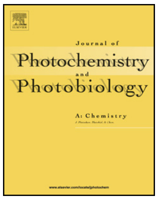
Journal of Photochemistry and Photobiology A: Chemistry 274 (2014) 7–12

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

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



Photocatalytic reduction of aromatic nitro compounds using CdS nanostructure under blue LED irradiation

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ARTICLE INFO

Article history:
Received 24 June 2013
Received in revised form
11 September 2013
Accepted 26 September 2013
Available online 8 October 2013

Keywords:
Photocatalysis
CdS nanostructure
Aromatic nitro compounds
LED irradiation

ABSTRACT

The aromatic nitro compounds reduced with a high selectivity to the corresponding amines under blue LED irradiation (3 W) using CdS nanostructure as photocatalyst. The reaction is relatively sensitive to the electron demands of the substituents. The nitro compounds with electron withdrawing groups (CN, COR, NO_2) give higher yields than with the electron donating groups (OMe, Me). In the nitro compounds with low activity, the high yields of corresponding amines were achieved by the addition of ammonium format. The CdS nanostructure showed excellent photocatalytic performance for the reduction of nitrobenzene compared with commercial CdS (Aldrich) under visible LED irradiation. The results demonstrated that CdS nanostructure have potential to provide a promising visible light driven photocatalyst for the selective reduction of nitro compounds to corresponding amines under mild conditions. The excellent reusability of the photocatalyst was examined for six runs.

1. Introduction

The selective reduction of aromatic nitro compounds to amines is one of the most important and fundamental transformations in organic synthesis, because the corresponding aromatic amines are widely utilized in the dyes, photographic, agricultural, and pharmaceutical industries [1]. Amines are often obtained by the catalytic hydrogenation of aromatic nitro compounds and many reducing agents have been applied for this transformation [2]. However, the selective reduction of the nitro group in the presence of other reducible functional groups in a molecule such as carbonyl, halide, cyano, and etc. is a challenging task. In addition, the reduction of aromatic nitro compounds often stops at an intermediate stage, producing hydroxylamines, hydrazines, and azoarenes as side products [3,4]. Due to the high importance of the selective reduction of aromatic nitro compounds, developing simple, green, and highly efficient methods is required [5].

Recently, photocatalysis as a promising and green technique has received increasing interest and provided an alternative to the conventional synthetic process [6]. The required mild conditions and the possibility to decrease the production of undesired substances highlight its potential as an efficient method for organic transformation [7]. Thus, considerable efforts are being paid to the photocatalytic selective reduction of nitro compounds. For instance, TiO_2 [8], N-doped TiO_2 [9] or dye-sensitized TiO_2 P25 [10,11], and $PbBiO_2X$ [12] under UV and visible light irradiation have been reported for the reduction of aromatic nitro compounds to corresponding amines.

In recent years, the search for the design of new visible-light-driven photocatalysts for organic transformation has significantly increased because of facile employment of sunlight due to its role in conservation of the global ecosystem [13]. In this regard, owing to the suitable band gap of CdS (2.4 eV) corresponding well with the spectrum of sunlight, the use of CdS is traditionally favored for many applications such as biological sensors [14], solar cells [15,16], field effect transistors (FET) [17,18], hydrogen evolution [19,20], and as photocatalyst in environmental purification [21]. In addition, the CdS has long been considered as a photocatalyst in organic transformations. For example, Yanigida et al. reported the photoreduction of aromatic ketones and olefins using CdS [22–24] and the first work on photocatalytic reduction of nitrobenzene to aniline using CdS was reported by Kuchmii et al. in 1989 [25]. More recently, CdS based graphene nanocomposite [26,27], commercial CdS [28] and synthesized CdS [29] applied as visible-light-driven photocatalysts for the selective reduction of limited nitro compounds under visible light irradiation. The disadvantage of pure CdS particles is the high recombination rate of photogenerated electron-hole pairs and susceptibility to agglomeration, restricting its wide application [19,30]. In order to solve

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http://dx.doi.org/10.1016/j.jphotochem.2013.09.011

these problems and enhance the photocatalytic activity of CdS particles, many approaches have been developed, including the preparation of quantum-sized CdS using various capping agents as the stabilizer [31] or combination with other components, including noble metals, semiconductors [32,33], and carbon materials [19,26,27,34]. Among different methods, aqueous synthesis of CdS using short chain thiols provides a useful alternative route to the preparation of CdS nanostructures. It is well known that characters of surface of nanoparticles such as excitation lifetimes, flat bond redox potentials, stability, solubility, and surface functionality can be influenced by end-chain substituents on chemisorbed thiols [35]. However, to our best knowledge, there has been little research investigating the reduction of nitro compounds using simply synthesized CdS nanostructure. This prompted us to undertake an investigation featuring the preparation of CdS nanostructure via a simple precipitation method using mercaptoethylamine hydrochloride (MEA) as a capping reagent [36]. MEA as an amine terminated thiol was selected with the expectation that the nanostructure surface would be positively charged at neutral pH and offer a strong binding interaction to the polar molecules [35]. The synthesized CdS was characterized by diffuse reflectance spectroscopy (DRS) technique, X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), TGA, and FTIR (see Supplementary Figs. S1–S5).

Recently, light emitting diodes (LEDs) with a low electrical power requirement in the visible spectra offer a promising replacement for conventional light sources in many applications [37–39]. Using LED lamps as a light source are associated with several advantages such as high photon efficiency, low voltage electrical power source, power stability, emission in broader spectral wavelength, and no need for cooling during long time operation for complete photocatalytic reactions [39]. Synthesized sample was utilized for the selective photoreduction of a wide range of aromatic nitro compounds to their corresponding amines under blue LED (3 W) lamp irradiation under very simple and mild experimental condition. The results demonstrated that the CdS nanostructure can be utilized as an efficient visible light driven photocatalyst for the selective reduction of aromatic nitro compounds to corresponding amines. The high photo activity of prepared sample attributed to the effect of MEA on CdS size reduction and its significant influence on the surface functionality and stability of CdS nanophotocatalyst during recycled experiments.

2. Experimental

2.1. Materials

Nitro compounds, sodium sulfide (Na_2S), and ammonium formate (HCO_2NH_4) were purchased from Merck Co. Cadmium acetate dehydrate Cd $(OAc)_2 \cdot 2H_2O$, mercaptoethylamine hydrochloride (MEA), and commercial CdS were supplied by Aldrich Co. Isopropanol was purchased from J.T. Baker Co. All other chemicals were used as received without further purification. Deionized water was used in all experiments.

2.2. Preparation of CdS nanostructures

To synthesize CdS nanostructure, aqueous solutions of cadmium acetate and sodium sulfide (0.1 M) were prepared by dissolving the respective salts in deionized water. 10 ml aqueous solution of mercaptoethylamine hydrochloride (MEA) as a capping reagent, containing 2 g MEA, was prepared and added to the 20 ml of cadmium acetate solution at room temperature. The resulting solution was stirred for 10 min, and then 20 ml of freshly prepared Na_2S solution was added dropwise to the mixture in 15 min under stirring. This mixture was stirred at room temperature for 45 min. During the reaction, the color of mixture gradually turned to pale yellow. After 1 h stirring, the precipitates were centrifuged and rinsed with deionized water several times, then dried in a desiccator for 48 h. Deionized water used for the preparation of CdS, was boiled and sparged continuously with argon while cooling to room temperature.

2.3. Photocatalytic activity

The photocatalytic reduction of nitro compounds to their corresponding amines was performed using CdS nanopowder under visible blue LED irradiation. Typically, 20 mg of the photocatalyst was added to the 5 ml of 1×10^{-2} M nitrocompounds solution in isopropanol. After that, the mixture was sunicated for 5 min to obtain a homogeneous dispersion of CdS nanostructure in *i*-PrOH, then purged argon (5 min) and then the vial was sealed up with a rubber stopper. The mixture was stirred magnetically during reaction (20 h) and illuminated with a visible blue LED (3 W) irradiation. After the reaction, for removing the photocatalyst particles completely, the mixture was centrifuged, and the remaining solution was analyzed with thin layer chromatography (TLC), and by Varian gas chromatograph (CP-3800). Conversion of nitro, yield of amine, and selectivity for amine were defined as follows:

$$\text{conversion}\quad(\%) = \left[\frac{(C_0 - C_{\text{nitro}})}{C_0}\right] \times 100$$

$$\text{yield}\quad(\%) = \frac{C_{\text{amine}}}{C_0} \times 100$$

$$\text{selectivity}\quad(\%) = \left[\frac{C_{\text{amine}}}{(C_0 - C_{\text{nitro}})}\right] \times 100$$

where C_0 is the initial concentration of nitro compound and C_{nitro} and C_{amine} are the concentration of the substrate nitro and the corresponding amine respectively, after the photocatalytic reaction.

3. Result and discussion

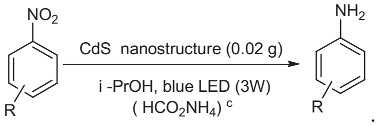
Since nanoparticles size directly affects exciton energies and electron–hole redox properties, it is important to well control the size of these photocatalytic nanoparticles. Also, the decrease in particles size to nanometer scale of CdS increases surface to volume ratio leading to an enhancement of the electron and holes surface access thereby enhances their photocatalytic activity for efficient oxidation and reduction processes respect to bulk material. Although several different methods have been developed to obtain nanostructures, convenient precipitation method was adopted to the synthesis of CdS nanostructures under mild conditions. MEA was used as a capping reagent and surface stabilizing ligand. Use of the MEA caused polar surface and enhanced the adsorption of compounds in the surface of photocatalyst. Moreover, CdS Q-dots synthesized by MEA derivatives as stabilizer reagent utilized as photocatalyst for the reduction of aryl azides to the corresponding arylamines in homogeneous solution [35]. However, using heterogeneous CdS photocatalyst allows much easier separation of the photocatalyst during product isolation. To evaluate the photocatalytic activity of the prepared nanostructure, reduction of nitro compound was performed under the blue LED ($\lambda \geq 420$ nm) irradiation. The photocatalytic activity of the prepared CdS nanostructure is initially examined by reduction of nitrobenzene to aniline under blue LED (3 W) irradiation. In order to determine the optimal experimental conditions, first the impact of solvents EtOH and *i*-PrOH was examined; it was found that reaction in

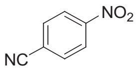
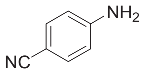
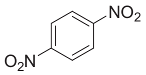
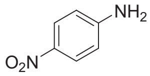
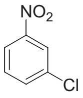
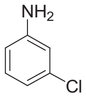
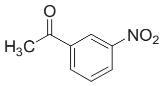
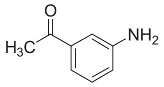
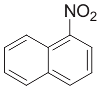
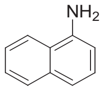
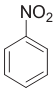
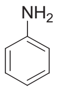
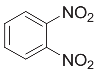
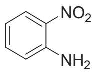
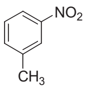
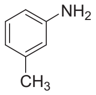
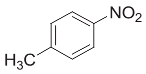
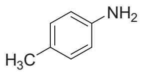
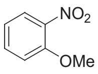
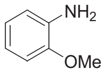
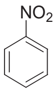
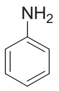
Table 1
Optimization of the photocatalytic reduction condition of nitro benzene with CdS nanostructure under blue LED (3 W) irradiation and argon atmosphere, irradiation time: 20 h.

Entry	Nitrobenzene (M)	Solvent	CdS (mg)	Aniline (%)[a]	Conversion (%)[a]	Selectivity (%)
1	0.01	EtOH	20	14	33	42
2	0.01	*i*-PrOH	40	52	90	57
3	0.01	*i*-PrOH	20	55	77	71
4	0.01	*i*-PrOH	10	25	50	50
5	0.001	*i*-PrOH	20	48	80	60
6[b]	0.01	*i*-PrOH	100	0	0	0
7	0.01	*i*-PrOH	0	0	0	0
8[c]	0.01	*i*-PrOH	20	0	0	0

[a] Determined by gas chromatography.
[b] In the dark.
[c] Under air atmosphere.

Table 2
Photocatalytic reduction of nitrobenzene derivatives to corresponding amines via CdS nanostructure.[a]



Entry	Starting material	Product (%)	Yield (%)[b,c]	Conversion (%)[b,c]	Selectivity (%)[c]
1			90	100	90
2			97	100	97
3			90	100	90
4			98	100	98
5			80	80	100
6			55 (97)	77 (100)	71 (97)
7			50 (100)	50 (100)	100 (100)
8			47 (100)	64 (100)	73 (100)
9			40 (100)	86 (100)	46 (100)
10			40 (100)	47 (100)	85 (100)
11[d]			19 (23)	21 (25)	90 (92)

[a] Photocatalyst, 20 mg; nitro compound alcoholic solution (1×10^{-2} M), 5 ml; irradiation with blue LED (3 W), 80 Lumen; irradiation time, 20 h.
[b] Determined by gas chromatography.
[c] Numbers in parentheses represent results in the presence of 50 mg of the HCO_2NH_4.
[d] In the presence of commercial CdS (Aldrich).

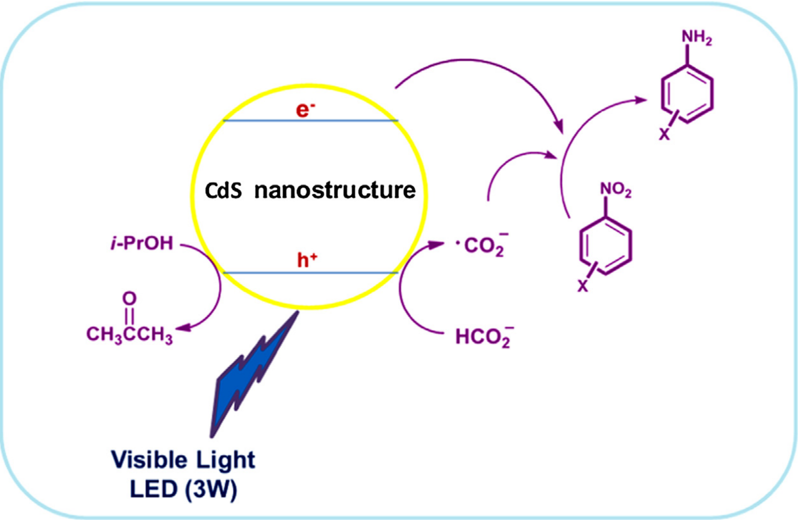


Fig. 1. Photocatalytic reduction of nitro compounds in the presence of HCO_2NH_4.

i-PrOH gives better results in term of product yields and selectivity to amine (Table 1, entry 3).

Notably, by increasing the amount of the CdS photocatalyst more than 20 mg, the nitrobenzene conversion increased, while aniline selectivity decreased. On the basis of these results, the 20 mg was chosen as optimum amount of CdS photocatalyst (Table 1, entry 3). The reduction of nitrobenzene in low concentration caused a high conversion but selectivity is lower than concentration 1×10^{-2} M (Table 1, entry 5). To ensure that CdS powder and light together are required for reduction, several control experiments were carried out. The obtained results indicate that the reduction of nitro compounds to amines is attributed to the photocatalytic activity of the CdS nanophtocatalyst (Table 1, entries 6, 7). In addition, photocatalytic activity was observed only in argon atmosphere (Table 1, entry 8). To demonstrate the general applicability of the CdS nanopowder for the reduction of aromatic nitro compounds and the scope of the process, various aromatic nitro compounds were investigated.

As shown in Table 2, the photocatalytic reduction of various aromatic nitro compounds including electron-rich and electron-deficient substrates proceeded readily at simple experimental condition to afford well to excellent yields of the corresponding amines (Table 2). Chemical yields depend strongly on the electron withdrawing or electron donating nature of the functional groups in the aromatic rings. For example, nitro compound with electron withdrawing groups (CN, NO_2, COR) have higher conversion and more selectivity than those with electron donating substituents (Me, OMe). During photocatalytic reduction of the nitro compounds, the cyano and carbonyl functionalities present in the aromatic ring remained unaffected (Table 2, entries 1, 4). Also, it can be seen that 3-chloronitrobenzene was reduced to the corresponding aniline in excellent yield without any dehalogenation which was often encountered with procedures such as hydrogenation (Table 2, entry 3).

It is interesting that using HCO_2NH_4 significantly enhanced the reduction of nitro compounds with low activity (Table 2, entries 6–10). Generally, HCO_2NH_4 used as a hole scavenger for the reduction of organic compounds [26–28,35]. In the presence of HCO_2NH_4 and absence of CdS, in a blank experiment, irradiation of an alcoholic solution of nitrobenzene led no reduction product, indicating that CdS is essential for the reduction of nitro compound. On the other hand, without irradiation under blue LED, no amine was detected too.

Indeed, HCO_2NH_4 can be oxidized by the photoexcited holes of the CdS photocatalyst, resulting in the formation of $^{\bullet}CO_2^{-}$ radicals [28]. It has been reported that $^{\bullet}CO_2^{-}$ radicals have strong reductive powers [$E^0(CO_2/^{\bullet}CO_2^{-}) = -1.9$ V vs NHE] [40] and are able to reduce nitro compounds. Therefore, nitro compounds might be reduced to corresponding amines by both photoinduced electrons from the conduction bond of the light activated CdS and $^{\bullet}CO_2^{-}$ in the experimental condition (Fig. 1). This can explain why the synthesized CdS photocatalyst shows excellent photocatalytic activity for the reduction of nitro compounds to corresponding amines in the presence of HCO_2NH_4 under visible LED irradiation.

The photoactivity of CdS nanostructure in the photoreduction of nitrobenzene was compared to that of commercial CdS (Aldrich) under identical conditions (with and without the addition of HCO_2NH_4). It was observed that the synthesized CdS nanostructure is more efficient than commercial CdS (Aldrich) (Table 2, entries 6, 11). A time course study of the photoreduction of 1,2-di-nitrobenzene to corresponding aniline with CdS nanostructure showed an increase in the rate of aniline formation from beginning of irradiation with blue LED lamp (Fig. 2.). This study indicates that no catalyst activation occurred during photocatalytic process as reported in the photoreductions of nitrobenzenes to anilines via dye-sensitized TiO_2 and metal salts [12].

The recyclability of CdS photocatalyst was also examined by the photocatalytic reduction of 3-nitroacetophenone as a test model.

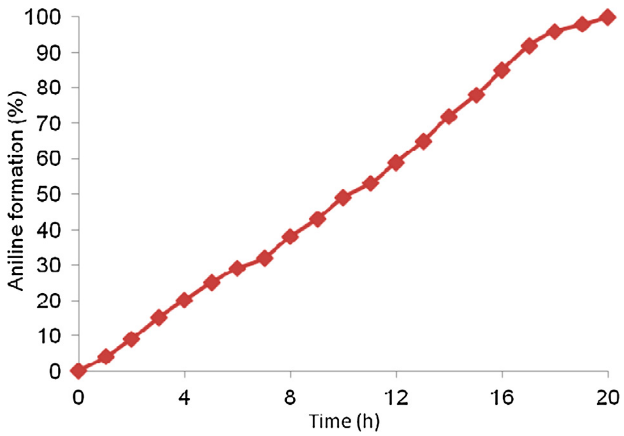


Fig. 2. Time course study of the reduction of 1,2-di-nitrobenzene to corresponding aniline via CdS nanostructure.

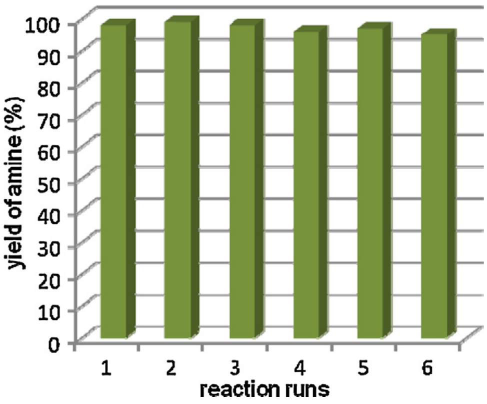


Fig. 3. Representation of 3-amino acetophenone yields at different reuses of the photocatalyst.

After the first use of CdS nanostructure in the photoreduction, the photocatalyst was isolated by centrifuge, washed thoroughly with EtOH or *i*-PrOH, and then dried in a desiccator at room temperature. The recycled catalyst showed excellent efficiency in 6 subsequent reaction runs (Fig. 3).

The photocorrosion is often a problem to prevent use of CdS photocatalyst ($CdS + h^+ \rightarrow Cd^{2+} + S$) [28]. The amount of Cd^{2+} is determined by atomic absorption spectroscopy (AAS) (less than the detection limit of 1 ppm), demonstrating that the photocorrosion of CdS nanostructure was negligible. In addition, the XRD analysis of CdS photocatalyst after the photoreduction was used for the investigation of the stability of CdS that clearly showed no change in the crystal structure under the experimental condition (Fig. 4). The XRD patterns of the catalyst can be well indexed to cubic zinc blend CdS (JCPDS card no. 80-0019).

The high efficiency of CdS nanostructure as a photocatalyst is attributed to large driving force for electron transfer from CdS nanostructure to nitro compounds. The reduction potential of aromatic nitro compounds has been reported between −0.59 and −0.25 V vs NHE [41] and much negative potential of excited CdS nanostructure (CB: −0.75 V vs NHE) [42] clearly recognized the thermodynamic aspect of electrons realizing from CdS conduction bond to the aromatic nitro compounds. In addition, using thiols as a capping agent is a proper way for passive surface dangling bonds and retarding recombination of photogenerated electron–hole pairs. It also provides stability and surface functionality of CdS nanostructure [43].

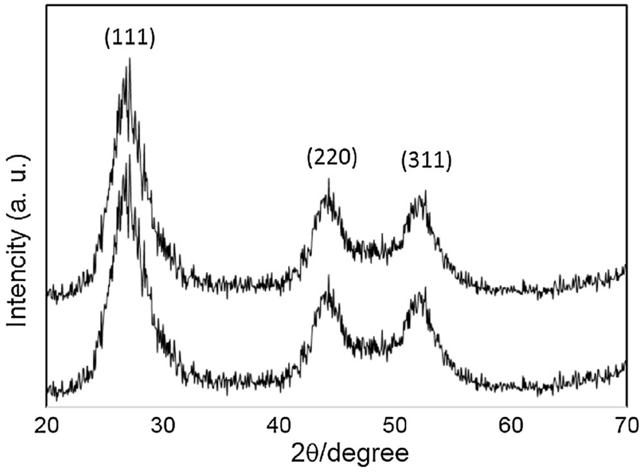


Fig. 4. X-ray powder diffraction patterns of CdS nanostructure before (upper) and after catalysis (lower).

4. Conclusions

It is evident that the CdS nanostructure prepared by MEA as a capping agent is an effective and reusable heterogeneous photocatalyst for the photoreduction of aromatic nitro compounds to their corresponding amines under blue LED (3 W) lamp irradiation. As synthesized CdS photocatalyst is capable of reducing a wide scope of nitro compounds, the efficient reduction of nitro compounds with low activity was also achieved by the addition of HCO_2NH_4. The reducible functionalities such as carbonyl and cyano groups remained intact under the reaction condition. The excellent reusability for six runs shows the good stability of synthesized sample. The time course study indicates that no catalyst activation occurred during photocatalytic process. In comparison with commercial CdS (Aldrich), the prepared CdS nanostructure shows superior photocatalytic activity. The high photoactivity of the CdS nanostructure under visible light irradiation can be attributed to the synergy effect of its high surface area, high photostability, and surface functionality.

Acknowledgment

The authors gratefully acknowledge the support provided by the Institute for Advanced Studies in Basic Sciences (IASBS).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jphotochem.2013.09.011.

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