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β-Cyclodextrin/TiO₂: Green Nest for Reduction of Nitroaromatic Compounds

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In this paper, highly efficient photocatalytic reduction of nitroaromatic compounds was investigated using β-cyclodextrin (β-CD) and commercial nano TiO₂ as a host–guest system in water under sunlight irradiation. The nitroaromatic compounds solubilized in water through encapsulation in β-CD formed an inclusion complex which was attached to TiO₂ under sunlight irradiation. This 'guest-host system' that we
10 call "Green Nest" showed high efficiency for the reduction of nitro compounds to the corresponding amines, and more interestingly, one pot reductive *N*-formylation and *N*-acylation from nitroaromatic compounds can be carried out in the presence of triethyl orthoformate, acetic and benzoic anhydride. The β-Cyclodextrin/TiO₂ were characterized by transmission electron microscopy (TEM), UV-Vis spectra, thermal gravimetric analysis (TGA), Brunauer–Emmett–Teller (BET), UV-Vis diffuse reflectance
15 spectroscopy (DRS), and Raman spectroscopy.

Introduction

The concept of photochemistry as green technology is more than a century old. Sunlight as an unending and natural source could be a key component of the industry in the
20 future. This delegates a key role to photochemistry in future industrial processes. Despite the advent of artificial light sources and other leaps in technology, it is not unexpected that mankind turns to the sun as a free energy and light source for organic photochemistry and true 'green' route in
25 organic synthesis[1]. On the other hand, selective transformation of organic compounds using metal oxide semiconductors as mediator is one of the hot challenging methods in organic synthesis from the viewpoints of renewable energy or environmental applications[2]. Owing to
30 its biochemical compatibility, low cost, non-toxicity, optical and electronic properties and high photo-activity, the main interest among the various metal oxide semiconductors has been shifted to TiO₂[3]. Also, because of its excellent photo-chemical properties, TiO₂ plays a crucial role in a wide range
35 of important redox organic transformations, especially in selective reduction of nitro compounds[4]. Up till now, a wide variety of traditional methods has been developed for the reduction of nitro compounds to corresponding amines using hazardous reagents but they show poor efficiency[5]. To
40 overcome these limitations, many attempts have been made at designing new sustainable and environmentally acceptable photocatalytic reductive methods for the nitro group without degrading the conjugated structure in a process that is direct and mild and could also allow its transformation to other
45 functional groups. In recent years, a great deal of attention has been paid to the photocatalytic transformation of nitro compounds into the amine, imine and benzeimidazole functionalities based on TiO₂[6].

Compared to other organic solvents, water is a green,
50 available, and more importantly cheap and safe solvent and has therefore attracted a lot of attention in organic synthesis[7]. In contrast to the popularity of 'TiO₂ nanoparticles' in photocatalytic transformations in organic solvents, their use in selective organic synthesis in water is still not quite widespread
55 because of some of the limitations or disadvantages associated with the low solubility of substrates and over-oxidation of organic compounds which are a result of the oxidant species produced (such as $^.OH$ and $O_2^{.-}/HO_2^.$) in a photocatalytic process[8]. Thus, overcoming these impediments in water is worth
60 highlighting in photocatalytic synthesis. Recently, molecular host–guest complexes have provided one of the promising routes to adsorption of organic molecules on the surface of metal oxide semiconductors in order to improve the interaction of organic substrates with the photocatalitically active sites when water is
65 used as the reaction medium. Quite recently, Nichols et al. demonstrated that cyclodextrin-TiO₂ nanowires with an open and porous structure show self-assembly capability as a result of simulated sunlight irradiation in water[9]. Their marine sponge-like structure, with high porosity and surface area, played a host role
70 for easy encapsulation of organic compounds. Recent studies indicate an increased photocatalysis performance when the surface of the TiO₂ particles has been modified with the host molecules such as β-cyclodexterin[10]. In other words, the modification of TiO₂ with cyclodexterin through interactions
75 between the hydroxyl groups of β-CD and TiO₂ draw the organic molecules near the surface of photocatalyst to enhance their interaction and also results in an increase in the photocatalytic redox ability of TiO₂[11]. In continuation of our effort to design novel systems for photocatalytic organic transformations[12], in
80 this work we wish to present a highly efficient and green photocatalytic system for selective reduction of the nitro group

under sunlight irradiation based on *in-situ* modification of TiO$_2$ P25 with *β*-CD in water. We believe that *β*-CD can enhance the dispersion of TiO$_2$ in water, and together produce a 'host nano-reactor system', that we call the "Green Nest", in order to compensate for the low interaction of the organic nitro compound with the surface of TiO$_2$ in an aqueous medium. On the other hand, *β*-CD can promote the charge transfer rate from the photo-excited TiO$_2$ to the electron acceptor guest molecule. Thus, it is assumed that the hydrophobic inner cavity of *β*-CD is a nano-photo-reactor in this system. To do this, first nitro compounds were added to the aqueous solution of *β*-CD, then this inclusion complex of *β*-CD-nitro compound was adsorbed on the surface of Titania by sunlight irradiation, and the reduction of the nitro group to amine function was carried out in the hydrophobic cavity of *β*-CD. Since, amide derivatives such as formanilides are valuable intermediates in organic synthesis[13] we attempted to expand this proposed photocatalytic system to one-pot reductive *N*-formylation and *N*-acylation.

Results and discussion

β-CD is well-known host molecule for organic compounds due to its hydrophobic cavity. The hydroxyl groups in inclusion complex of organic compound/*β*-CD make it soluble in water[14]. Besides, recent research in the development of high efficiency photocatalysis processes shows that the presence of a host molecule such as *β*-CD is very profitable. With this in mind, nitro compounds were added to a solution of *β*-CD, and then this inclusion complex of *β*-CD-nitro compound was adsorbed on surface Titania by sunlight irradiation. Initial experiments were carried out with a water solution containing *β*-Cyclodextrin (0.1 mmol), 3-nitro acetophenone (0.1 mmol), and commercial TiO$_2$ (30 mg) under sunlight irradiation for 4 h (Table 1, Entry 1) resulting in a 49% conversion according to gas chromatography (GC). Addition of ammonium formate or oxalic acid as a hole scavenger under the same conditions was investigated (Table 1, Entries 5, 2). No conversion of 3-nitro acetophenone was observed without TiO$_2$ or dark condition (Table1, Entries 6, 7).

Table 1 Photoreduction of 3-nitroacetophenone using *β*-CD-TiO$_2$ in various conditions under sunlight irradiations.
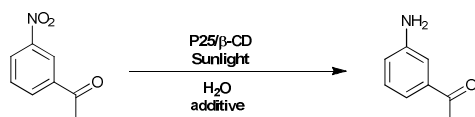
| Entry	Additive	Time(h)	Yield (%)
1	-^{b}	4	49
2	Oxalic acid	1	100
3	Potassium iodide	3	46
4	Sodium sulfate	3	31
5	Ammonium formate	3	95
6	-^{c}	6	-
7	-^{d}	6	-

^{a} GC yield , Luximetry 10-80× 10^3 Lux. ^{b} without additive, ^{c} without TiO$_2$ P25^d in dark condition.

β-CD can play a more crucial role in the above mentioned reaction in water. First, *β*-CD is the host molecule for the nitro compounds and increases solubility. This fact can be easily observed through the disappearance of nitrobenzene in water in a separate test.

Also, it was reported that the formation of a host-guest complex between *β*-CD and organic compounds in water, affect the UV-vis properties [15]. Therefore, as can be seen in Fig 1, the intensity of UV-vis spectra of an aqueous solution of *p*-Nitro phenol increases with the addition of a *β*-CD solution resulting in the formation of a host-guest complex.

Also using polyethylene glycol/water, EtOH/water and prototype polyhydroxyl carbohydrates such as glucose showed that although the solubility of nitrobenzene increased the conversion and product selectivity decreased. An increase in the visible-light activity of TiO$_2$ can be achieved in combination with *β*-CD because of hydroxyl group's interaction with h$^+$ on the surface of photocatalyst [16]. To show this fact, the above reaction was carried out in the absence of *β*-CD. It was observed that the reduction of nitrobenzene in water without *β*-CD was not a selective and clean reaction with a conversion of 30% after 3 h. On the other hand, we used a mixture of water and ethanol or poly ethylene glycol instead of *β*-CD to increase the solubility of the nitro compounds in water. Nevertheless, a mixture of products for this condition was observed. *β*-CD molecule built up from glucose units, that can also diminish electron-hole recombination rate [17]. To show importance of hydrophobic cavity in *β*-CD, glucose/TiO$_2$ was used in similar manner to *β*-CD/TiO$_2$. The low yield of arylamine confirmed the crucial role of *β*-CD cavity in high performance of photocatalytic reduction of nitroaromatic compounds in water. Also, in a model experiment, changing the acidity of the mixture through attachment of *β*-CD to TiO$_2$ was measured and an increase of acidity from 7 (in the absence of *β*-CD) to 4 (in the presence of *β*-CD under sunlight irradiation) was observed. These *p*H changes can be due to the surface adsorption of the *β*-CD to TiO$_2$ particles and formation of the *β*-CD/TiO$_2$ composite in water under sunlight irradiation [18] (Scheme 1).
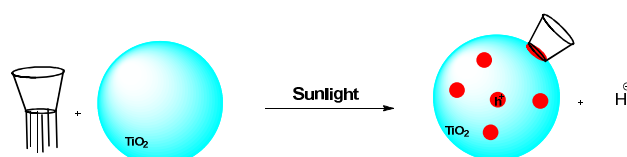
Scheme 1 *p*H enhancement of the *β*-CD -TiO$_2$ solution during sunlight irradiation results in deprotonation from a hydroxyl group of the CD molecules on TiO$_2$.
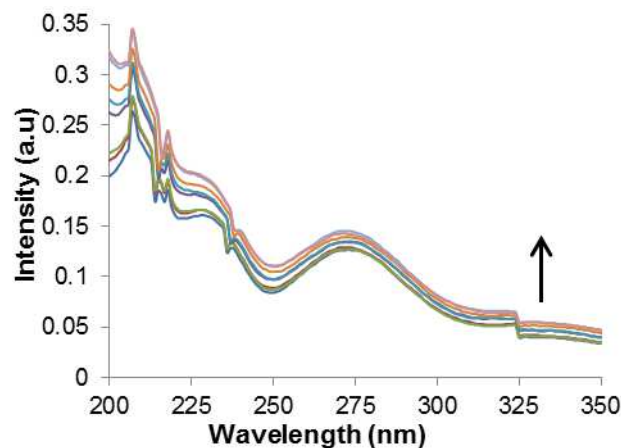
Fig.1 UV–vis absorption spectra of *p*-nitrophenol (1×10^{-4}M) in aqueous media and titration of this solution by *β*-cyclodextrin (1×10^{-3} M).

In next step, studies were extended with the reduction of different types of nitroaromatic including functional groups such as carbonyl, nitrile and halide using the *β*-CD/TiO$_2$ system in water under sunlight irradiation (Table 2). Several aromatic nitro compounds with the electron-donating or electron-withdrawing functional groups were reduced into the corresponding amines (Table 2, Entry 8-13). Consequently, the higher reduction conversion of the nitroaromatic compounds in the presence of electron-withdrawing groups was observed. High chemoselectivity of the reaction was showed with reduction of nitro functional group in the presence of other sensitive functional groups such as carbonyl, and nitrile that were remained intact along photocatalytic reduction reaction (Table 2, Entry 4, 11). Also, reduction of 1, 2-dinitrobenzene to corresponding diamine was carried out (Table 2, Entry 6). When the same reaction was used in a solution of ethanol /water (2/13 ml), benzimidazole was obtained with 88% yield (Table 2, entry 7). When the reaction carried out in more scale, 2 mmol of nitrobenzene, the product (aniline) was obtained in 83 % isolated yield after 12 h under solar light irradiation (Table 2, entry1[b]).

The mole ratio of nitro to ammonium formate is 1 to 3.2 and nitro to oxalic acid is 1 to 1.7. The ammonium formate and oxalic acid convert to ammonia, carbon dioxide or carbon dioxide during photocatalytic reaction respectively. We found that, in experimental control test, when the reaction carried out in the presence of excess amount of ammonium formate, amine product was obtained in quantitative yield after separation by extraction with EtOAc. The aqueous phase including excess of ammonium formate can be used for next reduction cycle without loss of the conversion yield (see supporting information, Scheme *S1*).

The important factors in the photocatalytic application in aqueous medium are the stability and reusability of the nanomaterial in the end of the reaction. To study this, the photocatalytic performance of *β*-CD/TiO$_2$ was investigated after four usages (Fig 2). At the end of each run, ethyl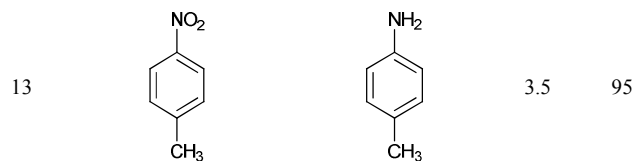 acetate was added to the aqueous mixture and sonicated for 5 min. The aqueous solution containing *β*-CD/TiO$_2$ nanoparticles was reused in the next run. A decrease in the photocatalytic efficiency can be due to the partial waste of photocatalyst during product separation. These results are consistent with the retention of the good photocatalytic activities of *β*-CD/TiO$_2$ after four usages.

**Table 2** Reduction of nitro compounds using β-Cyclodextrin/TiO$_2$ in water under sunlight irradiation

Entry	Substrate	Product	Time [h]	Yield [%][a]
1	nitrobenzene (NO$_2$)	aniline (NH$_2$)	3	100 (83)[b]
2	3-nitroacetophenone	3-aminoacetophenone	1	100
3	3-nitrochlorobenzene (Cl)	3-chloroaniline (Cl)	2	100
4	3-nitrobenzaldehyde (CHO)	3-aminobenzaldehyde (CHO)	1.5	92
5	4-nitro-N-phenylbenzamide (NHPh)	4-amino-N-phenylbenzamide (NHPh)	3	95
6	1,2-dinitrobenzene (NO$_2$, NO$_2$)	1,2-diaminobenzene (NH$_2$, NH$_2$)	3.5	95
7[c]	1,2-dinitrobenzene (NO$_2$, NO$_2$)	2-methylbenzimidazole (CH$_3$)	5	88
8	4-nitrobenzophenone (COPh)	4-aminobenzophenone (COPh)	2	100
9	4-fluoronitrobenzene (F)	4-fluoroaniline (F)	3	96
10	4-nitrophenol (OH)	4-aminophenol (OH)	4	89
11	4-nitrobenzonitrile (CN)	4-aminobenzonitrile (CN)	1.5	100
12	4-nitroacetophenone	4-aminoacetophenone	1.5	100
13	4-nitrotoluene (NO$_2$, CH$_3$)	4-methylaniline (NH$_2$, CH$_3$)	3.5	95

[a] GC yield using an internal standard (biphenyl) method unless otherwise stated. Reaction condition: nitro compounds (0.1 mmol), TiO$_2$ (30 mg), β-Cyclodextrin (0.1 mmol), water (15 ml) and oxalic acid (15 mg) or ammonium formate (25 mg) was degassed by Ar gas and irradiation with solar light. [b]The reaction carried out in 2 mmol of nitrobenzene in the following reaction condition: nitro compounds (2 mmol), TiO$_2$ (0.5 g), β-Cyclodextrin (0.8 mmol), water (60 ml) and ammonium formate (0.1 g), 12 h, under solar light irradiation, isolated yield. [c]For synthesis of benzeimidazole: In the same condition using mixture of ethanol (2 ml) and water (13ml). Daily sunlight (9 am– 3pm; sunlight intensity between 10-80× 10^3 Lux).
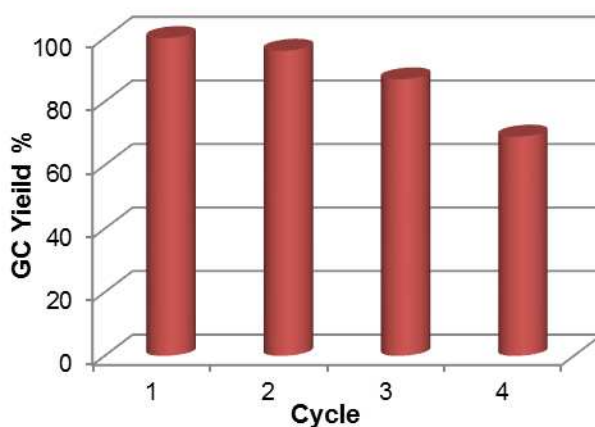

Fig. 2 Reusability and photocatalytic efficiency of the β-CD/TiO$_2$ aqueous solution for reduction of nitrobenzene under sunlight irradiation after 3 h.
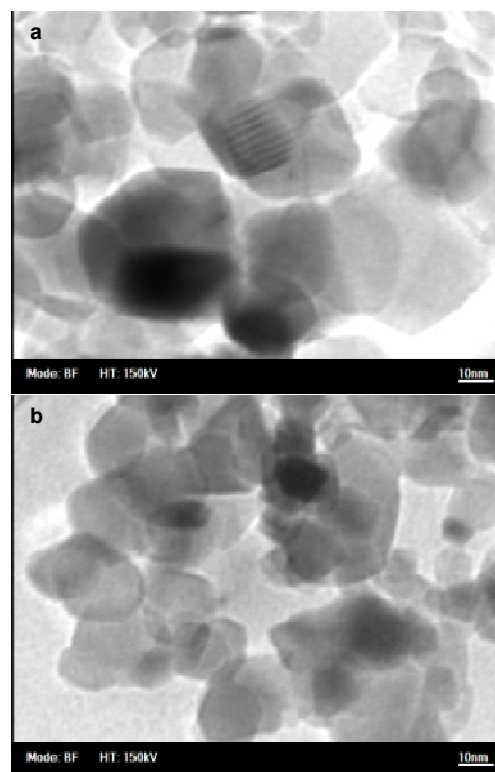
Scheme 2. TEM images of β-CD/TiO$_2$ (a) and TiO$_2$ (b)

Various characterizations of β-CD/TiO$_2$ confirm the presence of β-CD in surface Titania after 3h sunlight irradiation of the solution and β-CD. Figure S5 shows the thermal gravimetric analysis (TGA) of β-CD/TiO$_2$ after separation and washing
5 several times with water. From the TGA curve it was observed that around 4% CD in β-CD/TiO$_2$. Raman spectra show band located that 2800-3000 cm^{-1} (C-H) which is evidence of β-CD in β-CD/TiO$_2$ nano composite (Fig. S9 in supporting information). However, as presented in Scheme 2, there were no differences in
10 the lattice structure in TEM images of β-CD/TiO$_2$ and TiO$_2$. Considering the DRS analysis of β-CD/TiO$_2$ (Fig. S6 in the supporting information), the latter displayed a higher absorption in the visible light region than TiO$_2$. Also, a decrease in surface area of β-CD/TiO$_2$ compared to TiO$_2$ based on the BET method
15 can be attributed to the attachment of β-CD to surface Titania under sunlight irradiation (Table S1 in the supporting information).
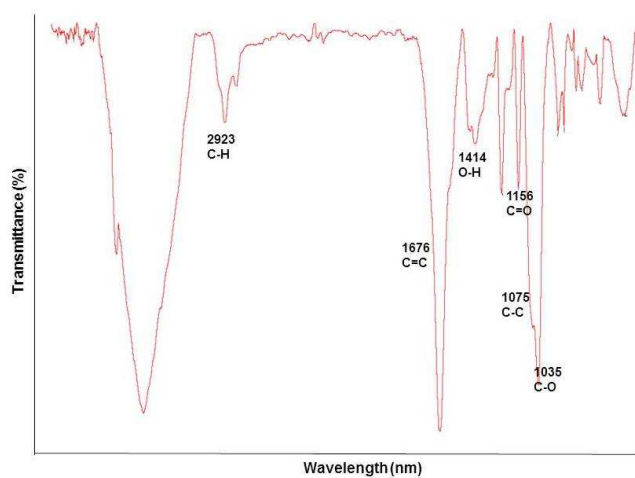
20 **Fig. 3** FT-IR Spectra of β-CD-TiO$_2$ hybrid nanoparticles

FTIR spectra analysis of β-CD/TiO$_2$ hybrid nanoparticles using TiO$_2$ as a reference was investigated (Fig 3). In comparison with P25 (Fig S11 in the supporting information), in TiO$_2$/β-CD the intensity increases at 3,400 cm^{-1}. This result can be due to the
25 presence of the O-H group's β-CD. Peak centred at 1,676 cm^{-1} was assigned as the stretching of the C=C bonds. Also, the absorption at 1,414 cm^{-1} was assigned to the O–H in-plane bending, while the antisymmetric C–O–C stretch was assigned at 1,156 cm^{-1}. The absorption at 1,030 cm^{-1} was assigned as the C–
30 O stretch vibrations [20].

Table 3. One-pot synthesis of amides from the photocatalytic reduction of nitro compounds using triethyl orthoformate or anhydride.

Entry	Substrate	Product	Time (h)	Yield (%)[a]
1	(acetic anhydride, H$_3$C-CO-O-CO-CH$_3$)	N-phenylacetamide	2.5	100
2	(benzoic anhydride, Ph-CO-O-CO-Ph)	N-(2-acetylphenyl)benzamide	1.5	91
3	(benzoic anhydride, Ph-CO-O-CO-Ph)	N-phenylbenzamide	3	97
4	(acetic anhydride, H$_3$C-CO-O-CO-CH$_3$)	N-(4-benzoylphenyl)acetamide	2	94
5	(acetic anhydride, H$_3$C-CO-O-CO-CH$_3$)	N-(4-methylphenyl)acetamide	3.5	100
6	CH(OEt)$_3$	N-phenylformamide	2	100 (66)[b]
7	CH(OEt)$_3$	N-(4-methylphenyl)formamide	3	94
8	CH(OEt)$_3$	N-(4-cyanophenyl)formamide	1	91
9	CH(OEt)$_3$	N-(4-benzoylphenyl)formamide	2.5	90
10	CH(OEt)$_3$	N-(4-hydroxyphenyl)formamide	4	89

[a] Isolated yields using column chromatography for *N*-acylation products
35 (1-5) and GC yields for *N*-formylation products (6-10). Reaction condition: nitro compounds (0.1 mmol), TiO$_2$ P25 (30 mg), β-Cyclodextrin (0.1 mmol), water (15 ml), ammonium formate (25 mg) and triethyl orthoformate (0.2 ml) or anhydride (0.12 mmol) under sunlight. Daily sunlight (9 am- 3 pm; sunlight intensity between 10-80×
40 10^3 Lux). [b] The reaction carried out in 2 mmol of nitrobenzene in the following reaction condition: nitro compounds (2 mmol), TiO$_2$ (0.5 g), β-Cyclodextrin (0.8 mmol), water (60 ml), ammonium formate (0.1 g), and triethyl orthoformate (4 ml), 12 h, under solar light irradiation.

In continuation we studied on a green, one-pot protocol for
45 further transformation of photocatalytic produced amines into valuable *N*-formylated and *N*-acylated amines in water (Scheme 3). Carboxylic anhydrides and triethylorthoformate were used as acylation and formyaltion agents. In this area, Lou et al. have reported the reductive
50 *N*-formylation of nitroarene compounds using Au-TiO$_2$ in the presence of ammonium formate at two temperatures

(room temperature and reflux condition) in CH_3CN as an aprotic solvent[21]. According to these findings, when an excess amount of ammonium formate was used in our method, no *N*-formylated product was detected after 5 h. Then, in the next attempt, triethylortho formate was used as a more active formalting agent. Interestingly, in the presence of triethylortho formate, high yield of the corresponding amide was achieved. Moreover, using carboxylic anhydrides as the acylation agent efficiently produced the corresponding amides too. As summarized in Table 3, various types of nitro aromatics including other functional groups were selectively transformed into their corresponding amide compounds in water. The photocatalytic system also showed excellent regioselective *N*-formylation of *p*-nitrophenol with very high yield (Table 3, Entry 10). As expected, when the reaction carried out in 2 mmol of nitrobenzene, the anilide was obtained in notable decreased isolated yield after 12 h.

To study the formylation step, in the control reactions, the same condition was used for the amine as the starting material, and the excellent yield of the corresponding formamide was obtained even in dark conditions, and in the absence of *β*-CD. This result demonstrated a high nonphotocatalytic activity of the formylation of amines. It's seemed that the formylation step had been carried out on the noncapsulated amine in *β*-CD. Therefore, to clarify this issue, the titration of *o*-nitro phenol and *o*-amino phenol with *β*-CD we were using UV-Vis data. As shown in Figures 3 and 4 (see supporting information), with the addition of the *β*-CD aqueous solution to *o*-nitro phenol and *o*-amino phenol, the UV-Vis intensity of *o*-NP increases more than *o*-AP because of the formation of the host-guest complex with *β*-CD in water. Thus, we suggest that the intrinsic physicochemical properties between amines (miscible) and nitro compounds (nonmiscible) caused the reduction of the nitro group in the hydrophobic cavity of *β*-CD and then *N*-formylation or *N*-acylation was performed in water.
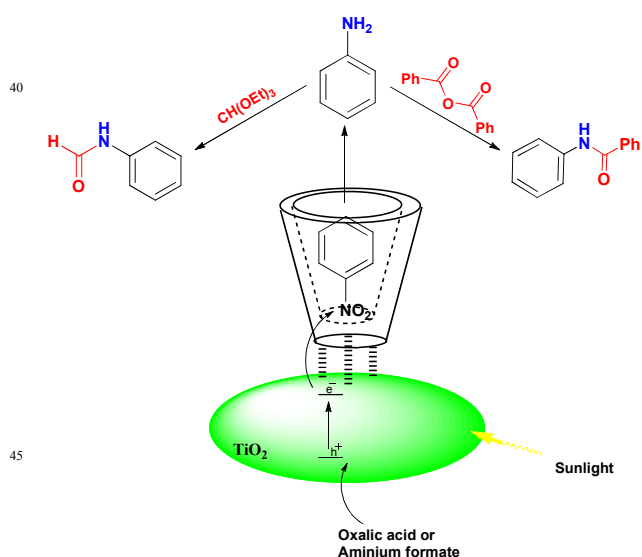
Scheme 3 One-pot *N*-formylation and *N*-acylation of photocatalytic produced amines through encapsulated nitrobenzene in *β*-CD under sunlight.

Conclusions

In this work we employed the self-assembly *β*-CD and commercial nano TiO_2 P25 under sunlight irradiation in water for green reduction of nitro compounds. This system shows a highly efficient, eco-friendly, clear and selective reduction of the nitro group into amines through the host-guest model. From the above mentioned result we suggest the encapsulation of guest molecules in inner *β*-CD cavities, followed by the binding of the subsequent host-guest complexes to the surface of TiO_2 nanoparticles. Interestingly, one-pot *N*-acylation and *N*-formylation of in situ prepared amines can be carried out in an aqueous medium using anhydride or triethyl orthoformate.

Experimental Section:

General procedure for the reduction of nitro compounds:

β-CD (0.1 mmol) was dissolved in water (15 ml) by warming to 60 $^\circ$C until a clear solution was formed. Nitro compounds (0.1mmol) were added to this solution and were sonicated for 10 min. Then, commercial TiO_2 (P25) (30 mg) and oxalic acid (15 mg) was added into a round bottom Pyrex flask (25 ml). The reaction mixture was degassed by Ar gas (20 min) and sealed with a septum. Afterwards, the flask was irradiated under stirring with sunlight according to the data in Table1. After the completion of the reaction, a suitable amount of $NaHCO_3$ were added *p*H to control the around 7 and the mixture was stirred at room temperature. The organic material was extracted with ethyl acetate. The organic phase was then dried using anhydrous $MgSO_4$. The reaction mixture was analyzed with Gas Chromatograph.

General procedure for one-pot *N*-formylation and *N*-acylation of the nitro compounds:

β-CD (0.1 mmol) was dissolved in water (15 ml) by warming to 60 $^\circ$C until a clear solution was formed. Nitro compounds (0.1mmol) were added to this solution and were sonicated for 10 min. Commercial TiO_2 (P25) (30 mg), ammonium formate (25 mg) and triethy orthoformate (0.2 ml) for formylation or anhydride (0.12 mmol) were added into a round bottom Pyrex flask (25 ml). The reaction mixture was degassed by Ar gas (20 min) and sealed with a septum. Afterwards, the flask was irradiated under stirring with sunlight according to the data in Table 3. The organic material was extracted with ethyl acetate. The organic phase was then dried (anhydrous $MgSO_4$), filtered, and the solvent was removed under vacuum. Pure products were obtained after recrystallization or by column chromatography on silica using the n-hexane and ethyl acetate mixture as an eluent (SiO_2; n-Hexane, EtOAc 5:1).

Acknowledgements

Notes and references

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† Electronic Supplementary Information (ESI) available: [It includes experimental details, ^{1}H NMR and ^{13}C NMR spectra of the synthesized compounds, UV-Vis spectra, TGA, Raman and, BET analysis]. See DOI: 10.1039/b000000x/

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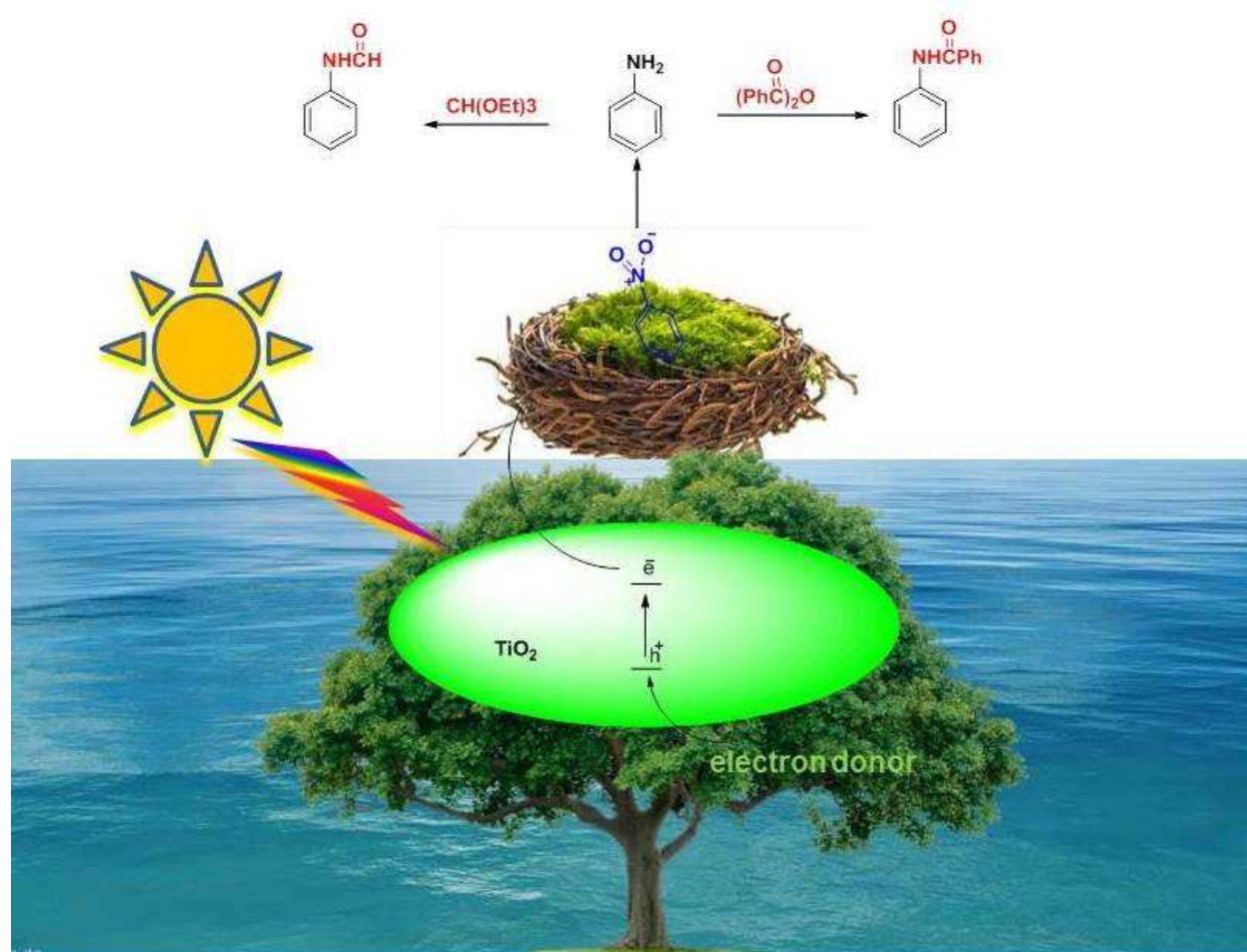21 X. B. Lou, L. He, Y. Qian, Y. M. Liu, Y. Cao, K. N. Fan. *Adv. Synth. Catal.,* 2011, **353**, 281.

Graphical Abstract

β-Cyclodextrin/TiO$_2$: Green Nest for Reduction of Nitroaromatic Compounds

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Highly efficient, eco-friendly and selective photocatalytic reduction of the nitro group into amines and one-pot *N*-acylation and *N*-formylation is reported through the "Green Nest" system.