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Graphene-supported CoS₂ Particles: an Efficient Photocatalyst for Selective Hydrogenation of Nitroaromatics in Visible Light

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 $CoS_2/graphene$ composite fabricated by a facile hydrothermal method exhibits excellent photocatalytic performance for selective hydrogenation of nitroaromatics to corresponding aniline employing molecule hydrogen as reducing agent under visible light irradiation (400-800 nm). The rate constant of the composite catalyst for nitrobenzene hydrogenation can achieve as high as 35.50×10^{-3} min⁻¹ with a selectivity of 100% toward the target product under mild conditions (30 °C and 0.25 MPa pressure of H₂). The catalyst also shows high recyclability, and there is no decrease in the catalytic activity after five successive cycles. There exists a synergistic effect between the graphene support and the CoS₂ particles: conductive graphene as the support can rapidly extract the photoexcited electrons and effectively suppress the recombination of photogenerated charges in CoS₂ particles, and then improve the photocatalytic performance. The photocatalytic reduction of nitrobenzene over the CoS₂/graphene catalyst to aniline occurs through the direct pathways in the presence of H₂.

1. Introduction

Aniline and its derivatives are important chemicals and intermediates for the synthesis of pharmaceuticals, dyes, pigments, polyurethanes, and agricultural products.^{1,2} However, selective reduction of nitro group in the presence of other reducible groups is a challenge in organic synthesis, and undesirable by-products are often produced in the processes.^{3,4} The conventional processes for amine production include catalytic hydrogenation of nitroaromatics, reduction of nitroaromatics with iron and iron salts, and amination of phenol.⁵ The use of stoichiometric reducing agent, such as oxalic acid,⁶ NaSH,⁷ NaBH₄,⁸ BH₃NH₃^{9,10} and hydrazine monohydrate,¹¹ usually results in large amounts of toxic wastes. The molecule hydrogen is the cleanest and most environmentally friendly reducing agent and has been used as the hydrogen source in many reduction processes of nitrobenzene. For instance, Keane et al. found that Mo₂Csupported Au-Pd could efficiently catalyze reduction of nitrobenzene, p-chloronitrobenzene and p-nitrobenzonitrile to the target amine.¹² Serp et al. showed that Ru@C₆₀ catalyst exhibited high catalytic activity for the chemoselective hydrogenation of nitrobenzene with H₂.¹³ Nevertheless, using H₂ as the hydrogen source, the reactions are usually conducted under elevated temperature or high H₂ pressure, which not only increases the energy consumption, but also causes

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potential safety problems.¹⁴ From the viewpoint of sustainable development and green chemistry, it is highly essential to develop green catalytic routes for selective reaction of nitroaromatics with H_2 to the corresponding amines. Photocatalytic reduction of nitroaromatics is such a novel and promising process. However, the proposed photocatalysts are mainly noble-metal-based catalysts, such as Au,^{15,16} Ag^{17,18} and Pt,¹⁸⁻²⁰ which are always limited by their scarce resources and high cost.

As an important kind of the transition metal dichalcogenides, cobalt disulphide (CoS₂) has excellent electronic conductivity and thermal stability. Due to good photoinduction effect, CoS₂ show commendable photocatalytic particles also performances in degradation of organics. For example, Oh's group reported that CoS₂ particles and their composites, such as CoS₂/graphene, CoS₂-graphene/TiO₂, CoS₂-C₆₀/TiO₂, CoS₂-CNTs/TiO₂ etc., could catalyze the degradation of methylene blue and Texbrite BA-L under visible light irradiation.²¹⁻²⁴ Peng et al. found that CoS₂ and nitrogen-doped-carbon coated CoS₂ showed superior performance for photocatalytic degradation of methylene bule.²⁵ Although CoS₂ particles have been investigated in various fields, their photocatalytic selective hydrogenation performance has not been reported as far as we know.

Graphene, a 2D material of sp² bonded carbon atoms, presents high conductivity, superior electron mobility and high surface area, which can not only improve the photocatalytic performance of semiconductor, but also protect the supported particles from oxidation.²⁶⁻²⁸ Herein we report that graphene-supported CoS₂ particles, as a novel photocatalyst, can catalyse selectively hydrogenation of nitroaromatics to corresponding aromatic amines under visible light irradiation

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and mild conditions (30 °C and 0.25 MPa pressure of H_2). It is the first report for selective photocatalytic hydrogenation of nitroaromatics with H_2 as hydrogen sources under visible light. The composite catalyst shows excellent photocatalytic activity, selectivity and stability.

2. Experimental section

2.1 Catalyst preparation

The synthesis of CoS₂/graphene composite was carried out in a Teflon-lined stainless steel autoclave. Typically, 5 mmol of cobalt nitrate ($Co(NO_3)_2 \bullet 6H_2O$) and 50 mg of graphene (~500 m^{2}/g) were dispersed into 40 mL of distilled water, and the suspension was magnetically stirred to form a homogeneous mixture of cobalt nitrate and graphene. After stirring for 2 h, another 20 mL of aqueous solution containing 5 mmol of sodium hyposulfite (Na₂S₂O₃•5H₂O) and 500 mg of polyvinylpyrrolidone (PVP, K30) were added dropwise into the mixture while keeping stirring for another 0.5 h. In the subsequent step, the suspension was transferred into a 100 mL stainless steel autoclave, and maintained at 160 °C for 24 h. Finally, the autoclave was cooled to room temperature naturally. The precipitate was filtered off, washed with neat ethanol and distilled water respectively, and dried in a vacuum environment at 40 °C for 12 h.

For comparison, $10-CoS_2/G$, $20-CoS_2/G$, $30-CoS_2/G$ and $40-CoS_2/G$ were prepared by the similar procedure in the present of 10 mg, 20 mg, 30 mg and 40 mg graphene, respectively. Pure CoS_2 particles were prepared using the same method in the absence of graphene.

2.2 Catalyst characterization

The crystalline phases of composites were measured by X-ray diffractometer (XRD, Rigaku D-Max/RB). The transmission electron microscopy (HRTEM, JEM-2100F) at accelerating voltage of 200 kV was used to investigate microstructures of the catalysts. Scanning electron microscopy (SEM, JSM-5600, Jeol, Tokyo, Japan) was used to observe the morphology and structure. X-ray photoelectron spectroscopy (XPS) was measured by using Al Ka (hk=1486.6 eV) X-ray line on a Kratos XSAM800 spectrometer. UV-vis diffuse reflectance spectra were recorded on a UV-visible absorption spectra (UV-3600, Shimadzu) using Al₂O₃ as a reference at room temperature. The fluorescence spectrophotometer (F-700 FL 220-240 eV, Tokyo, Japan) was used to measure the photoluminescence (PL) spectra of samples, and the excitation wavelength was 280 nm.

The hydrogen temperature-programmed desorption (H₂-TPD) experiments were conducted by a commercial chemisorption analyser (TP-5080, Xianquan, China). In the H₂-TPD experiments, 100 mg of catalyst sample was pre-treated in N₂ flow (25 mL/min) at 573.15 K (5 K/min) for 2 h. After the pre-treatment, the temperature was naturally decreased to 303.15 K in N₂ flow (25 mL/min). Then 0.081 mL H₂/N₂ (~10% of H₂ in volume) was inducted to expose the catalyst sample for 1 min and the spectra of H₂ were recorded. The adsorption was repeated 10 times until the spectra of hydrogen were not changed. At last, the adsorption capacities of the catalyst samples were calculated by the spectra of H_2 .

2.3 Photocatalytic hydrogenation of nitroaromatics

The photocatalytic selective hydrogenation of nitroaromatics reactions were conducted in a 50 mL sealed stainless autoclave with a quartz window for light irradiation. A typical reaction process is described as follows: 1.0 mmol of nitroaromatics and 40 mg of CoS₂/graphene catalyst were dispersed in 10 ml of neat ethanol, and the suspension was then sealed in the autoclave under 0.25 MPa of H₂ with magnetically stirring. A 300 W Xe lamp was employed as the light source (light wavelength from 400 to 800 nm), and the light intensity was 0.45 W/cm². The reaction temperature was carefully controlled at 30 °C by the circulating cooling water for 1.5 hours unless otherwise specified. The dependence of the catalytic activity on the irradiation intensity (0.2-0.45 W/cm²) was investigated by adjusting the electric current of light source. A series of optical pass filters were used to adjust light source to obtain a specified wavelength range of irradiation while the same irradiation intensity was kept at 0.45 W/cm². For example, a 700 nm optical filter allows the light with a wavelength range from 700 to 800 nm to pass. After reaction, the products were collected and analysed by Gas chromatography mass spectroscopy (GC-MS, Bruker SCION SQ 456 GC-MS system, Karlsruhe, Germany).

As the reaction process was the pseudo-first-order kinetics with respect to the concentration of nitrobenzene, the rate constant (κ) could be calculated following the equation 1: $\kappa = \frac{1}{t} ln \frac{C_t}{C_o}$ (1)

where C_t and C_0 were the concentrations of nitrobenzene at the reaction time t and 0, respectively.

The contribution of different wavelengths was calculated as the following: contribution of light induced by different wavelengths (%) =[conversion of nitrobenzene at a specific wavelength range (%) \times selectivity (%)]/[conversion of nitrobenzene (%) without any filter \times selectivity (%) – conversion of nitrobenzene in dark (%) \times selectivity (%)].

3. Results and Discussion

3.1 Catalyst characterization

From the field-emission scanning electron microscopy (FESEM) image shown in Fig. 1A, CoS_2 particles show a subsphaeroidal morphology with a mean diameter of about 300 nm. The interplanar crystal spacing of the particles is 0.32 nm (inset of Fig. 1A), which matches well with the (111) plane of CoS_2 .²⁹ Fig. 1B shows a FESEM image of the CoS_2 /graphene composite. The subsphaeroidal CoS_2 particles with a mean size of about 300 nm are uniformly dispersed on the graphene sheets. Similarly, the lattice spacing of CoS_2 particles in the composite also corresponds to the CoS_2 (111) crystal face (inset of Fig. 1B), indicating that graphene does not change the crystal lattice of CoS_2 in the composite. The X- ray diffraction (XRD) patterns of CoS_2 particles and the CoS_2 /graphene composite are shown in Fig. 1C. The strong diffraction peaks are assigned to a cubic

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(A)

(C)



Fig. 1 FESEM images of CoS₂ (A) and CoS₂/graphene (B) catalysts, XRD patterns (C) and UV-vis diffuse reflection spectra (D) of CoS₂ and CoS₂/graphene catalysts; the inset pictures in A and B are the size distributions of CoS₂ particles and HRTEM images.

JCPDS No.89-1492

phase of CoS₂ with a space group of Pa-3 (JCPDS Card No. 89-1492). No characteristic diffraction peaks for graphene are observed in the XRD patterns of the $CoS_2/graphene$ composite. This could be due to the low amount (~7.5 wt. %) and the relatively low diffraction intensity of graphene.³⁰ The ultraviolet-visible (UV-vis) diffuse reflection spectra of CoS₂ particles and the CoS₂/graphene composite are shown in Fig. 1D. CoS₂ particles and the composite have strong absorption at about 300 nm, and in the range of 450-800 nm, indicating that both CoS₂ particles and CoS₂/graphene composite have good ability for UV and visible light absorption. According to literature, we speculate that the strong absorption around 300 nm may be associated with the charge-transfer from the valence band to the conduction band within CoS₂ samples.³¹ The absorption band in the range of 450-800 nm could be ascribed to the d-d transitions of Co(II) ions in CoS_2 catalysts, in which Co is in octahedral coordination.³² Comparing the two absorption spectra, it can be seen that the composite exhibits stronger UV and visible light absorption than the CoS₂ particles alone, suggesting that the light energy can be better exploited by the composite.

3.2 Photocatalytic performance

The catalytic performances of graphene, CoS_2 and $CoS_2/graphene$ for the hydrogenation of nitrobenzene were investigated, and the results are summarized in Table 1. The rate constants are calculated following equation 1 (Figure S1). From the table, it is clear that the hydrogenation reaction cannot occur under the given conditions without catalyst or using only graphene as the catalyst (entries 1 and 2, Table 1). When only CoS_2 particles are used as the catalyst, the conversion of nitrobenzene is 72% and the rate constant is

 Table 1
 Experimental results of photocatalytic hydrogenation of nitrobenzene under given reaction conditions.

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 13.75×10^{-3} min⁻¹ (entry 3, Table 1). However, the CoS2/graphene composite exhibits more excellent catalytic activity under the same conditions. The conversion of nitrobenzene exceeds 99%, and the rate constant as high as 35.50×10^{-3} min⁻¹ (entry 5, Table 1). Evidently, the catalytic activity of the composite catalyst is higher than that of lone CoS₂ particles. According to the thermodynamic parameters for the hydrogenation of nitrobenzene in the temperature range between 30 and 60 °C under irradiation,³³ the activation energies of photocatalytic hydrogenation of nitrobenzene over CoS₂ and CoS₂/graphene catalysts are calculated to be 74.4 and 48.6 kJ/mol respectively, based on Arrhenius equation (Figure S2).³⁴ The evident difference in the activation energy indicates that the photocatalytic reaction undergoes different potential energy surfaces.³⁵ Compared to some reports of nitrobenzene hydrogenation reactions which were conducted in the presence of hydrogen, it can be observed that CoS₂/graphene catalyst can efficiently drive the reaction to obtain a good aniline yield under milder conditions (Table S1). Employing water as the solvent, the activity of the composite catalyst decreases to 11.50×10^{-3} min⁻¹ (entry 7, Table 1). This decrease is possibly due to the low solubility of nitrobenzene in water or H₂O molecules occupying the catalytic active sites of CoS₂/graphene catalyst. When the reaction is conducted under an argon atmosphere, almost no nitrobenzene is converted (entry 8, Table 1), indicating that H₂ is the sole hydrogen source of the reaction. For comparison, the performance of CoS₂ and CoS₂/graphene catalysts in dark were also investigated. Under the same conditions, the activity are only 1.45×10^{-3} min⁻¹ (entry 4, Table 1) and 3.30×10^{-3} min⁻¹ (entry 6, Table 1), respectively, which is far lower than the reaction rate driven by light. Therefore, the irradiation of visible light plays the dominative role in the hydrogenation of nitrobenzene.

3.3 Effect of light intensity and wavelength

To further confirm the contribution of light irradiation to the catalyst activity, the reactions were conducted under different

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Fig. 2 Dependence of the catalytic performance of $CoS_2/graphene$ for nitrobenzene hydrogenation on the irradiation intensity (A) and irradiation wavelength (B).

light intensities. The reaction results are shown in Fig. 2A. It can be seen that the conversion of nitrobenzene grows linearly with the irradiation intensity. This indicates that the photocatalytic process is first order in photon and the reaction is dominated by a single photon adsorption.³⁶ Fig. 2B shows the light wavelength dependence of the photocatalytic activity. Without any filter, the light wavelength ranges from 400 to 800 nm, the conversion of nitrobenzene is 99%. When the irradiation is limited in a wavelength range of 450-800, 500-800, 550-800, 600-800, 650-800 and 700-800 nm, the conversion of nitrobenzene is 93%, 84%, 72.5%, 58.1%, 41.6% and 31.1%, respectively. By eliminating the contribution of heating, the contribution induced by 400-450 nm light is 7.9% ((99-93) / (99-23) × 100%). Similarly, the contribution of 450-500, 500-550, 550-600, 600-650, 650-700 and 700-800 nm light accounts for 11.8%, 15.1%, 18.9%, 21.7%, 13.8% and 10.7%, respectively. It indicates that the light in the 500-700 nm makes a major contribution to the photocatalytic hydrogenation, which is well in accord with the UV-vis diffuse reflection spectrum.

3.4 Selective hydrogenation of nitroaromatics

Aniline derivatives, such as p-chloroaniline, are important for

both industry and organic synthesis.37 Hence the high chemoselectivity of catalyst for the reduction of the nitro group is highly desirable. A series of nitroaromatics were employed to investigate the chemoselectivity of CoS₂/graphene catalyst in this category of hydrogenation reactions. From the results shown in Table 2, the yield of all target products is 99% except p-dinitrobenzene and o-nitro anisole. The reaction of p-dinitrobenzene takes longer reaction time than others because two nitro groups need to be hydrogenated (entry 1, Table 2). The activity of o-nitro anisole is slightly lower than others, possibly due to the strong sterically hindering effect between adjoining nitro and methoxy group (entry 8, Table 2). However, no matter electron-withdrawing (entries 1-5, Table 2) or electrondonating substitutes (entries 6-9, Table 2) in nitrobenzene, only nitro group could be reduced to the amino group under the giving condition. It can be explained that the chemoselectively of photocatalytic nitroaromatics reduction depends on the ability of nitro group and other functional group to accept photogenerated electrons.¹⁴ Obviously the nitro group is easier to be activated by photogenerated electrons than other reducible groups in this work.

3.5 Proposed mechanism

Under the irradiation of visible light, the electrons of CoS_2 are excited from its valence band (VB) to its conduction band (CB), and thus photogenerated holes are left at VB. When CoS_2 particles are supported on graphene, the conductive graphene

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Fig. 3 Photoluminescence spectra of CoS_2 (a) and $CoS_2/graphene$ (b) (excitation wavelength, 280 nm).

 Table 3. The adsorption capacities of hydrogen and photocatalytic performance of different catalysts for hydrogenation of nitrobenzene.

 \frown $CoS_2/graphene + H_2$

NH₂

Entry	Catalyst	H₂/µmol∙g⁻¹	Conv.(%)	Select.(%)
1	CoS ₂	71.10	72	100
2	10-CoS₂/G	93.03	77	100
3	20-CoS₂/G	124.52	81	100
4	30-CoS ₂ /G	163.85	88	100
5	40-CoS ₂ /G	204.39	93	100
6	CoS ₂ /graphene	241.69	99	100

sheets can rapidly extract photogenerated electrons from CoS₂ particles. As a result, the recombination of photogenerated electrons and holes is effectively suppressed, which can be proved by the obvious decrease of the photoluminescence intensity of the CoS₂/graphene composite compared with that of CoS_2 particles (Fig. 3).^{38,39} Besides, as a high surface area support, graphene offers more adsorption and catalytic reaction sites.^{28,30} For comparison, 10-CoS₂/G, 20-CoS₂/G, 30- CoS_2/G and 40-CoS_2/G were prepared by the similar procedure. The adsorption capacities of hydrogen on the catalysts were measured in a flow of H_2/N_2 (10% in volume) by H_2 -TPD experiments and the catalytic activities of catalysts with different content of graphene were tested under giving condition. As shown in Table 3, the H₂ adsorption capacities of the catalysts increase with the content of graphene in catalyst, which leads to the increase of the photocatalytic activity of hydrogenation.^{28,40} Besides, within a certain range, the higher content of graphene in catalyst is more effectively suppressed recombination of photogenerated electrons and holes, which can be certified by the photoluminescence (PL) spectra shown in Figure S3. In summary, graphene enhances the photocatalytic performance of the catalyst in two ways. Firstly,



Fig. 4 The conversion of nitrobenzene in the dark reaction and photocatalytic reaction with 0.6 mL of TEA.

graphene can rapidly transfer the photoexcited electrons and effectively suppress the charge recombination of CoS_2 particles. Secondly, as a high surface area support, graphene can offer more adsorption and catalytic reaction sites.

Since the photogenerated electrons in CoS₂ have been extracted to the graphene sheets, especially on the interface between CoS₂ and graphene, abundant holes are left in the CoS₂ particles. When 0.6 mL of triethanolamine (TEA), a hole scavenger, 41 was employed to trap the photoexcited holes of CoS₂, the conversion of nitrobenzene decreased sharply from 100% to 27% at a H₂ pressure of 0.25MPa. The value is almost same as that in the dark reaction. With increasing the H₂ pressure, the conversion of nitrobenzene shows a similar increase curve with that in the dark (Fig. 4). Similarly, the addition of 5,5-Dimethyl-1-pyrroline N-oxide (DMPO), an electron-trapping agent,⁴² also resulted in a decline of photocatalytic hydrogenation. And the reactivity of conversion of nitrobenzene decrease to 28% when the volume of DMPO increases to 0.9 mL (Figure S4). The above phenomena indicate that the light induced hydrogenation reaction is almost quenched in the absence of photoexcited electrons or holes. Based on the above results, it is proposed that the photoexcited holes on the surface of CoS₂ can activate H₂ molecules and produce active hydrogen species. Simultaneously, the N-O bonds in the nitrobenzene which adsorbed on the surface of catalyst are activated by the photogenerated electrons. Then the active hydrogen species migrate to activated nitrobenzene molecules and couple together to form the aniline and water.

Despite many reports on the reduction of nitrobenzene to aniline, the reaction mechanism has not been clearly understood. As early as 1898, Haber have proposed a mechanism for the reduction of nitrobenzene, including direct and indirect reaction pathway (Scheme S1), which is generally accepted so far.⁴³ According to the mechanism, nitrosobenzene and hydroxylamine are intermediates for the

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Entry	Reactant	Conv. (%)	Select. (%)
1		71	100
2	NO NO	87	100
3	Мнон	95	100
4 ^b		<mark>1</mark> 92	97
5		8	93
6		17	100

Table 4. Experimental results of photocatalytic hydrogenation of various intermediates under the given reaction conditions.^a

 a Reaction conditions: 40 mg of catalyst, 1.0 mmol reactant, 10 mL of ethanol at 30 °C, 0.25 MPa of H₂ with light intensity of 0.45 W/cm² for 1 h. b 0.5 mmol nitrosobenzene and 0.5 mmol hydroxylamine.



Fig. 5 The proposed nitrobenzene hydrogenation photocatalytic mechanism of CoS₂/graphene composite.

hydrogenation of nitrobenzene to aniline in the direct pathway, whereas nitrobenzene was firstly reduced to azoxybenzene and azobenzene in the indirect pathway.⁴⁴ In order to clarify the photocatalytic reaction path of nitrobenzene in the presence of H₂, nitrosobenzene, hydroxylamine, azoxybenzene and azobenzene are used as reactants in the giving reaction conditions.⁴⁵ When using nitrosobenzene or hydroxylamine as reactants, the conversions are higher than the conversion of nitrobenzene (79%) (entries 1-3, Table 4), and the selectively of aniline are 100%. However, when the mixture of nitrosobenzene and hydroxylamine are used as reactants, the conversion of reactant is 92%, and only a small quantity of azoxybenzene is detected (Selectively of 3%, entry 4, Table 4), indicating that it is hard to produce azoxybenzene in our catalytic system. Most importantly, azoxybenzene and



Fig. 6 Photocatalytic stability of CoS_2 and $CoS_2/graphene$ catalysts in five cycles.

azobenzene gave a lower yield of aniline than nitrobenzene (entries 5 and 6, Table 4). Therefore, it is suggested that aniline is produced in direct pathway in our work. On the basis of the results described above, a proposed photocatalytic mechanism of the hydrogenation of nitrobenzene on the $CoS_2/graphene$ catalyst is sketched in Fig. 5.

3.6 Stability

The stability and recyclability is one of the most important properties of heterogeneous catalysts. However, the main issue of non-noble-metal-based materials such as FeS₂ is instability in the successive reactions.⁴⁶ To investigate the recyclability of lone CoS₂ and CoS₂/graphene catalysts, the catalysts were tested for five rounds at the same reaction conditions. The experiment results in Fig. 6 show that there is no significant decrease in the catalytic activity of CoS₂/graphene after five successive reactions, suggesting that the CoS₂/graphene catalyst has excellent stability. However, a slight decrease in the activity of CoS₂ is observed. From the Xray photoelectron spectroscopy (XPS) profiles of used CoS₂ and CoS_2 /graphene, it can be seen that the intensity of the peak of SO_4^{2-} in CoS_2 catalyst significantly increases after five cycles (Figure S5A), indicating a part of S_2^{2-} have been oxidized to SO_4^{2-} , whereas no SO_4^{2-} was produced in CoS_2 /graphene (Figure S5B).⁴⁷ The oxidation of CoS₂ leads to the decrease in the catalyst activity. Comparing the stability of CoS₂ and CoS_2 /graphene catalysts, it is further proved that the graphene sheets can protect CoS₂ particles from oxidization. The FESEM analysis confirms that the morphology of CoS₂/graphene and CoS₂ particles in the used catalysts has no obvious change (Figure S6).

4. Conclusions

In summary, the present work shows that CoS_2 /graphene composite can efficiently photocatalyze the chemoselective hydrogenation of nitroaromatics into corresponding amines under mild conditions (30 °C and 0.25 MPa pressure of H₂) with excellent activity, high selectivity and good stability. Using H₂ as hydrogen source, the photocatalytic reduction of

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nitrobenzene to aniline on the present catalyst occurs through the direct pathway. And graphene plays an important role in stabilizing CoS_2 particles and improving the photocatalytic performance of CoS_2 /graphene catalyst. The catalytic system not only provides a low energy-consumption and environmentally friendly route for the synthesis of aromatic amines, but also enriches the strategies for the design of graphene-supported semiconductor systems for different photo-based applications.

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Graphene-supported CoS₂ Particles: an Efficient Photocatalyst for Selective Hydrogenation of Nitroaromatics in Visible Light

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 CoS_2 /graphene composites fabricated by a facile hydrothermal method show excellent photocatalytic performance for selective hydrogenation of nitroaromatics to corresponding aniline employing molecule hydrogen as reducing agent under visible light irradiation (400-800 nm). There exists a synergistic effect between the graphene support and the CoS_2 particles: conductive graphene as the support can rapidly extract the photoexcited electrons and effectively suppress the recombination of photogenerated charges in CoS_2 particles, and then improve the photocatalytic performance.