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Development of chemoselective photoreduction of nitro compounds under solar light and blue LED irradiation

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ABSTRACT

Solar light and blue light irradiation of the commercially available heterogeneous nano photocatalyst TiO_2–P25 leads to reduction of nitro compounds to give the corresponding amines. The methodology provides a green and mild approach to this useful class of organic compounds. Aromatic nitro compounds containing a wide range of functional groups tolerated the conditions to give, chemoselectively the corresponding amines in excellent yields.

Aromatic amines are an important class of compounds frequently used as key intermediates in the synthesis of dyes, pharmaceuticals, and agrochemicals.[1] Several methods have been developed for the preparation of amines, mainly involving reduction of the corresponding nitro compounds. Reagents that are traditionally used for these reductions, including catalytic transfer hydrogenation and metal-mediated methods[2] are often toxic, and show poor efficiency. Therefore, from the standpoint of environmental and economic concerns, an efficient approach for cleaner and cheap production of amines is still a challenge in organic synthesis. Photoreduction strategies are attractive alternative means of attaining this goal in organic transformations.[3]

Photocatalytic reactions using semiconductor nanomaterials have attracted much attention. One of the most promising semiconductors for photocatalytic applications is titanium dioxide, particularly due to its low cost, chemical and thermal stability as well as nontoxicity. Degussa P25, which is frequently used as a benchmark in heterogeneous photocatalysis in many instances shows unsurpassed photocatalytic activity. The high photoactivity of this material is because of a delayed electron/hole recombination between the anatase (80%) and rutile (20%) phases.[4]

In 1993, Li et al. reported the first example of photoreduction of nitroaromatic compounds to anilines using TiO_2 Degussa P25 under UV irradiation.[5] Recent research in semiconductor photocatalysis has focused on visible light activity. Konig and co-workers reported the photoreduction of nitroaromatic compounds to the corresponding anilines using dye-sensitized TiO_2–P25[6] or $PbBiO_2X$,[7] which represent the first examples of photoreduction of nitro compounds using LED irradiation. Swaminathan and co-workers regenerated ketones from ketoximes with various semiconductor oxides including TiO_2 (anatase), TiO_2–P25, and Ag–TiO_2 under solar and UV-A light irradiation.[8] They also reported photocatalytic syntheses of benzimidazoles and indazole by Pt–TiO_2, Ag–TiO_2, and TiO_2–P25 nanoparticles under UV and solar light.[9] Gong and Li et al. reported photocatalytic oxidation of benzyl alcohol into benzaldehyde over single-crystalline rutile TiO_2 nanorods under visible light.[10] We have reported activated amorphous TiO_2 incorporated into periodic mesoporous organosilicas (PMOs) as an efficient photocatalyst for regeneration of ketones and aldehydes from the corresponding oximes under sunlight irradiation.[11] From the viewpoint of environmentally friendly or 'green' chemistry, it is of significant importance to develop processes for synthesizing useful organic compounds utilizing solar energy.[12] In the context of developing eco-friendly green chemical procedures, we decided to investigate the use of the commercial catalyst, TiO_2–P25 for the reduction of nitro compounds by LED and solar light irradiation,[13] without an additive or dye-sensitizer.

The photoreduction of nitrobenzene using TiO_2–P25 by solar light was investigated as a model reaction, and the results are shown in Table 1. A solution of nitrobenzene (0.002 mmol) in ethanol (4 mL) containing 0.005 g of the TiO_2–P25 photocatalyst was irradiated with solar light for 6 h. The reaction conversion was monitored by gas chromatography (GC). A 60% conversion of

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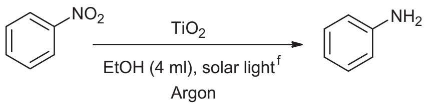
Table 1
Photoreduction of nitrobenzene to aniline in the presence of TiO_2–P25 using solar light



Entry	TiO_2 (g)	Nitrobenzene (mmol)	Time (h)	Conversion[a] (%)
1[b]	0	2×10^{-3}	8	0
2	0.005	2×10^{-3}	6	60
3	0.007	2×10^{-3}	3	80
4	0.01	2×10^{-3}	1	100
5	0.005	2×10^{-2}	8	40
6	0.01	2×10^{-2}	1.5	100
7	0.01	2×10^{-1}	8	30
8[c]	0.007	2×10^{-3}	3	75
9[d]	0.007	2×10^{-3}	3	85
10[e]	0.01	2×10^{-3}	8	0

[a] Determined by integration of the signals in GC chromatograms.
[b] Reduction of nitrobenzene without TiO_2.
[c] In 2-propanol.
[d] In methanol.
[e] In the dark.
[f] (8 am–4 pm, sunlight intensity between 80 and 10×10^3 Lux).

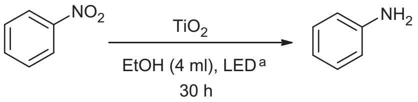
nitrobenzene was obtained with 0.005 g of the photocatalyst (Table 1, entry 2). Increasing amounts of TiO_2–P25 led to a significant enhancement of the photoreduction: 80% conversion using 0.007 g in 3 h, and 100% using 0.01 g in 1 h (Table 1, entries 3 and 4).

Next, we investigated the effect of increasing the concentration of nitrobenzene on the conversion. The results showed a quantitative conversion (100%) for 0.02 mmol nitrobenzene using 0.01 g TiO_2 after irradiation for 1.5 h. The results also showed neither irradiation alone nor the catalyst without light irradiation afforded any conversion of nitrobenzene (Table 1, entries 1 and 10). It is also known that the alcohol solvent is a sacrificial reagent, the electron hole in the valence band of an excited semiconductor transfer to alcohol. This photocatalytic reaction of nitrobenzene with TiO_2 was investigated in solvents such as methanol and isopropanol with irradiation for 3 h and the results are given in Table 1 (entries 8 and 9). There was no significant difference between ethanol and methanol, so we used ethanol owing to its low cost and toxicity.

Recently, visible light emitting diodes (LED) sensitized by low power have been applied as an attractive means to initiate photocatalytic reactions. Several advantages are associated with the use of LED lamps as a light source such as high photon efficiency, low voltage of electricity, and power stability.[14] Due to the high importance and advances in the application of visible light in photocatalytic reactions, we studied the reduction of nitro compounds using LEDs. The reduction of nitrobenzene under blue light LED (4×3 W) irradiation at an initial concentration of 2×10^{-3} mmol was examined using TiO_2–P25 over 30 h. We observed that 45%, 100%, and 100% conversions of nitrobenzene (2×10^{-3} mmol) were obtained when using 0.05 g, 0.08 g, and 0.1 g of TiO_2–P25, respectively (Table 2, entries 2–4). The photoreduction was also investigated for 2×10^{-2} mmol of nitrobenzene using 0.1 g of TiO_2–P25. The result showed that the efficiency of the reduction was decreased when the concentration of nitrobenzene increased (Table 2, entry 5). In general, the observations clearly confirm the beneficial role of TiO_2–P25 under LED irradiation in the reduction of nitrobenzene (Table 2).

Next, we investigated the effect of the TiO_2–P25 amount on the conversion of nitrobenzene under solar light and LED irradiation. The analysis revealed that high conversions of nitrobenzene were possible using solar light and low amounts of TiO_2–P25 (Fig. 1). The trend observed with solar light and TiO_2–P25 was found to be more efficient than LED. This is most likely due to the high intensity and UV absorption of solar light.

Table 2
Photoreduction of nitrobenzene to aniline in the presence of TiO_2–P25 using LED



Entry	TiO_2 (g)	Nitrobenzene (mmol)	Conversion[b] (%)
1[c]	0	2×10^{-3}	0
2	0.05	2×10^{-3}	45
3	0.08	2×10^{-3}	100
4	0.1	2×10^{-3}	100
5	0.1	2×10^{-2}	15
6[d]	0.1	2×10^{-3}	0

[a] Four blue LEDs with 3 W electrical power, 80 Lumens.
[b] Determined by integration of the signals in GC chromatograms.
[c] Reduction of nitrobenzene without TiO_2.
[d] In the dark.

Kisch has proposed that a photocatalyst concentration around the plateau onset should be selected in order to ensure optimal light absorption.[15] Only in this case is a comparison of apparent quantum yields or rates of various photocatalytic reactions meaningful. Therefore, we selected 0.01 g and 0.08 g as the optimum amounts of TiO_2–P25 for solar and LED conditions respectively. The results (Tables 1 and 2) revealed the high photocatalytic efficiency of TiO_2–P25 under visible light. After optimization of the reaction conditions for both solar light and LEDs, the substrate scope was investigated. Table 3 summarizes the results for the photoreductions of nitro compounds using both LED and solar light. In general, the products obtained via LED irradiation were similar to when using solar light (Table 3), but the photoactivity of TiO_2 was found to be higher in the presence of solar light compared to blue light LEDs.

Nitro aromatic compounds possessing functional groups such as carbonyl, cyano, and halide were reduced selectively into their corresponding amines (Table 3, entries 4–7 and 9). 1,4-dinitrobenzene and 1,2-dinitrobenzene gave both nitroaniline and diamine (Table 3, entries 2 and 3). We found that 2-methoxynitrobenzene has higher conversion under solar light irradiation than with LEDs (Table 3, entry 11). Nitromethane failed to react under the experimental conditions. Nitromethane is weak electron acceptor compared to nitrobenzenes,[16] this discrepancy is obvious in the

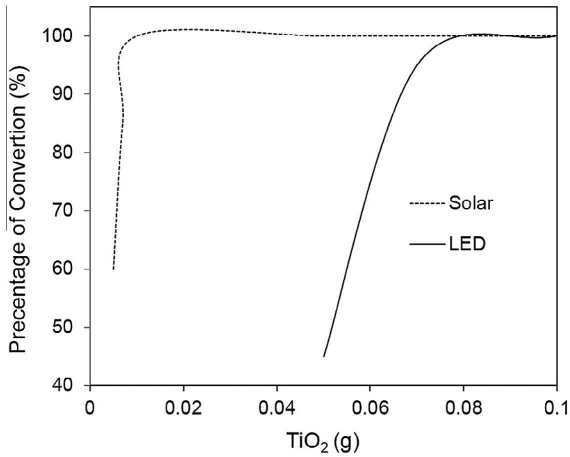
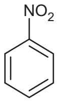
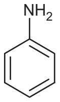
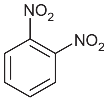
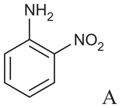
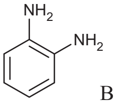
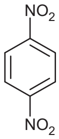
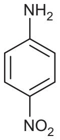
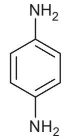
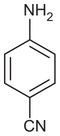
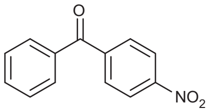
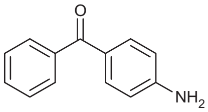
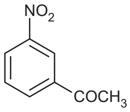
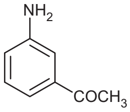
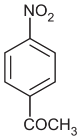
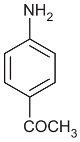
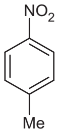
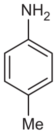
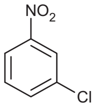
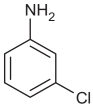
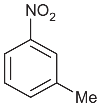
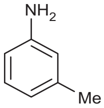
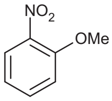
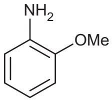


Figure 1. Effect of the TiO_2 amount on the photocatalytic conversion of nitrobenzene. Reaction conditions: nitrobenzene (2×10^{-3} mmol) in ethanol (4 mL) under LED irradiation for 30 h, solar light (1–6 h).

Table 3
Photoreduction of nitrobenzene derivatives using TiO_2–P25 under blue light LED or sunlight irradiation

Entry	Nitro compound	Product		Solar light[b]		LED[c]
				Yield[a] (%)	Time (min)	Yield[a] (%)
1				55	90	70
2		 A	 B	A: 55 B: 30	90	A: 70 B: 25
3		 C	 D	C: 60 D: 30	120	C: 50 D: 25
4				100	60	100
5				100	75	100
6				100	45	100
7				100	75	100
8				90	240	60
9				100	180	75
10				80	240	55
11				85	210	25
12	CH_3NO_2	–		0	480	0

[a] GC yield.

[b] Reaction conditions: nitro compound (2×10^{-2} mmol), TiO_2 (0.01 g), EtOH (4 mL), and irradiation with solar light (10 am–4 pm, sunlight intensity between 80 and 10×10^3 Lux).

[c] Reaction conditions: nitro compound (2×10^{-3} mmol), TiO_2 (0.08 g), EtOH (4 mL), and irradiation with four blue light LEDs (3 W electrical power, 80 Lumens), 30 h.

photoreduction process using TiO_2–P25. The results indicate that solar light and LEDs are efficient light sources for the photoreduction of nitroarenes by TiO_2–P25 without addition of a dye-sensitizer or additive.

We also investigated the recycling of the TiO_2–P25 photocatalyst from the reaction mixture of nitrobenzene. The catalyst was successfully reused in four consecutive runs and showed only a slight decrease of the catalytic activity after each recycling.

Next, we examined the efficiency of TiO_2–P25 under visible light irradiation. The UV–Vis absorption spectra of TiO_2–P25 and emission of blue LEDs are shown in Figure 2. The emission spectrum overlaps with a part of the UV–Vis absorption spectrum

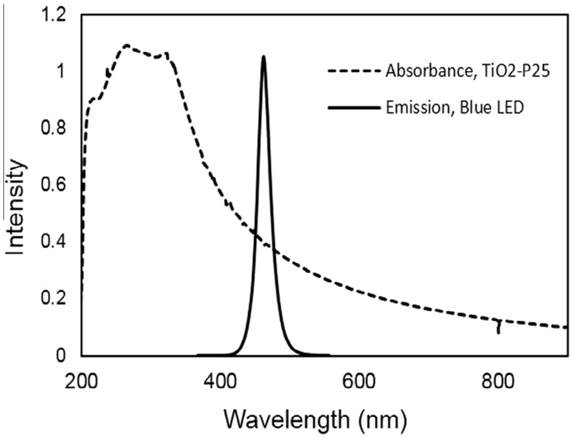


Figure 2. UV–Vis absorption spectrum of TiO_2–P25 and the emission spectrum of the blue LED lamp.

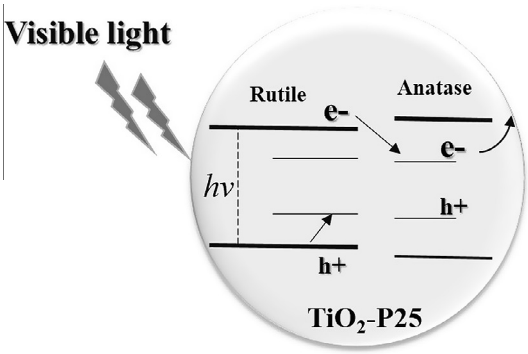


Figure 3. Schematic illustration of a rutile antenna and charge transfer between anatase and rutile in TiO_2–P25.

of TiO_2–P25. It enables TiO_2–P25 to reveal photocatalytic properties under high intensity of blue light LED lamp during long reaction time.

Results showed the efficiency of the TiO_2–P25 (anatase/rutile) for its photoactivity in visible light. The junction between anatase and rutile phases exhibit high rate of the charge separation in comparison to pure phases.[4] Gray and Thurnauer reported, the presence of small rutile crystallites creates a structure where rapid electron transfer from rutile to lower energy anatase lattice trapping sites under visible illumination leads to a more stable charge separation and the photoactivity of TiO_2–P25 in visible light (Fig. 3). The rutile phase for TiO_2–P25 acts as an antenna to extend the photoactivity into visible wavelengths.[17]

In conclusion, the use of TiO_2–P25 enables efficient reduction of nitroarenes under visible light irradiation. This process has significant advantages, for example: (a) uses energy efficient blue light LEDs or direct sunlight, (b) it does not require the use of a dye or additive, (c) mild ambient conditions, (d) selective and clean conversion of nitrobenzene derivatives. Therefore, this process might be useful as a method for the sustainable synthesis of anilines from nitroaromatic compounds.

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13. *Photocatalytic synthesis of aromatic amines.* Photocatalytic reactions were carried out in a round bottomed Pyrex flask and irradiated using four high power blue light LEDs 3 W lamp or by solar light under magnetic stirring at room temperature. Reaction conditions with solar light: the reduction of the aromatic nitro compounds (0.02 mmol) was carried out in the presence of TiO_2–P25 (0.01 g) in EtOH (4 mL) with irradiation for 1–4 h. Reaction conditions with LED irradiation: the reduction of aromatic nitro compounds (0.002 mmol) was carried out in the presence of TiO_2–P25 (0.08 g) in EtOH (4 mL), with irradiation for 30 h. While stirring, the mixture became heterogeneous as the reaction progressed. The product yields were determined by gas chromatography monitoring.
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