DE GRUYTER

Chemical Papers
DOI: 10.1515/chempap-2015-0231

ORIGINAL PAPER

Photocatalytic reduction of nitro aromatic compounds to amines using a nanosized highly active CdS photocatalyst under sunlight and blue LED irradiation

[a]Ali Asghar Safari, [a,b]Foad Kazemi*

[a]*Department of Chemistry,* [b]*Center for Climate and Global Warming (CCGW), Institute for Advanced Studies in Basic Sciences (IASBS), Gava Zang, Zanjan, 45137-66731, Iran*

Received 28 January 2015; Revised 12 August 2015; Accepted 22 August 2015

A variety of aromatic nitro compounds were chemoselectively reduced to the corresponding anilines using conveniently prepared nanosized CdS as a photocatalyst under the sunlight and blue LED irradiation. The results demonstrated that synthesized CdS nanostructures have the potential to provide a promising visible light driven photocatalyst for chemoselective reduction of nitro aromatics in the presence of nitrile and carbonyl groups to the corresponding amines under both sunlight and blue LED irradiation. Photoreduction of nitro aromatics by the prepared nanosized CdS with high surface area was faster than when using the commercially available CdS under both sunlight and LED irradiation. Nanosized CdS photocatalyst was prepared by a simple method without any capping agent. X-ray diffraction (XRD), energy dispersive spectrometry (EDAX), transmission electron microscopy (TEM), scanning electron microscopy (SEM), N_2 absorption–desorption, diffuse reflectance spectroscopy (DRS), and flat band potential methods were employed for the characterization, which revealed that the prepared CdS nanoparticles have a well-resolved cubic structure with the size of around 10–30 nm and a band gap of 2.37 eV.

Keywords: photoreduction, nanosized CdS, aromatic nitro compounds, LED, sunlight

Introduction

Synthesis of organic compounds via heterogeneous photocatalysis using semiconductor materials is an unconventional technology and an attractive field for many scientists (Abedi et al., 2013; Herrmann, 2005; Kakroudi et al., 2014; Ohtani et al., 2003; Wang et al., 2013). Recently, design and synthesis of new visible light-driven photocatalysts for organic transformations have attracted the attention of researchers because of their uncomplicated application, low costs and favorable environmental aspects of sunlight and visible light (Ananthakrishnan & Gazi, 2012; Prier et al., 2013).

Yet, the stringent UV light limitations in semiconductors caused by the wide band gap such as in TiO_2 motivate the researchers to find new reaction routes under visible light irradiation (In et al., 2011; Schultz & Yoon, 2014). In this connection, CdS with a suitable band gap (2.4 eV) corresponding well with the spectrum of sunlight has been studied for many photocatalytic applications such as sensors (Wang et al., 2003), solar cells (Britt & Ferekides, 1993; Chun et al., 2011), hydrogen evolution (Bao et al., 2008; Li et al., 2011), and pollutants decontamination (Veréb et al., 2012).

Aromatic amines are important key intermediates in the production of dyes, antioxidants, pharmaceutics, and agricultural chemicals which can be obtained by the reduction of aromatic nitro compounds (Kumar et al., 2001). Applications of heterogeneous photocatalysis for chemoselective reduction of nitro aromatic compounds to the corresponding amines have also been studied using a variety of semiconductors

*Corresponding author, e-mail: kazemi f@iasbs.ac.ir and modified semiconductors such as: TiO_2 (P-25 and rutile) (Flores et al., 2007; Imamura et al., 2011; Kaur & Pal, 2014), N-doped TiO_2 (Wang et al., 2009) or dye-sensitized TiO_2-P25 (Füldner et al., 2010, 2011), TiO_2 co-catalyst (Hakki et al., 2009), Ru(II) complex immobilized ZnO hybrid in the presence of a Pt(II) co-catalyst (Bhar & Ananthakrishnan, 2015), and ZnS nanostructures (Pal & Pal, 2015). Low band gap, which leads to fast recombination of photogenerated electron–hole pairs, is the main limitation of the commercial CdS particles and limits their application in semiconductor photocatalysis (Li et al., 2011; Sheeney-Haj-Ichia et al., 2005). Employing the nanosized CdS is one of the approaches developed in order to widen the CdS band gap and avoid the fast recombination of electron–hole pairs (Eskandari et al., 2013).

Very recently, chemoselective photocatalytic reduction of nitroaromatics by various nanostructured photocatalysts under visible blue LED irradiation has been reported (Eskandari et al., 2014; Kakroudi et al., 2014; Zand et al., 2014). In continuation of our studies, considering the great importance of visible light applications in photocatalytic reactions as a green method, chemoselective reduction of nitro aromatics to the corresponding amines was also investigated using a simply prepared nanosized CdS (CdS-NP) photocatalyst in propan-2-ol as an appropriate solvent under the sunlight and blue LED irradiation. Photocatalytic activity of the catalyst was compared with that of commercial Aldrich CdS (CdS-Ald) as a typically available photocatalyst.

Experimental

All solvents, sodium sulfide (Na_2S), nitro compounds, and cadmium sulfate ($CdSO_4 \cdot 8/3H_2O$) were purchased from Merck (Germany). Cadmium sulfide (CdS-Ald) was supplied by Sigma–Aldrich (UK). All other chemicals were used as received without further purification.

CdS nanoparticles were prepared according to literature (Hopfner et al., 2002) and were characterized in detail by TEM, porosimetry, powder XRD, diffuse reflectance spectra (DRS), and EDAX elemental analysis. Band edge positions of both CdSs were estimated by measuring the photovoltage as a function of the suspension pH according to the reports of Roy et al. (1995) and White and Bard (1985). The surface area and pore volume of the photocatalysts were determined from the nitrogen adsorption–desorption isotherm by the BET and BJH methods, respectively.

As optimized reaction conditions, a solution of nitroaromatic compounds (0.01 M) in an appropriate solvent and 20 mg of CdS-NP were sonicated and slowly purged with N_2 for 5 min. Then, the reaction vessel was sealed up with a rubber stopper and the mixture was stirred magnetically and irradiated with blue LED (4×1 W, $\lambda \geq 420$ nm, intensity: 80 lumen) or sunlight (of daily ambient temperature and sunlight intensity range of 80–100 × 10^3 lux).

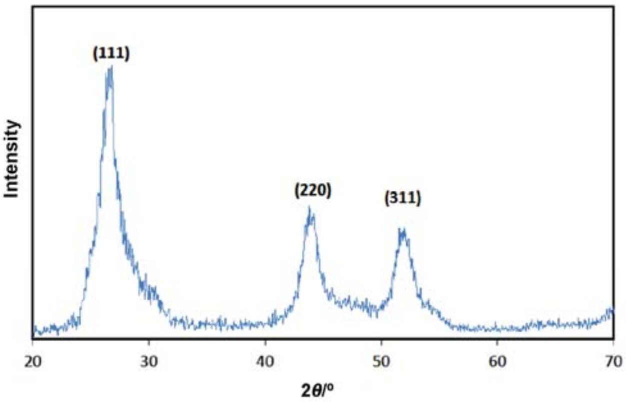


Fig. 1. X-ray powder diffraction patterns of CdS-NP.

The reaction conversion was monitored by thin layer chromatography (TLC). After completing the reaction, the mixture was centrifuged and supernatant was removed and analyzed on a GC Alient gas chromatograph (Nonpolar CP-Sil 8 column (30 m × 0.32 mm), Varian Chrompack (Middelburg, The Netherlands).

Results and discussion

In continuation of our previous studies on the enhancement of the nitroaromatics photocatalytic reduction yield using CdS based photocatalysts, highly photoactive CdS nanoparticles prepared according to literature (Hopfner et al., 2002).

Nanosized CdS was synthesized using the very easy method and was able to effectively reduce high concentrations of nitroaromatic compounds (0.01 M) via blue LED and sunlight irradiation in the absence of any additives (ammonim formate, oxalates, . . .) in short reaction times compared with other reported CdS based photocatalysts at the same reaction conditions (Eskandari et al., 2013, 2014).

XRD pattern of the prepared CdS nanoparticles is shown in Fig. 1. According to the main diffraction peaks it can be well matched with a standard cubic zinc blend structure (JCPDS card no. 80-0019).

SEM and TEM images indicated inhomogeneous dispersion of the prepared CdS nanoparticles within the diameter range of 10–30 nm (Fig. 2). According to the TEM image, CdS-Ald (commercial CdS) is agglomerated to the size of more than 100 nm (Fig. 2).

EDAX measurements of the nanoparticles indicated the presence of both cadmium and sulfur elements in a roughly 1 : 1 mole ratio. In order to determine the band gap energy of CdS-Ald and the prepared CdS-NP, the modified Kubelka–Munk function $[F(R_\infty)hv]^2$ was plotted vs. the incident photon en-

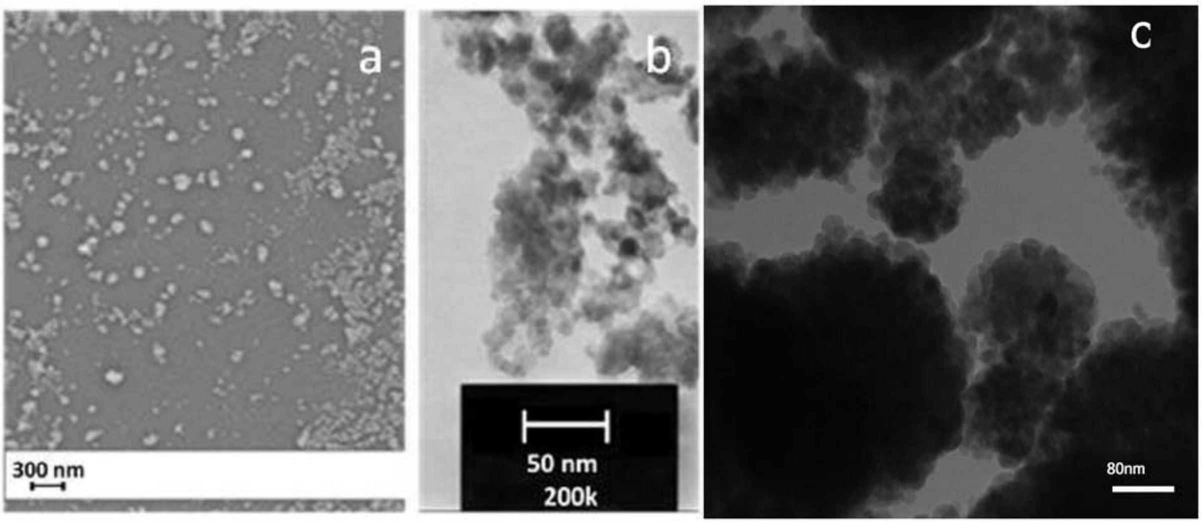


Fig. 2. SEM (a) and TEM (b) image of prepared CdS, and TEM image of CdS-Ald (c).

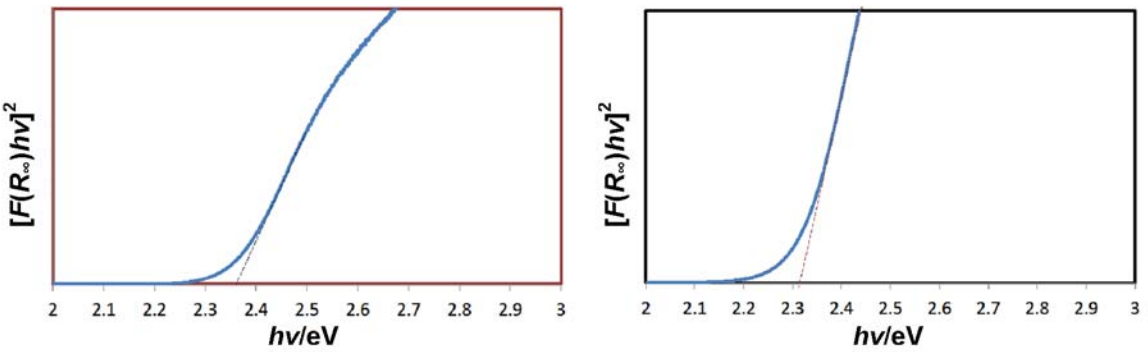


Fig. 3. Diffuse reflectance spectra of CdS-NP (a) and CdS-Ald (b).

ergy considering diffuse reflectance spectroscopic analysis data (Fig. 3, Table 1). As shown in Table 1, band gap energy of commercial CdS-Ald is 2.31 eV whereas that of the prepared CdS-NP was by 0.06 eV higher (2.37 eV) due to the quantum size effect (Eskandari et al., 2014).

Band edge positions of both prepared and commercial CdSs were obtained by measuring the photovoltage as a function of suspension pH according to literature (Table 1) (Roy et al., 1995; White & Bard, 1985). The band edge positions were determined as –0.38 and –0.42 for CdS-NP and CdS-Ald, respectively (Table 1). Since the flat band potential could be measured only in aqueous suspension, it was approximately estimated that the value in propan-2-ol (solvent used in the photoreduction reaction) changes similarly at both CdS band edge positions (Hopfner et al., 2002; Roy et al., 1995; White & Bard, 1985).

The estimated valence band of CdS-NP and CdS-Ald was calculated by subtracting the band gaps from the band edge values ($E_{\mathrm{Fb}} - E_{\mathrm{bg}}$) (Table 1) (Hopfner et al., 2002).

The surface area and pore volume of CdS-NP and CdS-Ald were determined from the nitrogen adsorption–desorption isotherm by the BET and BJH methods, respectively (Table 1).

For the primary reaction test, the photocatalytic reduction of nitrobenzene to aniline using CdS-NP was investigated and the optimum reaction conditions were determined. Typically, photoreduction of nitrobenzene using CdS under blue LED irradiation was investigated to determine the optimum concentration of the photocatalyst and a suitable solvent (Table 2).

Our present as well as previous studies (Eskandari et al., 2014) showed that propan-2-ol is the best solvent for photocatalytic reduction of nitrobenzene to aniline considering ethanol, methanol and propan-2-ol (Table 2, entries 4, 6, and 7) under the same conditions and in the presence of CdS as the photocatalyst.

Under optimized reaction conditions, the results showed that both CdS-NP and CdS-Ald photocatalysts converted nitrobenzene to aniline by 91 % and 46 %, respectively (Table 2, entries 4 and 8), and no product was detected under catalyst free or dark conditions (Table 2, entries 11 and 12).

Table 1. Characterization, band gap energies, and photoelectrochemical data

Sample	$E_{\mathrm{bg}}^{a,b}$ eV	$E_{\mathrm{Fb}}^{a,b,c}$ vs. NHE V	$E_{\mathrm{vb}} = (E_{\mathrm{Fb}} - E_{\mathrm{bg}})$ vs. NHE V	Surface area^d $\mathrm{m^2\ g^{-1}}$	Pore volume^e $\mathrm{cm^3\ g^{-1}}$
CdS-NP	2.37	–0.38	1.99	76.1	0.162
CdS-Ald	2.31	–0.42	1.88	23.4	0.049

a) Mean value of three independent measurements; *b*) reproducibility was better than ± 0.01 eV; *c*) measured according to Roy et al. (1995) and calculated for pH 7; *d*) BET surface area; *e*) BJH pore volume.

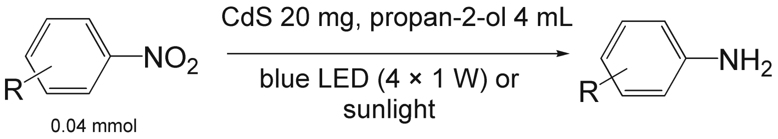
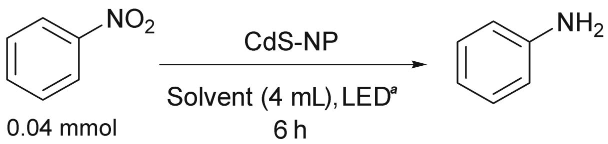


Fig. 4. Photocatalytic reduction of nitroaromatics under LED and sunlight irradiation.

Table 2. Photoreduction of nitrobenzene to aniline in the presence of CdS under LED irradiation



Entry	CdS-NP/mg	Solvent	Yield^b/%
1	8	Propan-2-ol	56
2	12	Propan-2-ol	74
3	16	Propan-2-ol	87
4	20	Propan-2-ol	91
5	24	Propan-2-ol	86
6	20	Methanol	48
7	20	Ethanol	45
8^c	20	Propan-2-ol	46
9^d	20	Propan-2-ol	89
10^{c,d}	20	Propan-2-ol	58
11^e	0	Propan-2-ol	0
12^f	20	Propan-2-ol	0

a) Blue LED (4 × 1 W), 80 lumen; *b*) GC yield; *c*) CdS-Ald as photocatalyst; *d*) sunlight irradiation (in the range of 80–100 × 10^3 lux) in 60 min; *e*) without catalyst; *f*) in dark.

Reactions under sunlight irradiation were also carried out at the same optimized condition as those under LED irradiation. The reaction under sunlight irradiation was found to be faster than under the LED irradiation (Table 2, entries 9 and 10).

The reaction of nitroarobenzene using the CdS-NP photocatalyst under sunlight irradiation was also found to be faster than when CdS-Ald was used (Table 2, entries 9 and 10).

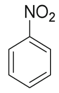
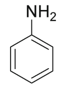
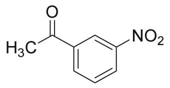
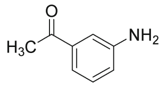
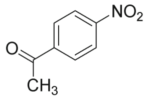
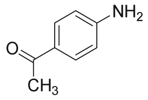
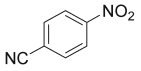
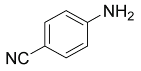
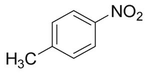
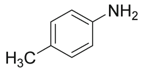
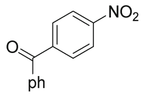
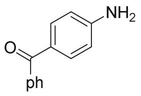
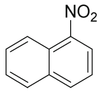
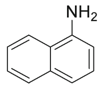
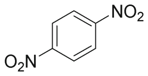
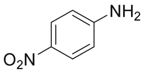
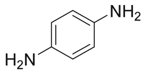
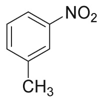
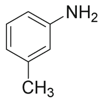
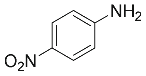
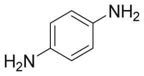
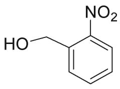
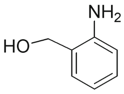
As shown in Table 1, conduction band positions of two photocatalysts are approximately close together. It seems that the thermodynamic reduction of nitroaromatics is almost similar in the presence of both photocatalysts. On the other hand, the valence band potential position (E_{vb}) of CdS-NP is by 0.11 eV more positive than CdS-Alds. This observation suggests that the valence band of CdS-NP has stronger holes for oxidation of the sacrificial solvent compared with CdS-Ald when using the proposed mechanism (Eskandari et al., 2014). On the other hand, surface area and pore volumes of CdS-NP are by approximately 3.3 fold higher than those of CdS-Ald (Table 1). High surface area of CdS-NP compared with that of CdS-Ald allows high adsorption of reactants and enhances the speed of the photocatalytic reaction. All results of the photocatalytic reactions (Fig. 4) under sunlight and LED irradiation are shown in Table 3.

As shown in Table 3 a variety of aromatic nitro compounds including electron-rich and electron-deficient substrates proceeded readily under blue LED and sunlight irradiation and simple experimental conditions to afford good to excellent yields of the corresponding amines.

Under blue LED irradiation, the yield depends strongly on the electron withdrawing or electron donating nature of the functional groups in the aromatic rings. The reactions generally take a long time (5–24 h) to complete whereas the same reaction under solar irradiation decrease to 45–120 min (Table 3).

Nitro compounds with electron withdrawing groups (CN, NO_2, COR) provided high yields in short reaction times compared with those containing electron-rich substituents (Me, NH_2) (Table 3). During the reactions under both LED and sunlight irradiation, the CN, COR, and CH_2OH functionalities in the aromatic ring remained unaffected (Table 3, entries 2, 3, 4, and 11). As shown in Table 3, sunlight affords the photoreduction of nitro compounds in high yields in short times in comparison with the photoreduction under LED irradiation. Photocatalytic reduction of 1,4-dinitrobenzene under LED irradiation showed of

Table 3. Photocatalytic reduction of nitroaromatics to corresponding amines using CdS-NP photocatalyst under blue LED and sunlight irradiation in propan-2-ol

Entry	Starting material	Product	Time/h (Yield/%)^{a,c}	Time/min (Yield/%)^{b,c}
1			6 (91)	60 (89)
2			5 (98)	45 (99)
3			8 (87)	60 (92)
4			6 (93)	60 (95)
5			8 (78)	60 (91)
6			10 (80)	70 (93)
7			14 (77)	120 (85)
8			24 (72)	120 (4)
			24 (11)	120 (84)
9			8 (85)	60 (90)
10			24 (21)	120 (70)
11			10 (63)	70 (71)

a) Blue LED (4 × 1 W, 80 lumen); *b*) sunlight irradiation (in the range of 80–100 × 10^3 lux); *c*) GC yield.

1,4-diaminobenzene and 4-nitroaniline yields of 11 % and 72 %, respectively, in 24 h. The same reaction under sunlight irradiation yielded 84 % and 4 % of 1,4-diaminobenzene and 4-nitroaniline, respectively (Table 3, entry 8). The data clearly show that the reduction of 1,4-dinitrobenzene to 4-nitroaniline under LED irradiation can be done chemoselectively.

Reusability of the CdS-NP photocatalyst was also investigated by the photocatalytic reduction of nitrobenzene as a test model. After each run, the photocatalyst was isolated by centrifugation, washed thoroughly with propan-2-ol (2 × 2 mL) and used in a new run.

Reusability of CdS-NP was also investigated for a 60 min and 6 h reaction under sunlight and LED irradiation, respectively. As shown in Table 4 after four runs, the yields decreased to 51 % and 13 % under LED and sunlight irradiation, respectively. Results of

Table 4. Reusability of CdS-NP in the reduction of nitrobenzene to aniline under sunlight and blue LEDs irradiation in propan-2-ol

Run	1	2	3	4
Conditions	Yield/%			
LED	91	88	75	51
Sunlight	90	63	30	13

atomic absorption spectroscopy showed the presence of low amounts of Cd^{2+} in the centrifuged solution after each reaction run under sunlight irradiation that can be attributed to the release of Cd^{2+} via photocorossion reaction ($CdS + h^+ \rightarrow Cd^{2+} + S$) causing a decrease of the reaction yield. On the other hand, diffuse reflectance spectroscopy results with CdS-NP revealed that the photocatalyst band gap energies remained unaffected after four runs under sunlight and LED irradiation.

Conclusions

In conclusion, we have demonstrated that simply prepared nanosized CdS is an efficient heterogeneous photocatalyst for the photocatalytic reduction of a variety of nitro aromatics containing electron withdrawing and donating groups to the corresponding amines under sunlight and blue LEDs irradiation. Photocatalytic reduction of amines in sunlight was faster than that under LEDs irradiation, but the reusability of the catalyst under LED irradiation was found to be better than sunlight.

Photocatalytic reaction under sunlight and LED irradiation showed that CdS-NP is a highly efficient catalyst for the reduction of nitrobenzenes to the corresponding anilines compared with CdS-Ald. High surface area, wide band gap and positive values of the CdS-NP valence band potential enhanced the photocatalytic ability of CdS-NP vs. CdS-Ald.

References

Abedi, S., Karimi, B., Kazemi, F., Bostina, M., & Vali, H. (2013). Amorphous TiO_2 coated into periodic mesoporous organosilicate channels as a new binary photocatalyst for regeneration of carbonyl compounds from oximes under sunlight irradiation. *Organic & Biomolecular Chemistry*, *11*, 416–419. DOI: 10.1039/c2ob26907d.

Ananthakrishnan, R., & Gazi, S. (2012). $[Ru(bpy)3]^{2+}$ aided photocatalytic synthesis of 2-arylpyridines *via* Hantzsch reaction under visible irradiation and oxygen atmosphere. *Catalysis Science & Technology*, *2*, 1463–1471. DOI: 10.1039/c2cy20050c.

Bao, N. Z., Shen, L. M., Takata, T., & Domen, K. (2008). Self-templated synthesis of nanoporous CdS nanostructures for highly efficient photocatalytic hydrogen production under visible light. *Chemistry of Materials*, *20*, 110–117. DOI: 10.1021/cm7029344.

Bhar, S., & Ananthakrishnan, R. (2015). Utilization of Ru(II)-complex immobilized ZnO hybrid in presence of Pt(II) co-catalyst for photocatalytic reduction of 4-nitrophenol under visible light. *RSC Advances*, *5*, 20704–20711. DOI: 10.1039/c4ra13746a.

Britt, J., & Ferekides, C. (1993). Thin-film CdS/CdTe solar cell with 15.8% efficiency. *Applied Physics Letters*, *62*, 2851–2852. DOI: 10.1063/1.109629.

Chun, S., Jung, Y., Kim, J., & Kim, D. (2011). The analysis of CdS thin film at the processes of manufacturing CdS/CdTe solar cells. *Journal of Crystal Growth*, *326*, 152–156. DOI: 10.1016/j.jcrysgro.2011.01.086.

Eskandari, P., Kazemi, F., & Azizian-Kalandaragh, Y. (2013). Convenient preparation of CdS nanostructures as a highly efficient photocatalyst under blue LED and solar light irradiation. *Separation and Purification Technology*, *120*, 180–185. DOI: 10.1016/j.seppur.2013.09.039.

Eskandari, P., Kazemi, F., & Zand, Z. (2014). Photocatalytic reduction of aromatic nitro compounds using CdS nanostructure under blue LED irradiation. *Journal of Photochemistry and Photobiology A: Chemistry*, *274*, 7–12. DOI: 10.1016/j.jphotochem.2013.09.011.

Flores, S. O., Rios-Bernij, O., Valenzuela, M. A., Córdova, I., Gómez, R., & Gutiérrez, R. (2007). Photocatalytic reduction of nitrobenzene over titanium dioxide: by-product identification and possible pathways. *Topics in Catalysis*, *44*, 507–511. DOI: 10.1007/s11244-006-0098-2.

Füldner, S., Mild, R., Siegmund, H. I., Schroeder, J. A., Gruber, M., & König, B. (2010). Green-light photocatalytic reduction using dye-sensitized TiO_2 and transition metal nanoparticles. *Green Chemistry*, *12*, 400–406. DOI: 10.1039/b918140g.

Füldner, S., Mitkina, T., Trottmann, T., Frimberger, A., Gruber, M., & König, B. (2011). Urea derivatives enhance the photocatalytic activity of dye-modified titanium dioxide. *Photochemical & Photobiological Sciences*, *10*, 623–625. DOI: 10.1039/c0pp00374c.

Hakki, A., Dillert, R., & Bahnemann, D. (2009). Photocatalytic conversion of nitroaromatic compounds in the presence of TiO_2. *Catalysis Today*, *144*, 154–159. DOI: 10.1016/j.cattod.2009.01.029.

Herrmann, J. M. (2005). Heterogeneous photocatalysis: state of the art and present applications. *Topics in Catalysis*, *34*, 49–65. DOI: 10.1007/s11244-005-3788-2.

Hopfner, M., Weiß, H., Meissner, D., Heinemann, F. W., & Kisch, H. (2002). Semiconductor photocatalysis type B: synthesis of unsaturated α-amino esters from imines and olefins photocatalyzed by silica-supported cadmium sulfide. *Photochemical & Photobiological Sciences*, *1*, 696–703. DOI: 10.1039/b204569a.

Imamura, K., Iwasaki, S. I., Maeda, T., Hashimoto, K., Ohtani, B., & Kominami, H. (2011). Photocatalytic reduction of nitrobenzenes to aminobenzenes in aqueous suspensions of titanium(IV) oxide in the presence of hole scavengers under deaerated and aerated conditions. *Physical Chemistry Chemical Physics*, *13*, 5114–5119. DOI: 10.1039/c0cp02279a.

In, S. I., Vesborg, P. C. K., Abrams, B. L., Hou, Y. D., & Chorkendorff, I. (2011). A comparative study of two techniques for determining photocatalytic activity of nitrogen doped TiO_2 nanotubes under visible light irradiation: Photocatalytic reduction of dye and photocatalytic oxidation of organic molecules. *Journal of Photochemistry and Photobiology A: Chemistry*, *222*, 258–262. DOI: 10.1016/j.jphotochem.2011.06.005.

Kakroudi, M. A., Kazemi, F., & Kaboudin, B. (2014). β-Cyclodextrin-TiO_2: Green nest for reduction of nitroaromatic compounds. *RSC Advances*, *4*, 52762–52769. DOI: 10.1039/c4ra08059a.

Kaur, J., & Pal, B. (2014). 100% selective yield of *m*-nitroaniline by rutile TiO_2 and *m*-phenylenediamine by P25-TiO_2 during *m*-dinitrobenzene photoreduction. *Catalysis Communications*, *53*, 25–28. DOI: 10.1016/j.catcom.2014.04.019.

Kumar, J. S. D., Ho, M. K. M., & Toyokuni, T. (2001). Simple and chemoselective reduction of aromatic nitro compounds to aromatic amines: reduction with hydriodic acid revisited. *Tetrahedron Letters*, *42*, 5601–5603. DOI: 10.1016/s0040-4039(01)01083-8.

Li, Q., Guo, B. D., Yu, J. G., Ran, J. R., Zhang, B. H., Yan, H. J., & Gong, J. R. (2011). Highly efficient visible-light-driven photocatalytic hydrogen production of CdS-cluster-decorated graphene nanosheets. *Journal of the American*

Chemical Society, *133*, 10878–10884. DOI: 10.1021/ja2025454.

Ohtani, B., Pal, B., & Ikeda, S. (2003). Photocatalytic organic syntheses: Selective cyclization of amino acids in aqueous suspensions. *Catalysis Surveys from Asia*, *7*, 165–176. DOI: 10.1023/a:1025389725637.

Pal, B., & Pal, B. (2015). Tuning the optical and photocatalytic properties of anisotropic ZnS nanostructures for the selective reduction of nitroaromatics. *Chemical Engineering Journal*, *263*, 200–208. DOI: 10.1016/j.cej.2014.10.109.

Prier, C. K., Rankic, D. A., & MacMillan, D. W. C. (2013). Visible light photoredox catalysis with transition metal complexes: applications in organic synthesis. *Chemical Reviews*, *113*, 5322–5363. DOI: 10.1021/cr300503r.

Roy, A. M., De, G. C., Sasmal, Z., & Bhattacharyya, S. S. (1995). Determination of the flatband potential of semiconductor particles in suspension by photovoltage measurement. *International Journal of Hydrogen Energy*, *20*, 627–630. DOI: 10.1016/0360-3199(94)00105-9.

Schultz, D. M., & Yoon, T. P. (2014). Solar synthesis: Prospects in visible light photocatalysis. *Science*, *343*, 1239176. DOI: 10.1126/science.1239176.

Sheeney-Haj-Ichia, L., Basnar, B., & Willner, I. (2005). Efficient generation of photocurrents by using CdS/carbon nanotube assemblies on electrodes. *Angewandte Chemie International Edition*, *44*, 78–83. DOI: 10.1002/anie.200461666.

Veréb, G., Ambrus, Z., Pap, Zs., Kmetykó, Á., Dombi, A., Danciu, V., Cheesman, A., & Mogyorósi, K. (2012). Comparative study on UV and visible light sensitive bare and doped titanium dioxide photocatalysts for the decomposition of environmental pollutants in water. *Applied Catalysis A: General*, *417–418*, 26–36. DOI: 10.1016/j.apcata.2011.12.018.

Wang, J., Liu, G. D., & Merkoçi, A. (2003). Electrochemical coding technology for simultaneous detection of multiple DNA targets. *Journal of the American Chemical Society*, *125*, 3214–3215. DOI: 10.1021/ja029668z.

Wang, H. Q., Yan, J. P., Chang, W. F., & Zhang, Z. M. (2009). Practical synthesis of aromatic amines by photocatalytic reduction of aromatic nitro compounds on nanoparticles N-doped TiO_2. *Catalysis Communications*, *10*, 989–994. DOI: 10.1016/j.catcom.2008.12.045.

Wang, H. Q., Yang, X. F., Xiong, W. F., & Zhang, Z. M. (2013). Photocatalytic reduction of nitroarenes to azo compounds over N-doped TiO_2: relationship between catalysts and chemical reactivity. *Research on Chemical Intermediates*, *41*, 3981–3997. doi: 10.1007/s11164-013-1504-6.

White, J. R., & Bard, A. J. (1985). Electrochemical investigation of photocatalysis at cadmium sulfide suspensions in the presence of methylviologen. *The Journal of Physical Chemistry*, *89*, 1947–1954. DOI: 10.1021/j100256a027.

Zand, Z., Kazemi, F., & Hosseini, S. (2014). Development of chemoselective photoreduction of nitro compounds under solar light and blue LED irradiation. *Tetrahedron Letters*, *55*, 338–341. DOI: 10.1016/j.tetlet.2013.11.023.