</td>
<td>40</td>
<td>90(75)</td>
<td>98(95)</td>
</tr>
<tr>
<td>8</td>
<td>Cl—Ph—NO₂</td>
<td>Cl—Ph—NH₂</td>
<td>10</td>
<td>85(47)</td>
<td>99(98)</td>
</tr>
<tr>
<td>9</td>
<td>Br—Ph—NO₂</td>
<td>Br—Ph—NH₂</td>
<td>10</td>
<td>82(69)</td>
<td>97(94)</td>
</tr>
</tbody>
</table>

*The data in parentheses are conversion and selectivity over blank-CdS under identical reaction conditions.
Figure 7. Chopping visible light photocurrent-voltage curves (a) and electrochemical impedance spectroscopy (EIS) Nyquist diagrams (b) of blank-CdS and 5%GR-CdS nanocomposite in 0.2 mol/L Na$_2$SO$_4$ aqueous solution (pH = 6.8)

Figure 8. Nitrogen adsorption-desorption isotherms and pore size distribution of blank-CdS (top panels) and 5%GR-CdS nanocomposite (bottom panels)

Furthermore, the Brunauer-Emmett-Teller (BET) surface area and porosity analysis of blank-CdS and 5%GR-CdS have also been conducted. The BET surface area of 5%GR-CdS is ca. 57 m$^2$/g, which is similar to that of blank-CdS (ca. 56 m$^2$/g). As reflected in Figure 8, nitrogen adsorption-desorption isotherm of blank-CdS exhibit type II isotherm and 5%GR-CdS nanocomposite shows type IV with a typical H3 hysteresis loop according to the IUPAC classification, indicating that blank-CdS belongs to non-porous structure, whereas 5%GR-CdS is characteristic of mesoporous solid [69]. This is also confirmed by their pore size distribution. The change in pore structure of 5%GR-CdS caused by the incorporation of GR nanosheets may induce the disparity of the adsorption capacity of the samples. The results of adsorption experiments in the dark for the substrates, aromatic nitro compounds, over blank-CdS and 5%GR-CdS (Figure 9) indicate that the alter-
ation in pore structure of 5%GR-CdS give rise to the distinction of adsorption capacity between blank-CdS and 5%GR-CdS. In particular, the higher adsorption capacity toward aromatic nitro compounds over 5%GR-CdS than blank-CdS indicates a higher accumulating concentration of reactants over the photocatalyst surface, which is beneficial to photoactivity improvement. The stability testing result for 5%GR-CdS is shown in Figure 10. Obviously, no evident loss of photoactivity takes place over 5%GR-CdS during four times successive recycles, demonstrating that GR-CdS nanocomposites are able to serve as stable photocatalysts for such reduction reactions. This can be ascribed to the addition of hole scavenger, ammonium oxalate which inhibits the photocorrosion of CdS effectively [70].

In view of the mechanism for the reduction of aromatic nitro organics, a photoinduced six-electron reduction process involving sequential electron transfer, protonation and dehydration is illustrated in Scheme 2 [58,71]. Evidently, a complete reduction of a nitro compound requires six electrons and leaves the same numbers of holes behind. In the present system, the photogenerated holes are quenched by the added scavenger, ammonium oxalate; meanwhile, the electrons reduce the nitro group. The flatband potential ($V_{fb}$) of 5%GR-CdS is measured to be approximately –0.68 V versus Ag/AgCl, –0.49 V versus normal hydrogen electrode (NHE) according to the Mott-Schottky plot [72]. The conduction band (CB) of CdS in 5%GR-CdS is more negative than the reduction potential of the aromatic nitro compounds [58]. Therefore, the reduction process triggered by the photoinduced electrons is thermodynamically permissible.

Accordingly, a reasonable model is proposed to illustrate the probable reaction mechanism for selective reduction of aromatic nitro compounds over GR-CdS nanocomposite photocatalysts, as portrayed in Scheme 3. With the illumination of visible light ($\lambda$ > 420 nm), the electrons are excited from the valence band (VB) of CdS in GR-CdS nanocomposites to its CB. The inert N$_2$ atmosphere and the addition of ammonium oxalate as holes scavenger; the conduction band edge ($E_{CB}$) of CdS and Fermi level ($E_F$) of graphene are relative to normal hydrogen electrode (NHE).

Figure 9. Remaining fraction of various aromatic nitro organics after the adsorption-desorption equilibrium is achieved over blank-CdS and 5%GR-CdS nanocomposite: (1) 4-nitroaniline, (2) 3-nitroaniline, (3) 2-nitroaniline, (4) 4-nitrophenol, (5) 3-nitrophenol, (6) 2-nitrophenol, (7) 4-nitrotoluene, (8) 4-nitroanisole, (9) 1-bromo-4-nitrobenzene, (10) 1-chloro-4-nitrobenzene

Figure 10. Cycling photocatalytic reduction of 1-bromo-4-nitrobenzene over 5%GR-CdS nanocomposite under visible light irradiation ($\lambda$ > 420 nm) in water with the addition of ammonium oxalate as quencher for photogenerated holes and N$_2$ purge

Scheme 2. Photocatalytic reduction of aromatic nitro compounds over semiconductor particles

Scheme 3. Model picture demonstrating the proposed reaction mechanism for the reduction of aromatic nitro compounds to the corresponding aromatic amines over GR-CdS nanocomposites under visible light irradiation ($\lambda$ > 420 nm) with the addition of ammonium oxalate as holes scavenger; the conduction band edge ($E_{CB}$) of CdS and Fermi level ($E_F$) of graphene are relative to normal hydrogen electrode (NHE)
presence of GR also increases the accumulating concentration of nitro organics over the surface of GR-Cds nanocomposites. Consequently, the adsorbed aromatic nitro compounds can be effectively reduced to aromatic amines by accepting the photogenerated electrons with prolonged life span.

4. Conclusions

In summary, GR-Cds nanocomposites prepared through a one-step solvothermal treatment are utilized to photocatalyze selective reduction of various aromatic nitro compounds to the corresponding aromatic amines in aqueous phase under visible light irradiation. As compared with blank-Cds, GR-Cds nanocomposites with an appropriate weight addition ratio of GR exhibit enhanced photocatalytic performance. This can be ascribed to the synergistic effect of three factors due to the introduction of graphene, including the increased visible light absorption intensity, the improved lifetime and transfer of charge carriers and the enhanced adsorption capacity of GR-Cds nanocomposite toward the substrates. It is expected that this work could give testimony to the potential of GR-based semiconductor photocatalysts for solar energy conversion in the field of selective organic transformations.

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References
