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Authors: Subhash Chandra Ghosh

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Visible-light-driven efficient photocatalytic reduction of organic azides to amine over CdS sheet-rGO nanocomposite

Krishnadipti Singha, Aniruddha Mondal, Subhash Chandra Ghosh* and Asit Baran Panda*

Abstract: CdS sheet-rGO nanocomposite as heterogeneous photocatalyst enables visible light induced photocatalytic-reduction of aromatic, heteroaromatic, aliphatic and sulfonyl azides to the corresponding amines using hydrazine hydrate as a reductant. The reaction shows excellent conversion and chemoselectivity towards the formation of the amine without self-photoactivated azo compounds. In the adopted strategy, CdS not only accelerate the formation of nitrene through photo-activation of azide but also enhance the decomposition of azide to a certain extent which entirely suppressed the azo compound formation. The developed catalyst CdS sheet-rGO nanocomposite is very active to provide excellent results under 40W simple household CFL lamp.

Introduction

Reduction of organic azide to the corresponding amine is one of the most important straightforward protocols for amine synthesis, owing to the easy accessibility of azides from respective halides, alcohols, and sulfonates and has potential industrial applications in organic chemistry, chemical biology as well as in chemical industry, e.g., synthesis of natural products and bioactive molecules.[1-3] A large number of synthetic protocols, using homogeneous sensitive reducing agents, have been developed for this reaction.[2] Although these developed protocols were ended with satisfactory results, however, most of them have several disadvantages concerning general applicability, cost, waste generation, safety, and most importantly chemo-selectivity and energy efficiency.[2] To overcome the drawbacks mentioned above, a heterogeneous catalyst using mild reducing agent was developed for this reaction.[3] Mainly, Ranu and co-workers utilized Cu(0) nanoparticle-$HCOONH_4$ system,[3a] and Pagoti et al.[3b] reported Fe_3O_4-N_2H_4 for azide to amine conversion. However, both the reaction needed higher reaction temperature (100-120°C) to complete the reaction. In addition to this, Cu(0) nanoparticle is not reusable.[3a] Thus, an efficient, simple heterogeneous catalyst system which can work at room temperature is highly desirable to make it energy efficient.

Recent years, development of efficient visible light driven photocatalytic chemical conversion, i.e., harvesting of solar energy to chemical energy, have been activated globally, as the solar energy is the only sustainable energy resource on earth and provides energy efficient greener routes. However, most of the organic molecules are photo transparent, and the photoactive molecules resulted in the undesired product.[4] Thus, a suitable light active catalyst is needed for desired photoinduced transformation. Most of the developed heterogeneous visible light active catalyst utilize precious metals [5] and till date, very few heterogeneous catalyzed photo induced organic transformations are known, such as alcohol to carbonyls/esters, nitro to amine, an amine to imine and hydrocarbon oxidation.[6] Thus, it is highly desirable to develop visible light active precious metal-free catalyst and exploration to photoinduced new organic transformations. Notably, the photo-induced selective transformation of azide to amine is challenging. Azides are photoactive and resulted in azo compounds through self-activation [4] and to the best of our knowledge; there is no such report on the photocatalytic reduction of organic azides to the corresponding amine.

CdS is an important visible light active, efficient semiconductor photocatalyst.[7] However; its photocatalytic activity is not satisfactory originating from tremendous photogenerated electron-hole recombination. The extent of recombination for 2D CdS nanosheets are quite low owing to their high surface area, quantum confinement and most importantly improved lifetime of photo-generated electron originating from transportation of electron through its long-range lattice periodicity.[8] Recently we have developed a simple procedure for the synthesis of ultrathin 2D sheet mediated CdS flower, which showed good photocatalytic activity.[9] In the recent past, CdS-reduced graphene oxide (rGO) nanocomposites have received tremendous attention as an efficient visible light active photocatalyst, owing to stabilization of photo-generated electron, due to shifting of an excited electron from CdS to conducting rGO.[10] Thus it is expected that the ultrathin CdS sheet-rGO nanocomposite would be the efficient photocatalyst, which has not been explored yet.

In continuation of our previous work on the development of visible light active potent photocatalyst for energy efficient green organic transformation,[9, 11] herein we report the selective reduction of organic azides to the corresponding amine at room temperature using ultrathin CdS sheet-rGO nanocomposite as photocatalyst and hydrazine hydrate ($N_2H_4 \cdot H_2O$) as hydrogen source under 40W simple household CFL lamp. Here it is essential to mention that we have used CFL lamp to make the procedure simple and acceptable, to avoid the required special

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K. Singha, A. Mondal, Dr. S. C. Ghosh, Dr. A. B. Panda
Central Salt and Marine Chemicals Research Institute (CSIR-CSMCRI) and CSMCRI-Academy of Scientific and Innovative Research (AcSIR)
G. B. Marg, Bhavnagar-364002, Gujarat,
India.
E-mail: scghosh@csmcri.org, abpanda@csmcri.res.in
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Results and discussion

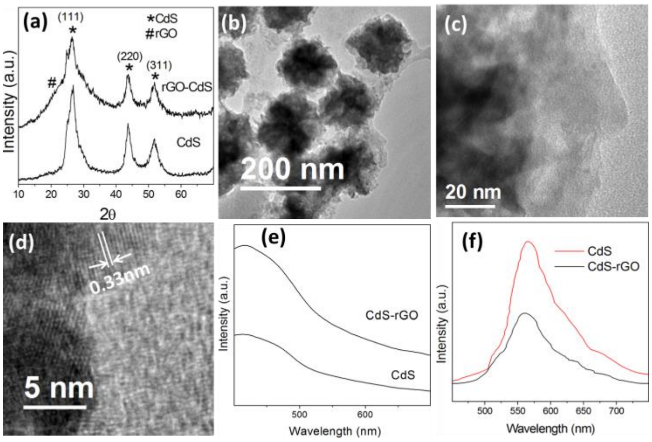

Fig. 1 (a) XRD pattern, (b-d) TEM and HR-TEM images, (e) UV-Vis. absorption spectra, and (f) PL spectra of the synthesized CdS sheet mediated flower and corresponding rGO composite (CdS-rGO).

precaution to manage enormous heat from commonly used high power Xe lamp for good activity. The developed catalyst synthetic strategy is based on the preparation of two separate colloidal suspensions of ultrathin (~0.8nm) sheet mediated CdS flower [9] in toluene, and DMF dispersed graphene oxide (GO). Then physical mixing of two suspended solutions followed ultra-sonication and addition of hydrazine hydrate to mixed suspension resulted in the precipitate of the desired composite. Addition of CdS sheet to GO, the CdS sheets were bound to the graphene surface through the interaction of a functional group of GO and Cd of CdS and then GO reduced to rGO by hydrazine.[12] (Experimental section, Supporting Information).

Figure 1a represents the XRD patterns of bare CdS flower and CdS flower /rGO composite. The X-ray diffraction peaks of bare CdS can be indexed to Zinc blend structure (cubic) of CdS (JCPDS File No. 01-75–1546). The CdS-rGO nanocomposite showed similar diffraction pattern to that of pristine CdS, except a hump in the 2θ range 20- 25°, indexed to rGO, indicate the successful incorporation of CdS in rGO moiety. TEM image of bare CdS confirmed that the synthesized CdS are a flower in shape, flowers are uniform, with a size of 100-125 nm and flowers are made of assembled ultra-thin sheets (Figure S1, Supporting Information). TEM image of corresponding CdS-rGO nanocomposite indicates the uniform distribution of CdS flower over graphene sheet (Figure 1b & Figure S2, Supporting Information). The magnified TEM image depicts the presence of two type of sheets, the dense sheets in inner part can be ascribed to the CdS, and lighter part in the outer side may be the rGO (Figure 1c & Figure S2, Supporting Information). As expected, HR-TEM image also showed the presence of two types of distinct fringes. The identifiable straight or cross fringes in inner side with an inter planner distance of 0.33 ± 0.05 nm, indexed to (111) plain of CdS ZB structure and random fringes in outer side ascribed to the rGO, the inherent characteristic of graphene sheet (Figure 1d & Figure S2, Supporting Information). Thus, TEM image confirms the formation of nanocomposite and revalidate the XRD result. AFM image of CdS-rGO nanocomposite also depicts the dispersion of nearly uniform spheres (~100 nm) over rGO surface (Figure S3, Supporting Information). In the FTIR spectrum of CdS-rGO nanocomposite, the C=C stretching at around 1650 cm^{-1} of pristine GO is shifted to 1580 cm^{-1}, ascribed to the interaction of aromatic ring π electrons with Cd of CdS. Also, the band intensity of all oxygen-containing functional groups of bare GO is reduced reasonably in nanocomposite (Figure S4, Supporting Information). The phenomena indicate the efficient reduction of GO by hydrogen and good interaction between CdS and rGO in the nanocomposite. Raman spectrum of CdS-rGO nanocomposite showed the presence of two intense peaks at 298 and 597 cm^{-1} ascribed to CdS, and two low intense peaks at 1354 and 1593 cm^{-1}, for D and G bands of GO (Figure S5, Supporting Information). The corresponding I_D/I_G ratios are 1.02 and 0.84 for rGO–CdS and bare GO. Enhancement of corresponding I_D/I_G ratios for CdS-rGO nanocomposite confirmed the reasonable reduction and retention of order structure of GO in the composite. Figure 1e illustrates the UV−Vis. absorption spectra of bare CdS and CdS/rGO composite. Bare CdS flower showed an unstructured spectrum with an absorption edge at ~407 nm. The obtained absorption edge is reasonably blue shifted compared to that of bulk CdS (490 nm, 2.5 eV), ascribed to the strong quantum confinement due to the ultra-thin sheet. Whereas, absorption spectra of CdS-rGO nanocomposite showed reasonably enhanced visible light absorption with identical absorption characteristic of CdS. Adsorption in the visible region can be ascribed to the absorption of rGO itself and further validate the composite formation. In corresponding PL spectra, reduction in PL peak intensity for CdS-rGO nanocomposite compared to that of PL of pristine CdS confirms the efficient interfacial charge transfer the junction of CdS and rGO (Figure 1f). Further, the photoluminescence lifetime experiment showed that the lifetime of rGO-CdS nanocomposite (0.6814 ns) is higher to that of bare CdS (0.4086 ns), and confirmed the reasonable enhancement in charge separation for CdS-rGO composites (Figure S6, Supporting Information). The PL observation confirms the CdS flowers formed an appropriate composite with rGO through strong electrostatic interaction.

Initially, reduction of o-azidonitrobenzene to o-nitroaniline was chosen as a model to check the catalytic efficiency of synthesized CdS sheet-rGO nanocomposite using hydrazine as a reducing agent under 40W simple household CFL lamp at room temperature. Amount of catalyst, hydrazine with a variation of solvent and time was varied to optimize the reaction condition (Table S1, Supporting Information). It was observed that the selective azide reaction in benzotrifluoride (BTF) solvent, with ten equivalent of hydrazine and 10 mg of catalyst for 0.25 mmol of the substrate provides the best result (100% selectivity, 95% isolated yield) after 4h of the selective azide reaction. Although the reaction proceeds quite satisfactory in toluene with 82% yield, but the reactivity in the tested other solvent, e.g., DMF, MeOH, and CH_3CN were unsatisfactory. Here it is essential to mention that till ten equivalent of hydrazine the reaction showed chemoselectivity and strictly the azide was reduced, but further increase in the amount of hydrazine to 15 equivalent the yield of nitroaniline was decreased drastically to 30%. The nitro group

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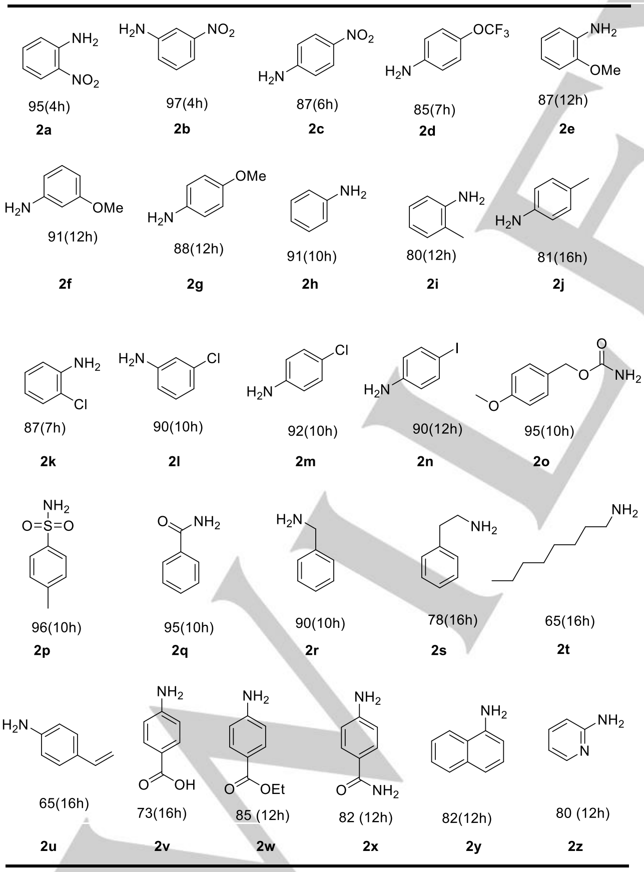
was started to reduce, and o-phenylenediamine became the major product (65%), which was further decreased gradually with enhancement of hydrazine amount and with 20 equivalent of hydrazine the yield of product 2-nitroaniline is reduced to 20%. From the result, it is evidenced that in the CdS-rGO nanocomposite/hydrazine system reduction of azide functionality is more facile to that of the nitro group, which required an enhanced amount of hydrazine.[3a] So, in a lesser amount of hydrazine, the azide group was reduced selectively.

As this methodology was found highly effective for selective photocatalytic reduction of o-azidonitrobenzene to o-nitroaniline, we extended the substrate scope to different aromatic azides, containing different functional groups to establish the chemo-selectivity, broad applicability of our developed catalyst and methodology. The results were summarized in (Table 1). To our delights, the reduction of azides took place very smoothly and selectively with excellent yield. However, depending upon the functional group present in the moiety reaction time differ. Similar to that of o-azidonitrobenzene, m- and p- azidonitrobenzene resulted in corresponding nitro aniline selectively with excellent yield (entries **2a-2c**, Table 1). Electron withdrawing trifluoromethoxy group at para to azide also worked very well (entry **2d**, Table 1). It was observed, that in the presence of the electron donating group, e.g. methyl and methoxy group, irrespective of the position in the aromatic ring, reaction needed longer time to complete and provided high to excellent yield (entries **2e- 2h**, Table 1). Chloro and iodo substituted azides also efficiently Reduced to the corresponding amine in high yields (entries **2k-2n**, Table 1). To our delight, other azides functionality like azidoformate, sulfonyl azide, benzoyl azide is also smoothly reduced to carbamate, sulphonamide amide respectively with excellent yield (entries **2o-2p**, Table 1). As expected, aliphatic azides also efficiently reduced to the corresponding amine in good to excellent yield (entries **2r-2t**, Table 1). 4-azido styrene is also efficiently reduced without affecting the double bond (entry **2u**, Table 1). Functional group like acid, ester, and amides are also well tolerated. Other aromatic and heteroaromatic azides especially 2-azido pyridines reduced to aminopyridines in good yields (entries **2Z**, Table 1). The obtained results for selective reduction of azide for different organic substance, which include aromatic azide, aliphatic, sulfonyl, and carbonyl azides, are comparable or sometimes better concerning the reported homogeneous and heterogeneous catalyst (Table S2, Supporting Information).

Table 1 Substrate scope of the chemoselective azide hydrogenation reaction.



Condition: 0.25 mmol substrate, 10 eq. Hydrazine hydrate, 10 mg CdS-rGO, 1.5 mL BTF and visible light irradiation using 40W CFL lamp.

To establish the necessity and superiority of CdS sheet-rGO nanocomposite, reduction of o-azidonitrobenzene to *o*-nitroaniline were performed using bare CdS sheet, CdS sphere, and corresponding rGO composite, bulk CdS and without catalyst (Table 2). It was observed that CdS sheet-rGO composite showed superior activity, particularly to that of rGO composite of 5nm CdS sphere. This is due to the horizontal dispersion of thin CdS sheet over rGO, as evidenced by TEM, which facilitate the maximum possible interaction and electron transportation through long-range lattice periodicity, in-turn charge separation, and showed enhanced activity. It is surprising to note that the all the azides resulted in an only single product of the corresponding amine after performed photocatalytic hydrogenation reaction.

Table 2. Variation of yield with catalyst

Entry	Catalyst(mg)	N2H4 (eqv.) [a]	Time	Yield [b]
1	CdSf [c]	0.15	4	73
2	CdSf-rGO	0.15	4	95
4	CdS(Bulk)	0.15	12	45
5	CdS sp [d]	0.15	6	69
6	CdS sp-rGO	0.15	6	84

[a] eqv.:Equivalent, [b] isolated yield, [c] CdSf: sheet mediated flower, [d] CdS sp: 5 nm spherical particle. Reaction condition: 2-azidonitrobenzene (0.25 mmol) , Catalyst (10 mg), hydrazine hydrate (10 eqv) , BTF (1.5 mL) in 40W CFL lamp.

Whereas the aromatic azides are very prone to photo-dissociate to corresponding reactive aryl nitrene, which subsequently dimerizes To azobenzene or rearrange to ketenimines, in the presence of amine, it produces 2-amino-3H-azepines (Scheme S1, entries **2r-2t**, Table 1).[6] Thus, the obtained results indicate that the self-transformation of nitrene was entirely suppressed by plenty of proton in the adopted experimental condition, which was subsequently resulted in the corresponding amine.

For further confirmation of the proposed mechanism and identify the origin of obtained 100% selectivity of the corresponding amine during performed photocatalytic

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hydrogenation of azide, we did some controlled reactions with p-nitroazide, a visible light active azide, in the absence of hydrazine or catalyst and both. keeping all other parameters identical (Scheme S2, Supporting Information). In the absence of hydrazine, the corresponding azo compound was found to be the only one product, which was 30% in the absence of a catalyst and 55% in the presence of a catalyst. This result indicates that the p-nitroazide was self-photo-activated under visible light and resulted in azo compound through nitrene intermediate with a very less conversion, but CdS accelerate the photoactivation, in-turn the conversion was increased. However, in the presence of hydrazine and absence of a catalyst, conversion of azide was 60%, with the 70% p-nitroaniline as the major product and 27% of the corresponding azo compound. Results indicate that hydrazine enhances the conversion of azide to a certain extent (60%) by shifting the reaction equilibrium through the formation of the corresponding amine. However, hydrazine alone cannot stop the azo compound formation. From the controlled reactions, it is evident that CdS not only accelerate the formation of nitrene through photo-activation of azide but also enhance the decomposition of azide to a certain extent which fully suppressed the azo compound formation.

Based on the experimental findings as mentioned above, a probable reaction mechanism is proposed for the effective photocatalytic reduction of azide to the corresponding amine. According to the proposed mechanism, at first, the catalyst CdS absorb energy (hν) from visible light, then the valence band electron transfers to its conduction band and generate a hole in the valence band. The electron in high energy state directly transforms to azide from CdS band or through rGO. After accepting the electron, the azide transformed to nitrene radical and liberated N_2. Simultaneously, the hydrazine was decomposed to N_2, proton (H+) and electron. Subsequently, the nitrene radical reacts with a proton from hydrazine and produced amine, whereas the electron was shifted to the photogenerated hole in VB of CdS (Figure 2, Scheme S3, Supporting Information). Thus, hydrazine plays a dual role in the performed reaction procedure; act as proton Source as well as a source of the electron, which diminished the possible photo-corrosion of CdS.

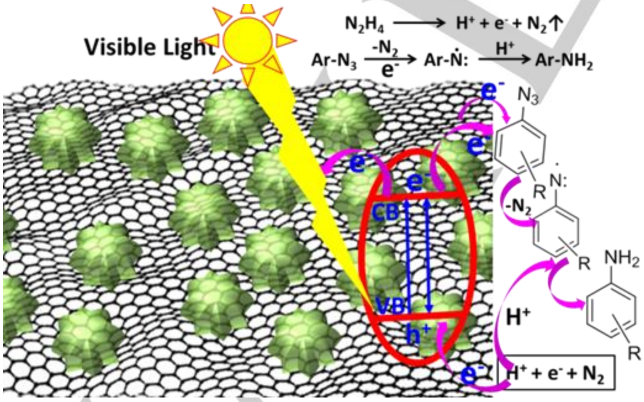

Fig. 2: A Probable proposed photocatalytic pathway for reduction of azide to the amine.

Re-usability of a heterogeneous catalyst is a vital parameter. The developed CdS sheet-rGO composite was reused consecutive four times, after separation from the reaction mixture and washing and no such substantial alteration in the catalytic efficiency were observed compared to that of the fresh catalyst (Figure S7, Supporting Information). There is a high probability of photocorrosion of the catalyst during the repeated reaction, which may cause the structural and morphological damage. So, we performed the XRD and TEM analysis of used CdS-rGO catalyst after the second cycle (Figure S8). No such distinct structural and morphological change is observed, and the issue of photocorrosion for adopted reaction procedure can be ruled out. Reduction of o-azidonitrobenzene in an identical reaction condition under dark the conversion was of negligible and confirmed that the performed reduction is strictly photocatalytic.

Conclusions

In summary, we have developed a simple visible light driven photocatalytic protocol for selective reduction of organic azides to corresponding amines using ultra-thin sheet mediated uniform CdS flowers-rGO nanocomposite and 40W CFL lamp as light source. The developed protocol showed excellent chemoselectivity and reduced azide group selectively in the presence of other functional groups such as nitro, carboxylic acid, ester, amide, ether, and halogen. The developed protocol is not only applicable for aromatic azide but also applicable aliphatic, sulfonyl, and carbonyl azides. The photocatalytic activity is comparable or sometimes better concerning the literature reported homogeneous as well as a heterogeneous catalyst. Finally, our catalyst is very active under 40W CFL lamp and can be utilized to develop a simple protocol of other organic transformations through visible light-induced photocatalytic reactions.

Experimental Section

Materials

Cadmium nitrate, 30% aqueous ammonium hydroxide solution were purchased from S. D. Fine Chemical, India. Decanoic acid ethyl xanthate and all the organic substrates were purchased from Sigma-Aldrich. All the chemicals were used without further purification. For all applications, water with a resistivity of 18 MΩ cm was used, obtained from a Millipore water purifier.

Synthesis.

Synthesis of CdS flower. The ultrathin sheet assembled CdS flower was synthesized following our previously reported method.[9] In a typical experiment procedure, in the 10 ml, aqueous solution with 0.5gm (1.88 mmol) cadmium nitrate 4ml 30% aqueous ammonium hydroxide solution was added dropwise to get a clear solution of cadmium ammonium complex solution. The prepared cadmium complex solution was added dropwise with constant stirring to a pre-prepared hot (~60°C) biphasic mixture of water (20ml) and decanoic acid (4g), which gave a transparent solution. A 10 ml aqueous ethyl xanthate (potassium salt, 0.32 g) solution was added to the resulted transparent changes to yellowish, but it remains transparent. 33 ml of the yellowish solution was transferred into a preheated (150°C) 50 ml Teflon-lined stainless autoclave for 2h with proper sealing, allowed to cool naturally and resultant yellow CdS flower was collected and washed with methanol for several times and dried in air. Monodispersed spherical CdS particles (5 nm) stabilized by decanoic acid has also been synthesized following our previously reported method (ESI).[11c]

Synthesis of the rGO-CdS nanocomposite. First CdS (0.5 mmol) was dispersed in toluene. Separately GO (5 weight %), synthesized following a typical modified Hummers method, was dispersed in DMF. Then dispersed solution of GO were added to CdS solution taking in a 500 mL beaker. The whole solution was stirred and sonicate for 12h. Then 1.5 mL hydrazine was added to this solution; again the whole solution was stirred for 2-3h. after that solution was centrifuged, collect solid catalyst, and the catalyst was dried in an oven at 60^{o}C for 12h.

Catalyst Characterization.
For evaluation of X-ray diffraction patterns of synthesized catalysts MINIFLEX-II (FD 41521) powder diffractometer was used. JEOL JEM 2100 transmission electronic microscope (TEM) was used for morphological and structural evaluation. Samples were prepared by mounting dichloromethane dispersed samples on lacey carbon formvar-coated Cu grids (300 mesh). The FT-IR spectroscopic measurements were carried out using a PerkinElmer GX spectrophotometer. The spectra were recorded in the range 400–4000cm^{-1} in KBr media. UV-Vis absorption spectra and photoluminescence spectra of toluene dispersed nanoparticles were recorded with a Shimadzu UV-2550 spectrophotometer and Fluorolog, Horiba Jobin Yvon fluorometer respectively.

General procedure for the selective reduction of azides to an amine using rGO-CdS.
Photocatalytic selective reduction of organic azides was performed in a 15 mL test tube under irradiation of 40 W visible light. In a typical process, a mixture of azide (0.25 mmol) in BTF (1.5 mL), rGO-CdS (10 mg) and hydrazine monohydrate (0.125 mL, 10 eq) was transferred into15 mL test tube and stirred for 10 minutes under N_2 atmosphere. Then the reaction mixture was irradiated by 40 W lamp for 4-16h, the reaction mixture was monitored by TLC. After the reaction, the mixture was centrifuged to remove the catalyst particle. The aqueous layer was extracted with ethyl acetate (3 x 10 mL). The combined organic extracts were washed with water and brine, dried over Na_2SO_4 and evaporated under reduced pressure. The crude product was purified by flash chromatography (EtOAc/hexanes eluent) to afford the desired pure amine. Most of the amines were analytically pure before flash chromatography. The recovered catalyst was washed with methanol (2 x 5 mL), dried under vacuum, and reused for the next cycle of the reaction.

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Keywords: Organic azide • Reduction• Photocatalysis • CdS • Visible light

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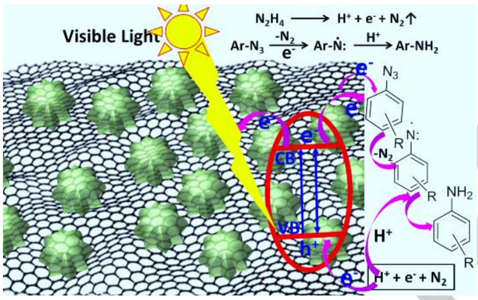
Entry for the Table of Contents

FULL PAPER

Visible light induced efficient photocatalytic reduction of aromatic, heteroaromatic, aliphatic and sulfonyl azides organic azides with corresponding amines using hydrazine hydrate as a reductant and CdS sheet-rGO nanocomposite as a heterogeneous catalyst. The developed catalyst is very active and provided excellent results under 40W simple household CFL lamp.



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Visible-light-driven efficient photocatalytic reduction of organic azides to amine over CdS sheet-rGO nanocomposite