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Photocatalytic Synthesis of Anilides from Nitrobenzenes under Visible Light Irradiation: 2 in 1 Reaction

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Abstract:

An efficient method has been developed for the synthesis of a series of anilides *via* a two in one reaction of nitrobenzenes with anhydride in the presence of TiO_2 as a nanocatalyst and photocatalyst under sunlight or blue LED irradiation. In this method simultaneously, nitrobenzenes convert to the corresponding anilines *via* photocatalytic reduction on the TiO_2 surface, and a condensation of aniline with the anhydride performed on the Lewis acid site of the TiO_2 surface. Interestingly amidation step leads to the promotion of better reaction and good selectivity in reduction of nitrocompounds. This method is simple, rapid, high yield, and green.

Keywords: Two in one reaction, Photocatalysis, Anilide. Visible light

Introduction

Anilide and its derivatives occupy pivotal positions in organic synthesis and synthesis of biologically and pharmaceutically active compounds [1-4]. Generally, the amides are produced through the reaction of a carboxylic acid or ester with an amine. Lately, one-pot reaction has become one of hot topics in green chemistry because it eliminates isolation of unstable intermediates and reduces waste production [5-8]. The conversion of nitroarenes to their corresponding acetanilides in a one-pot reaction is an important transformation in organic chemistry. As nitrobenzenes are readily available industrial chemicals, it is more efficient to start directly from the nitrocompound rather than to start from the corresponding amine or isocyanate [9]. In general, direct conversion of nitroarenes to acetanilides are carried out by iron powder with acetic acid [10], Pt nanoparticle ZrO₂ and acetic anhydride [11], molybdenum hexacarbonyl/acetic acid [12], and also anilides have been obtained either *via* nickel [13] or rhodium [14] or platinum [15] catalyzed carbonylation of nitroarenes. However, 50 to 100 atm CO required in each case.

In the last decades, the increasingly serious energy crisis has led to an aggressive search for conversion of light energy into chemical energy by photocatalysis processes. [16-25] The Design of heterogeneous photocatalysis systems that encourage efficient one-pot synthesis is currently the focus of attention [26]. Photocatalyst TiO_2 is able to promote two different transformations in one-pot by employing both photocatalytic and catalytic actions.

Lately, some successful examples of photocatalytic reduction of nitro compounds have been reported. TiO₂ [27-29], and N-doped TiO₂ [30], have been investigated for the reduction of nitrobenzenes to their corresponding anilines under UV light irradiation. On the other hand, CdS/Graphene [31-32], dye-sensitized TiO₂ P25 [33-34], and PbBiO₂X [35] have been employed to reduce these molecules by visible light irradiation. Shiraishi *et al.* reported one-pot synthesis

of benzimidazoles and imines by simultaneous photocatalytic and catalytic reactions on $Pt@TiO_2$ nanoparticles [26, 36]. Also, Sa *et al.* reported one-pot photo-reductive N-alkylation of aniline and nitroarene derivatives with primary alcohols over Au–TiO₂ [37]. Considering that the solar energy is an endless resource, recently significant progresses have been seen in heterogeneous photocatalysis for the synthesis of organic compounds using sunlight. Swaminathan et al. reported one-pot photocatalytic syntheses of benzimidazoles and indazole by Pt-TiO₂, Ag-TiO₂, and TiO₂-P25 nanoparticles under UV and sunlight [38-39]. Lately our group have reported on activated amorphous TiO₂ coated into periodic mesoporous organosilicas (PMOs) [40], TiO₂-N Doped [41], β -Cyclodextrin / TiO₂ [42], and CdS [43-44] as efficient photocatalysts for synthesis of selective organic transformation under visible light. Moreover, we have reported that TiO₂-P25 showed selectivity of over 80% for reduction of a series of nitrobenzens under sunlight and LED irradiation [45]. TiO₂-P25, which is frequently used as a standard in heterogeneous photocatalysis, consists of a mixture of anatase (75%) and rutile (25%) phases. The junction between anatase and rutile phases in TiO₂-P25 exhibit high rate of the charge separation in comparison to pure phases. Also, the rutile phase for TiO₂-P25 acts as an antenna to extend the photoactivity into visible wavelengths [45].

Experimental

Photocatalytic synthesis of anilide. Photocatalytic reactions were carried out in a round bottom 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 aromatic nitro compounds (0.05 mmol) and anhydride (0.052 mmol) were carried out in the presence of TiO₂-P25 (0.03 g) in EtOH (10 mL) and irradiated under sunlight for 1-4 h. Reaction conditions with blue LED irradiation: aromatic nitro compounds (0.002 mmol) and anhydride (0.0025

mmol) were carried out in the presence of TiO_2 -P25 (0.08 g) in EtOH (4 mL), and irradiated by four high power blue light LEDs 3 W lamp for 30 hours. While stirring, the mixture became heterogeneous as the reaction progressed. The product yields were determined by gas chromatography monitoring. The structure of products were confirmed by NMR (see ESI⁺).

Results and Discussion

In continuation of our work on visible light photoreduction of nitroaromatic compounds using sunlight and blue LED irradiation [45], in order to develop and improve this method, we present a strategy for one-pot synthesis of anilides using nitrobenzens and anhydride as the reactants and TiO₂-P25 nanoparticles as a heterogeneous catalyst at room temperature under visible photoirradiation. According to the best of our knowledge, the photoamidation of nitro compounds and anhydride under blue LED lamp irradiation using TiO₂-P25 has not been addressed before.

Initially, the photosynthesis of *N*-phenylacetamide using TiO₂-P25 was investigated as a model reaction, and the results are shown in Table 1. The results of this experiment showed that by employing an ethanol solution containing nitrobenzene (0.02, 0.05, and 0.1 mmol) and acetic anhydride (0.022, 0.052, and 0.12 mmol) with TiO₂-P25 (0.01, 0.03, and 0.05 g) under argon and irradiation sunlight, *N*-phenylacetamide is obtained at 100% yield in a full conversion (Table 1, entries 1-3). The results have shown that *N*-phenylacetamid can be synthesized efficiently without the addition of a base or an additive [47]. Under the same reaction conditions, we found that the reduction of nitrobenzene in the absence of acetic anhydride gives selectivity with 55% yield, while in its presence it shows 100% yield (Table 1, entries 2 and 6). This result suggested that one-pot reaction causes a promotion of photoreduction of nitrobenzene with amidation step.

The reaction is initiated by photoexcitation of TiO_2 , producing electron (e⁻) and positive hole (h+) pairs under visible light. The (e⁻) reduces nitrobenzene to aniline and EtOH is oxidized by the hole. The catalytic condensation of the formed aniline and anhydride on the Lewis acid site of TiO₂ [26, 48] produces *N*-phenylacetamide (Scheme 1).

Please, insert Scheme 1, here.

The catalytic condensation of aniline with anhydride on the Lewis acid site of TiO_2 is confirmed by the reaction of aniline with acetic anhydride in at 298 K. As results shown, the absence of catalyst gives *N*-phenylacetamide with 10% yield, while in the presence of TiO_2 shows 80% yield, indicating that this catalyst promotes condensation (Table 1, entries 4 and 5). Under the above optimized conditions (Table 1, entry 2), various anilides were synthesized in the condensation reaction of a series of nitrobenzenes with anhydrides using TiO_2 -P25 under sunlight. The obtained results are summarized in Table 2.

Nitrobenzene containing functional groups (CN, OMe, NO₂, and COCH₃) with acetic anhydride gave the corresponding *N*-phenylacetamide in excellent yields (Table 2, entries 3 and 6-10). This method was also applied to the one-pot synthesis of the *N*-phenylbenzamide of benzoic anhydride (Table 2, entries, 2, 5, and 8). It is also possible to carry out this reaction for synthesis of *N*-phenyl, 3-methylbenzamide of 3-methylbenzoicanhydride in 100% yield (Table 2, entry 4). Thus, a series of anilides were synthesized using the conditions reported herein.

Please, insert Table 1, here.

Corresponding to, recently visible light emitting diodes (LED) sensitization with a low power is an attractive means to initiate photocatalytic reactions. Several advantages are associated with the use of LED lamps as a light source. For example, high photon efficiency, need low voltage of electricity, power stability, emit broader spectral wavelength [49].

In continuation, according to our previous report on photoactivity TiO_2 -P25 under blue LED, we were encouraged to turn our attention to the use of blue LED for one-pot photosynthesis of anilides.

Please, insert Table 2, here.

Interestingly, our investigations showed that the photocatalytic conversion of nitrobenzene and acetic anhydride to *N*-phenylacetamide could be carried out successfully by using TiO_2 -P25 under blue LED with high yield (Table 1, entry 7). We also found that high selectivity reduction of nitrobenzene is observed in the presence of acetic anhydride than photoreduction nitrobenzene in its absence (Table 1, entries 7 and 9). This result suggested that one- pot reaction led to the promotion of better reaction and good selectivity (Table 1, entry 7). After optimizing the reaction conditions a variety of nitrobenzenes and anhydrides were reacted successfully under blue LED. (Table 2)

Nitrobenzene containing chemical functional groups, which are often prone to either oxidation or reduction (e.g., carbonyl, cyanide, and methoxy), were found that gave anilide with good selectivity (Table 2, entries 3, 7, 8, and 10). Comparing these results with our previous report [45], we saw an increase in selectivity reduction of nitro compound (Table 2 entries 10 and 11). These results confirm that one-pot reaction forms an efficient and selective condition for synthesis of anilides.

In summary, the presented results propose that nano TiO_2 -P25 photocatalyst can be used for the synthesis of anilides from nitrobenzene and anhydride in one-pot reaction with high yield under sunlight or blue LED irradiation. Photocatalyst TiO_2 is able to promote two different transformations in one-pot by employing both photocatalytic and catalytic actions on the TiO_2

surface. The one-pot reaction leads to both an enhancement of selectivity and yield of products. According to 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. Therefore efficient synthesis anilide under blue LED, has the great potential to be used as a sustainable method for anilide photosynthesis. The reported approach is facile, mild, green, and high yield.

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† Electronic Supplementary Information

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Captions

Scheme 1. Synthesis of N-phenylacetamide from nitrobenzene and acetic anhydride using TiO₂-P25 under visible light.

Table 1. Photosynthesis of N-phenylacetamid from nitrobenzene and acetic anhydride in the presence of TiO₂- P25 under sunlight and blue LED irradiation.

Table 2. Photosynthesis of anilides from nitrobenzenes and anhydride in the presence of TiO₂- P25 under sunlight and blue LED irradiation.

A COLORINA

	Ň	NO_2 O O O O EtC	O TiO ₂ -P DH, Argon, ligh	25 >	NHCMe		21	
Entry	Nitrobenzene (mmol)	Acetic anhydride (mmol)	$TiO_{2}(g)$	EtOH (ml)	Light	Time (h)	Conversion (%)	Select (%) ^a
1	0.02	0.022	0.01	4	*	1	100	100
2	0.05	0.052	0.03	10	*	2	100	100
3	0.1	0.12	0.05	20	*	4	100	100
4 ^b	0.02	0.022	-	4	-	10	10	
5°	0.02	0.022	0.01	4	-	10	80	
6 ^d	0.05	0	0.03	10	*	4	100	55
7	0.002	0.0025	0.08	4	LED	30	100	100
8	0.005	0.0055	0.1	4	LED	48	35	18
9 ^d	0.002	0	0.08	4	LED	30	100	70

Table 1. Photosynthesis of *N*-phenylacetamid from nitrobenzene and acetic anhydride in the presence of TiO₂- P25 under sunlight and blue LED irradiation.

^{a)} Reaction conditions room temperature (25-35 °C) and sunlight irradiation (intensity =90–100 × 10³ lux). Selectivity= $c_p/(c_{r0}-c_r)$ 100%, c_{r0} : the initial concentration of nitrobenzene; c_r : the concentration of nitrobenzene during the reaction; c_p : the concentration of the product during the reaction. GC yield based on an internal-standard method. ^(b) Aniline with acetic anhydride in the absence of TiO₂. ^(c) Aniline with acetic anhydride in the presence of TiO₂. ^(c) Aniline with acetic anhydride in the absent the acetic anhydride.

				Solar light ^b		LED °
Entry	Nitrocompound	Anhydride	Product	Time(h)	Yield (%) ^a	Yield (%) ^a
1	NO ₂		A Office A	2	100	100
2	NO ₂	Ph O Ph	B	2.5	100	100
3	O ₂ N CN		C C	1.5	100	100
4	NO ₂	Ç İÇ	D	3	100	80
5	O ₂ N NO ₂	Ph O Ph	O ₂ N E	2	80	75
6	Me NO2		Me NHCCH ₃	3	100	85
7		<u>L</u>	G	1	100	100
8	NO2 COCH3	Ph O Ph	H CCCH3	1	100	100
9	Me NO2		I Ne O NH CH ₃	2.5	100	75
10	NO ₂ OMe		J OMe	2	90	70
11	NO ₂ OMe	-	NH ₂ OMe	3.5	80	45

Table 2. Photosynthesis of anilides from nitrobenzenes and anhydride in the presence of TiO_2 - P25 under sunlight and blue LED irradiation.

^a GC yield, ^b Reaction conditions: nitro compound (0.05 mmol), anhydride (0.052 mmol), TiO₂ (0.03 g), EtOH (10 ml) and irradiation with sunlight (10 am-2 pm, sunlight intensity between 90-10×10³ Lux). ^c Reaction conditions: nitro compound (2×10^{-3} mmol), anhydride (2.5×10^{-3} mmol), TiO₂ (0.08 g), EtOH (4 ml) and irradiation with four blue light LEDs (3 W electrical power, 80 Lumens), 30 h.





- Anilide was synthesized from nitrobenzene under sunlight or blue LED irradiation. •
- Photocatalyst TiO₂ is able to promote two different transformations. •
- The 2 in 1 reaction leads to enhancement of selectivity and yield of products. •

Acceleration