Chem. Pap.
DOI 10.1007/s11696-016-0106-3

ORIGINAL PAPER

A photocatalytic green system for chemoselective reduction of nitroarenes

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Received: 15 June 2016 / Accepted: 9 November 2016

Abstract A highly efficient photocatalytic reduction of nitroarenes using TiO_2/polyethylene glycol 400-water (TiO_2/PEG–H_2O) is reported. This system at deoxygenated and illuminated (sunlight or violet LED) conditions efficiently reduced nitroarenes using oxalic acid or ammonium formate as a sacrificial electron donor. Reducible functional groups such as chloro, hydroxy, flouro, bromo and carbonyl were intact under the optimized reaction conditions. The 0.1 and 0.5–1 mmol amount of nitroarenes was used under sunlight and violet LED (400 nm) irradiation, respectively. Reusability of the nanotitania was successfully carried out four times. The analyses of the recovered catalyst after five runs including TEM, XRD, TGA and CHN were done and results showed that PEG is located on TiO_2; no change in morphology, crystallinity and particle sizes was observed.

Keywords Violet LED · Sunlight · PEG-TiO_2 · Photocatalytic · Chemoselective · Green synthesis

Introduction

Energy consumption is a future challenge. Therefore, renewable and natural energy sources, such as sunlight, can be employed as a green source of energy (Zhou and Hu 2010). To this aim, nanochemistry allows the use of inexpensive materials and inexpensive processing technologies to harvest sunlight and open up new views to attain higher solar energy conversion performance at lower costs (Atwater and Polman 2010; Scholes et al. 2011; Schuller et al. 2010; Schwede et al. 2010). In addition, recently, light-emitting diodes (LED) have been applied as a marvelous instrument to initiate photocatalytic reactions. LEDs can emit light of different wavelength (infrared, visible, or near-ultraviolet).

Since the 1970s, photocatalytic processes have attracted substantial attention and are still very active and evolving research areas (Chen and Mao 2007). Heterogeneous photocatalysis by semiconductor materials has been gaining increasing interest in photocatalytic water cleavage (Brimblecombe et al. 2008; Esswein and Nocera 2007; Kanan and Nocera 2008; Tang et al. 2008), photodegradation of dyes (Shan et al. 2008) and phenols (Lea and Adesina, 2001) and in organic synthesis (Di Paola et al. 2008; Mahdavi et al. 1993; Rios-Berny et al. 2010; Gao et al. 2015; Flores et al. 2007; Ramdar et al. 2016; Friedmann et al. 2016) due to its likely potential for solar energy conversion. TiO_2, because of its unique chemical and physical properties, such as high efficiency, low cost, physical and chemical stability, widespread availability, and noncorrosive property is broadly used in the fields of solar energy conversion and photocatalysis (Di Paola et al. 2008). TiO_2-P25 as an active and available catalyst is used widely in photodegradation and organic synthesis. Li et al. first reported a photoinduced reduction of nitro compounds

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Electronic supplementary material The online version of this article (doi:10.1007/s11696-016-0106-3) contains supplementary material, which is available to authorized users.

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to the corresponding amines using TiO_2-P25 as a catalyst under UV light; they used 2 ml of a 0.01 M solution of nitrobenzene in the reaction (Mahdavi et al. 1993).

Gray and Thurnauer reported that TiO_2-P25 can also be active in visible light. They reported the presence of small rutile crystallites causes rapid electron transfer from rutile to lower energy anatase lattice trapping sites under visible illumination leading to a more stable charge separation and the photoactivity of TiO_2-P25 in visible light. It was concluded that extension of the photoactivity into visible wavelengths is due to antenna effect of the rutile phase (Hurum et al. 2003). The selective reduction of nitroarenes with sunlight and blue LED irradiation using TiO_2-P25 in ethanol as solvent was reported by us (Zand et al. 2014). In addition, we reported (Abdollahi et al. 2014b) aqueous-phase chemoselective reduction of a wide range of aromatic nitro substrates (0.1 mmol scale) in the presence of β-cyclodextrin-TiO_2 (β-CD-TiO_2) under sunlight irradiation. The β-CD was introduced as a green nest for reduction of nitroarenes. Through this method, overcome of some semiconductor limitations in water, associated with the low solubility of substrates and overoxidation of organic compounds which are a result of the oxidant species produced (such as $^{\cdot}OH$ and $O_2^{-\cdot}/HO_2^{\cdot}$) in a photocatalytic process, was achieved.

PEGs as green inexpensive phase transfer catalysts have other properties such as low toxicity, water solubility, ease of recoverability, thermal stability, low volatility and biodegradability. Among PEGs, liquid PEG-400 can be used as solvent with or without water addition (Harris et al. 1982; Ido et al. 1997; Mates and Ring 1987; Hasan Nia et al. 2015; Sheftel and Victor 2000).

Now, based on our experience of working with semiconductor photocatalysts such as TiO_2 and CdS in nitro reduction in aqueous and organic phases (Abedi et al. 2013; Eskandari et al. 2013, 2014; Abdollahiet al. 2014a, b; Zand et al. 2014; Safari and Kazemi 2016), we report here a protocol for selective photocatalytic reduction of nitroarenes in water using TiO_2/PEG–H_2O photocatalytic condition under sunlight and violet LED irradiation. We introduce a method that would increase the amount of substrate to 0.5–1 mmol of nitroarenes.

Experimental

Nitro compounds, polyethylene glycol-400 (PEG-400) and oxalic acid were purchased from Merck Co. Ammonium formate (HCO_2NH_4) and titanium dioxide (TiO_2-P25) were supplied by Fluka and Degussa Co., respectively. All chemicals were used as received without further purification. Deionized water was used in all experiments. CHNS analysis was recorded with ElementarVario EL III. TEM images were obtained with Philips CM120, VEGA\-TESCAN-XMU. Thermogravimetric analysis was conducted from room temperature to 700 °C in a nitrogen flow using a NETZSCH STA 409 PC/PG instrument. Nitrogen sorption analysis (Belsorp, BELMAX, Japan) was used for further analysis of the catalyst. FTIR spectra were recorded on Bruker-vector 22.

Nitro compounds (0.1 mmol under sunlight and 0.5 mmol under UV LED irradiation) were dissolved in PEG-400 (1.5 ml) and then 10 ml of water was added to the solution; commercial TiO_2 (P25) (40 mg) and oxalic acid (1.5 equimolar) were added into a round bottom Pyrex flask (25 ml).The reaction mixture was degassed by Argon gas (20 min) and sealed with a septum. Afterwards, the flask was irradiated under stirring with sunlight or violet LED (see the data in Table 2). After the completion of the reaction according to GC monitoring, $NaHCO_3$ was added to increase pH = 7 and the mixture was stirred at room temperature. The aqueous layer was extracted with EtOAc (2 × 10 ml). The organic layer was dried with sodium sulfate, filtered and evaporated in vacuum.

Results and discussion

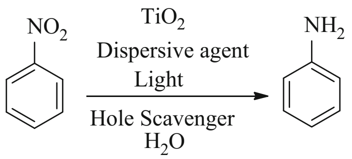
One problem of heterogeneous photocatalytic reactions is low amount of substrate (Eskandari et al. 2014; Hakki et al. 2013; Mahdavi et al. 1993; Shiraishi et al. 2012; Wang et al. 1997; Zand et al. 2014). In our previous report (Abdollahi et al. 2014b), we used β-CD-TiO_2 for the reduction of nitroarenes (1:1 β-CD:nitroarene, 0.1 mmol scale) in water under sunlight irradiation. The guest–host nitroarenes-β-CD solubilized in water and also the dispersity and aggregation prevention of TiO_2 were demonstrated to have been improved. Today, the LED irradiation has many advantages; LEDs are inexpensive and available in different forms, but unfortunately, the β-CD-TiO_2 photocatalysis was unsuccessful under blue LED irradiation. PEGs are known as available, nanoparticle stabilizer, nonexpensive and water dispersive agents (Hasan Nia et al. 2015). Also PEG was used for preparation of TiO_2 (Bu et al. 2004) and combination of PEG-TiO_2reduces TiO_2 cytotoxicity (Mano et al. 2012). Herein we report a new method for nitro aromatic reduction in water under sunlight and violet LED and in the presence of PEG-400-modified TiO_2 as catalyst.

Nitrobenzene was chosen as a model compound for the study of optimized reaction conditions. Oxalic acid was chosen as a sacrificial reagent as in our previous work (Abdollahi et al. 2014b). The reduction reaction was carried out under sunlight irradiation. 0.1 mmol of nitrobenzene dissolved in 1.5 ml of different water dispersive agents: diethylene glycol, triethylene glycol, PEG-400 and diglyme (Table 1, entries 4,6–8). These solutions were added to 10 ml of water including 40 mg of TiO_2-P25. The reaction progress was monitored with GC (Table 1). Excellent results were obtained for triethylene glycol, PEG-400 and diglyme. The PEG-400 was selected for its availability and low cost. The optimization of PEG amounts was carried out and 1.5 ml of PEG-400 was chosen (Table 1, entries 2–5).

The photocatalytic behavior of the reaction was confirmed through reactions in the absence of photocatalyst and light at separate experiments (Table 1, entries 13, 14).

The effect of nitrobenzene amounts (0.05, 0.1 and 0.2 mmol) was optimized. The best conversion was obtained for 0.1 mmol of nitrobenzene after sunlight irradiation for 3.5 h (Table 1, entries 15,16).

Table 1 The optimization on photocatalytic reduction of nitrobenzene in the presence of TiO_2-P25



Entry	Dispersive agent (ml)	Hole scavenger	Light source	TiO_2 amount (mg)	Yield (%)[a]
1	–	Oxalic acid	Sun	40	38
2	PEG 400 (0.5)	Oxalic acid	Sun	40	44
3	PEG 400 (1)	Oxalic acid	Sun	40	91
4	PEG 400 (1.5)	Oxalic acid	Sun	40	96
5	PEG 400 (2)	Oxalic acid	Sun	40	98
6	Diethylene glycol (1.5)	Oxalic acid	Sun	40	41
7	Triethylene glycol (1.5)	Oxalic acid	Sun	40	97
8	Diglyme (1.5)	Oxalic acid	Sun	40	100
9	PEG 400 (1.5)	–	Sun	40	43
10	PEG 400 (1.5)	EtOH	Sun	40	70
11	PEG 400 (1.5)	Ammonium formate	Sun	40	95
12	PEG 400 (1.5)	Sodium sulphite	Sun	40	61
13[b]	PEG 400 (1.5)	Oxalic acid	Sun	–	0
14[c]	PEG 400 (1.5)	Oxalic acid	–	40	0
15[d]	PEG 400 (1.5)	Oxalic acid	Sun	40	100
16[e]	PEG 400 (1.5)	Oxalic acid	Sun	40	76
17	PEG 400 (1.5)	Oxalic acid	Sun	30	50
18	PEG 400 (1.5)	Oxalic acid	Sun	35	86
19	PEG 400 (1.5)	Oxalic acid	Sun	50	97
20	PEG 400 (1.5)	Oxalic acid	Sun	60	96
21	PEG 400 (1.5)	Oxalic acid	Blue LED	80	0
22[f]	PEG 400 (1.5)	Oxalic acid	Violet LED	40	100
23 [g]	PEG 400 (1.5)	Oxalic acid	Violet LED	40	100
24 [h]	PEG 400 (1.5)	Oxalic acid	violet LED	40	100(92[i])
25[j]	β-cyclodextrin	Oxalic acid	violet LED	40	2(8[k])

[a] Sunlight intensity between (870 and 1070 Lux)

[b] Without TiO_2

[c] In dark

[d] 0.05 mmol nitrobenzene was used

[e] 0.2 mmol nitrobenzene was used

[f] Nitrobenzene (0.1 mmol) oxalic acid (0.15 mmol), 3 h

[g] Nitrobenzene (0.5 mmol) oxalic acid (0.75 mmol), 7 h

[h] Nitrobenzene (1 mmol) oxalic acid (1.5 mmol), 13 h

[i] Isolated yield

[j] β-CD (1 mmol), nitrobenzene (1 mmol), oxalic acid (1.5 mmol), 13 h

[k] 0.1 mmol β-CD was used

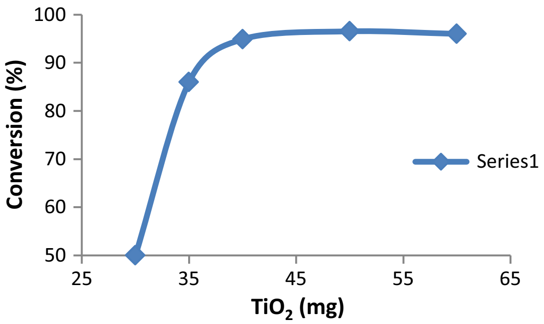


Fig. 1 The optimization of TiO_2 amount used in the reduction of nitrobenzene under sunlight irradiation

To exploit the optimal light absorption (Kisch 2010), we investigated the effect of TiO_2-P25 amounts on the conversion of nitrobenzene under the above conditions. The best result was found when 40 mg of TiO_2 was used for 0.1 mmol of nitrobenzene, 1.5 ml of PEG-400, 10 ml of water and 0.15 mmol of oxalic acid under sunlight irradiation (Table 1, entries 17–20; Fig. 1).

The effect of the sacrificial additives on the reduction of nitrobenzene as a model reaction has been checked out by comparing preliminary yields in the presence and absence of additives. In the absence of any additive in the reaction conditions just 43% conversion was observed due to reducing ability of PEG (Table 1, entry 9). Among the used additives, oxalic acid and ammonium formate were found as excellent reducing agents (Table 1, entries 10–12).

In addition, it is well known that a primary alcohol (such as methanol or ethanol) can be used as both a hole scavenger and solvent in the photocatalytic reduction of nitroaromatics, generating corresponding aldehydes as the oxidation product. Since these aldehydes are toxic, a ‘‘greener’’ sacrificial reagent converting to a nontoxic compound is preferable. Oxalic acid and ammonium formate are green sacrificial hole scavengers because they are easily oxidized to carbon dioxide (CO_2) (Imamura et al. 2011).

Similar to our previous report (Zand et al. 2014), we tried to use blue LED as a light source. We found even in much lower concentration of nitrobenzene (0.01 mmol), TiO_2-P25(80 mg), oxalic acid (0.015 mmol), PEG (1.5 ml) and water (10 ml) under blue LED (4 × 3 W); after 24 h no reduction occurred (Table 1, entry 21). Because of LED importance, we were encouraged to use more powerful LEDs; the reaction was repeated with violet LED (395–405 nm) (2 × 3 W). Very interestingly, the reaction was completed after 3 h (Table 1, entry 22). This fantastic result led to testing the reaction for the practical reduction of nitrobenzene (1 mmol) (Table 1, entries 22–24). Again the reaction was completed after 13 h with a 92% isolated yield. Fluorescence spectrum of TiO_2/polyethylene glycol 400–water mixture at excitation wavelength of 400 showed emissions at 524.2 and 470.89 nm. This fact confirmed the activity of the catalyst under violet LED irradiation. The TiO_2/polyethylene glycol 400–water mixture did not show any emission at 440 nm, and this evidence also confirmed inactivity of the photocatalyst under blue LED irradiation (see Figure S1, S2 in Supporting Information). For comparison, the use of violet LED was also checked by β-CD-TiO_2 method. Using TiO_2 40 mg, 1:1 and 1:10 β-CD:nitrobenzene (1 mmol scale of nitrobenzene) in water under violet LED (2 × 3 W), only 2 and 8% conversion was shown, respectively, after 13 h (Table 1, entry 25).

After optimizing the reaction conditions, to consider the scope of the developed method, the reduction of various nitro compounds containing different functional groups was performed. As shown in Table 2, the photocatalytic reduction of diverse aromatic nitro compounds including electron-rich and electron-deficient functional groups proceeded readily at experimental conditions and afford well to excellent yields of the corresponding aromatic amines (Table 2). For example *m*-chloronitrobenzene and m-nitrotoluene both converted to the *m*-chloroaniline and *m*-toluidine after 3 h with excellent yields (Table 2, entries 2, 5). It seems that solubility of nitroarenes and their corresponding products has major role in the reactivity. It was observed that *p*-nitrophenol with appropriate solubility but with an electron donating group was completely converted to the *p*-aminophenol (Table 2, entry 7). In contrast, *p*-nitrobromobenzene, the low water solubility including electron-withdrawing group, only converted to the *p*-bromoaniline with 36% (Table 2, entry 8). Then with increasing the amount of PEG from 1.5 to 2 ml, increased solubility condition of substrate, the conversion enhanced to 100% (Table 2, entry 8). Under LED irradiation, due to higher concentration of nitroarenes (0.5 mmol) compared to sunlight irradiation, the importance of solubility and also adsorption and desorption of material (nitro and its amine) on titania, increased, e.g., no products were found for 1,2-dinitrobenzene and *o*-nitroaniline (Table 2 entries 10, 11) and conversion yield of nitronaphthalene decreased to 34% (Table 2 entry 9).

There is an enormous interest in developing efficient, active and environmentally sustainable systems that would perform the selective reduction of nitro compounds in the presence of other reducible functional groups, such as ketones, aldehydes or halides (Tafesh and Weiguny 1996). In our present method, any dehalogenation was not occurred when we used 1-chloro-3-nitrobenzene and 1-bromo-4-nitrobenzene as nitro compound, which has been observed in some previously reported methods (Table 2, entries 2, 8). Under the present reaction conditions, high chemoselectivity with an excellent yield was observed when 3-nitroacetophenone was used and no

Table 2 Reduction of nitro compounds using TiO_2/PEG–H_2O under sunlight and violet LED irradiation

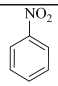
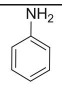
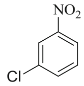
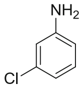
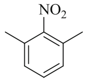
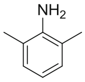
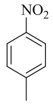
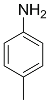
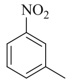
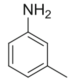
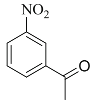
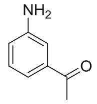
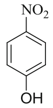
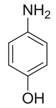
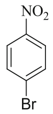
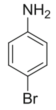
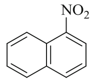
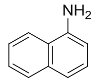
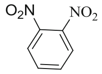
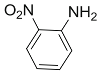
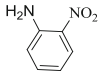
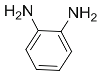
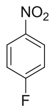
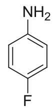
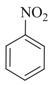
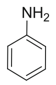
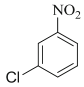
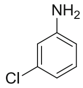
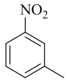
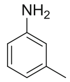
Entry	Nitro	Time (h) In sun	Time(h)in LED	Amine	Yield (%) In sun[b]	Yield (%) In LED[c]
1		3.5	16		96	100[a]
2		3	22		95	100
3		3.5	26		100	100
4		4.5	28		88	92
5		3	22		100	100
6		3	18		100	98
7		4	44		100	100
8		3	22		36(100)[d]	100
9		4.5	22		80	34
10		5	24		73	0
11		6	24		32(41)[d]	0
12		3.5	12		100	100
13[e]		3.5	-		100	-

Table 2 continued

Entry	Nitro	Time (h) In sun	Time(h)in LED	Amine	Yield (%) In sun[b]	Yield (%) In LED[c]
14[e]		3	-		98	-
15[e]		3	-		99	-

[a] 1 mmol Of nitrobenzene is used

[b] Reaction conditions: nitro compound (0.1 mmol), TiO_2 (0.04 g), H_2O (10 ml), oxalic acid (0.15 mmol, PEG-400 (1.5 ml) and sunlight intensity between 870 and 1070 Lux

[c] Reaction conditions: nitro compound (0.5 mmol), TiO_2 (0.04 g), H_2O (10 ml), oxalic acid (0.75 mmol, PEG 400 (1.5 ml) and with two 400-nm LEDs irradiation (2 × 3 W)

[d] Reaction was carried out in the presence of 2 ml of PEG-400

[e] Reduction was carried out in the presence of 40 mg of separated PEG-TiO_2 under sunlight irradiation

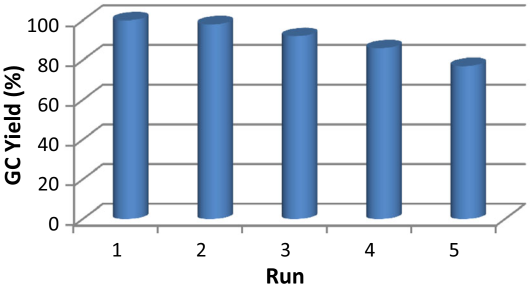


Fig. 2 Reusability of the catalyst in nitrobenzene reduction under sunlight

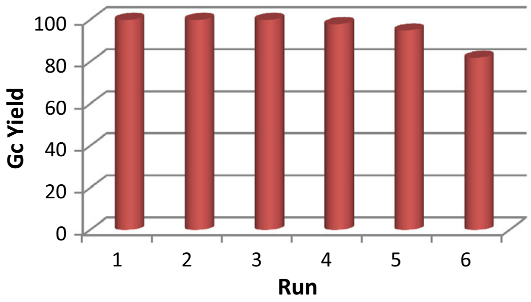


Fig. 3 Reusability of the catalytic mixture through stepwise addition of reactants under sunlight

Table 3 CHN analysis data for recycled PEG-TiO_2 catalyst and PEG-TiO_2 before reaction

Catalyst	%N	%C	%H
PEG-TiO_2	0.0	7.297	1.151
Washed TiO_2-PEG	0.0	1.04	0.2
Reused separated PEG-TiO_2-P25	0.716	11.53	2.136

unwanted reduction of the carbonyl group was observed (Table 2, entry 6). A good regioselectivity was observed in the reduction of 1,2-dinitrobenzene (Table 2, entry 10).

To consider reusability of the TiO_2/PEG–H_2O catalytic system, the reduction of nitrobenzene at optimum condition was monitored for five runs and the catalyst showed good activity. The little decrease after the fifth run can be due to removing PEG and TiO_2 under washing step (Fig. 2), see also Supporting Information). In addition, to better study the catalyst photoactivity, prevention of removing PEG and TiO_2, and scalability of the reaction, we examined the stepwise increasing of nitrobenzene to the optimized reaction. In each step in the presence of 40 mg of TiO_2, 0.1 mmol of nitro benzene and 0.15 mmol of oxalic acid were added stepwise to the reaction mixture. The excellent results were achieved even after five runs in only 40 mg starting TiO_2. This fact shows scalability of the reaction in addition to high activity and stability of the catalyst in this method (Fig. 3).

The main question about nature of catalyst is: what is the role of PEG? Then, study of adsorption of PEG on TiO_2 can be useful. For this purpose, the TiO_2 was added to PEG/water (1.5 ml/10 ml) and TiO_2 was separated after 3 h. The separated TiO_2 was used for reduction of some nitroarenes without the addition of PEG. Very interestingly, the excellent results were obtained for nitrobenzene, 3-chloronitrobenzene and 3-nitrotoluene without any PEG 400 addition (Table 2, entries 13–15). CHN analysis of the separated TiO_2 showed 7.3% weight carbon (Table 3) and TGA analysis showed 12.96% weight loss can be refer to polyethylene glycol located on the titania (see Figure S3 in Supporting Information). In addition, the FTIR of separated TiO_2-P25 (PEG-TiO_2) confirmed the organic moiety (see Figure S5 in Supporting Information). To show that how

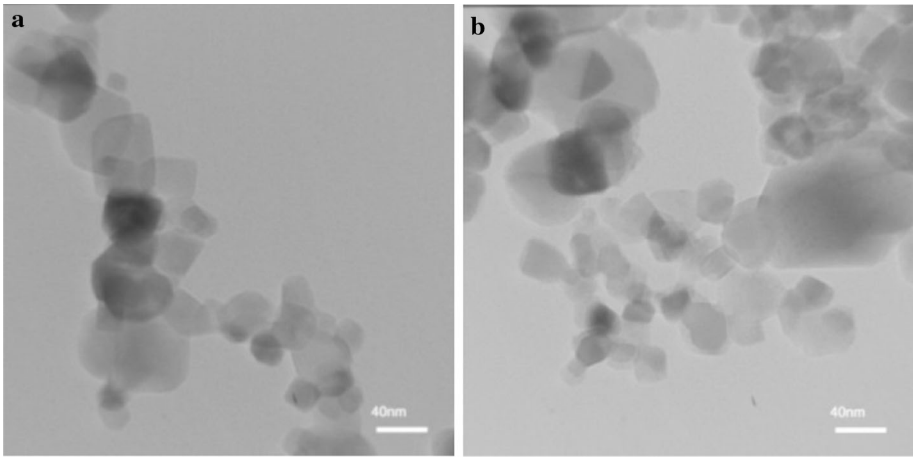


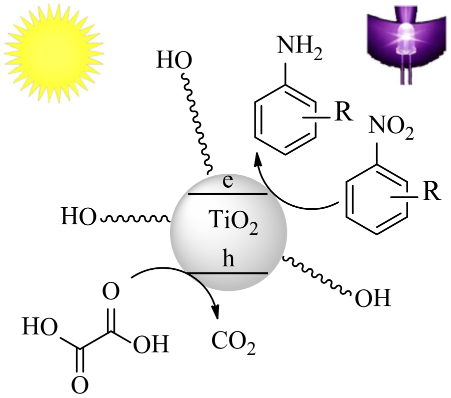
Fig. 4 TEM images of: **a** PEG-TiO_2 and **b** reused separated PEG-TiO_2-P25

absorption of PEG-400 takes place on TiO_2, several experiments were carried out; first, PEG-TiO_2 was washed in 60 °C and CHN analysis showed a decrease on PEG, so this can be due to physical adsorption on TiO_2 surface (physisorption) (Table 3). The pH change of TiO_2/PEG–H_2O was measured under sunlight irradiation and no change was observed, this also confirms the physisorption of PEG on TiO_2 surface. Astruc et al. also show H-bonding interaction between triethylene glycol and surface OH bonds of metal oxides (Deraedt et al. 2015). These results can be explained through adsorption of PEG on the surface of titania and organic moieties mounted during reduction of nitrobenzene. CHN analyses of the PEG-TiO_2, washed PEG-TiO_2 and reused separated PEG-TiO_2 catalysts showed 7.29, 1.04 and 11.53% w/w of carbon (Table 3). In addition, TGA analyses showed 12.96 and 13.1% weight loss for PEG-TiO_2 and reused separated PEG-TiO_2, respectively (see Figure S3, S4 in Supporting Information).

XRD pattern of reused separated PEG-TiO_2 catalyst did not show any change in the TiO_2 crystalline phase (Figure S6 in Supporting Information).

TEMs of PEG-TiO_2 and reused separated PEG-TiO_2 catalysts show no change in the particle size (Fig. 4, Scheme 1).

In summary, we have reported a highly efficient photocatalytic reduction of nitro aromatic compounds employing TiO_2/PEG–H_2O. In this method, nitroarene, with electron-donating and electron-withdrawing groups, has been employed successfully. The relatively high scale of 0.1 and 0.5–1 mmol nitro compounds was used under violet LED (400 nm) and sunlight irradiation, respectively. The study of the catalytic system showed that PEG attached physically on the surface of nanotitania. PEG-TiO_2 is a very efficient photocatalyst. PEG caused better water dispersity and stability of the catalyst against agglomeration. Excellent reusability, environmentally benign and high-scale amount of starting materials make this method a promising one for practical reduction of nitroarenes. In addition, the physisorbed PEG-TiO_2 catalyst was separated from TiO_2/PEG–H_2O mixture and interestingly showed highly efficient activity in aqueous photocatalytic reduction of nitroarenes.



Scheme 1 Reduction of nitrobenzene using TiO_2/PEG–H_2O under sunlight and violet LED irradiation

Acknowledgements We thank the Institute for Advanced Studies in Basic Sciences (IASBS) for financial support in this work. We also thank Dr. Hamed Zandi for editing the manuscript.

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