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A Tandem Aerobic Photocatalytic Synthesis of Benzimidazoles by Cobalt Ascorbic Acid Complex Coated on TiO_2 Nanoparticles Under Visible Light

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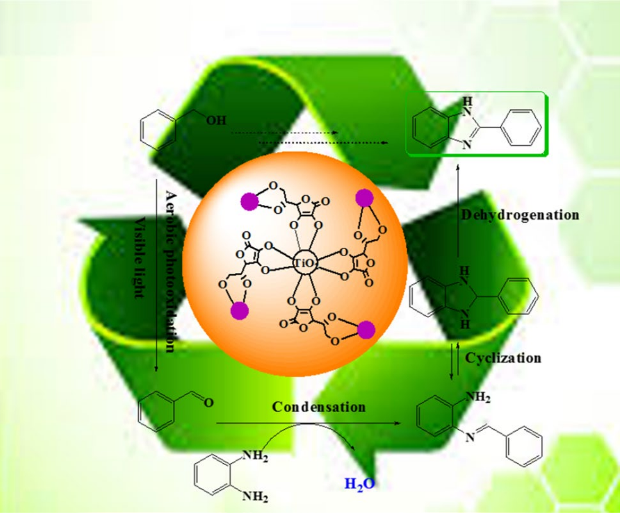
Abstract In this study, we developed methods for the one pot environmentally benign synthesis of benzimidazoles by cobalt ascorbic acid complex coated on TiO_2 nanoparticles via aerobic photooxidative cyclization reactions. Easy work-up procedure, reusability of the catalyst and scalable to the multi-mole scale, which is valuable for an industrial process make these catalytic systems highly attractive. Also, the combination of photocatalytic and catalytic reactions presented here may help to develop a new strategy towards the development of photocatalysis-based organic synthesis.

Graphical Abstract



Keywords Benzimidazole · Cobalt nanocatalyst · One-pot tandem synthesis · Photocatalysis · Aerobic photooxidation

1 Introduction

Achieving high synthetic efficiency and atom economy has been an important goal for development of synthetic organic chemists. Tandem reactions which complete several chemical transformations in one vessel, are a powerful strategy in which not only reduce the number of reaction steps, energy consumption and waste but also minimize the use of solvents and reagents [1]. So, these cascade reactions are sustainable green processes that illustrate the concepts of efficiency and atom economy.

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The photocatalysis of organic synthesis has become an important research area in photochemistry in the past two decades [2–4]. The photocatalytic reaction demonstrates the possibilities of converting light energy into chemical energy providing a new synthetic route [5, 6].

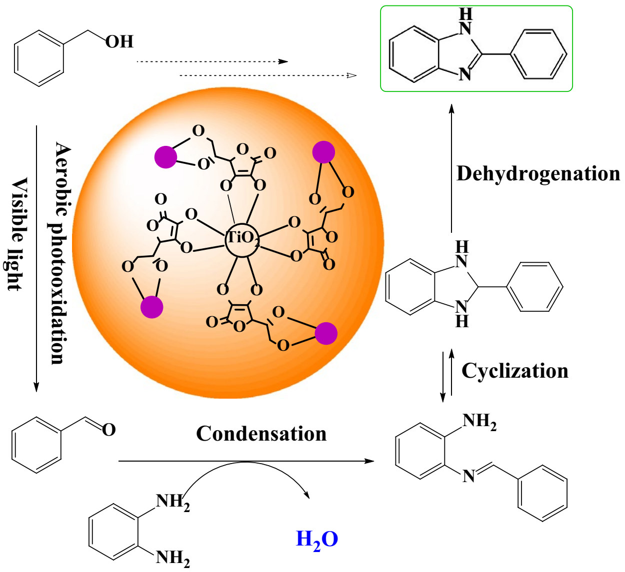
The title method in comparison to the commercially used synthetic methods, which involve long reaction times, expensive and hazardous reagents, and side product formation, is cost-effective, highly selective, rapid, and eco-friendly.

Benzimidazoles, which are known as important building blocks for the construction of pharmaceuticals, natural products, functional materials, and agrochemical compounds, have attracted much attention in organic synthesis in recent decades [7–48].

Among reported methods, the use of alcohols as starting materials is suitable alternatives for integrates considerations of economic viability and environmental integrity because of wide availability of alcohols [39–48].

In view of the above and during our research on development of heterogeneous nanophotocatalysts performance for organic synthesis in green conditions [49–54], recently we reported the selective aerobic benzylic C–H oxidation of alcohols and hydrocarbons by TiO_2/AA/Co nanohybrid in ethyl acetate [52]. In a continuous study, we envision a direct and green method for benzimidazols synthesis by aerobic oxidative cyclocondensation of alcohols and *o*-aminoanilines in visible light (Scheme 1).

This catalyst system involves photooxidation of alcohols to aldehydes followed by cyclocondensation with 1,2-phenylenediamine to afford benzimidazoles in one-pot operation with good to excellent yield.



Scheme 1 Aerobic oxidative cyclocondensation of alcohols and *o*-aminoanilines catalyzed by TiO_2/AA/Co nanohybrid in visible light

Various catalytic systems that enable one-pot organic transformations have been reported [39–48], but one-pot systems that combine photocatalysis and catalysis are limited [55, 56] Meanwhile, these systems use a homogeneous photocatalyst (photoredox catalyst) and an organocatalyst to effect the one-pot transformations.

2 Experimental

2.1 General Remarks

All chemicals were purchased from Merck and Fluka Chemical Companies. The FT-IR spectra were recorded on NICOLET system. TEM images were obtained by TEM instrumentation (Philips CM 10). Progresses of the reactions were monitored by TLC using silica-gel SIL G/UV 254 plates. NMR spectra were recorded on a Brucker Avance DPX 250 and 400 MHz instruments.

2.2 Preparation of TiO_2/AA/Co Nanohybrid (See Supporting Information) [52]

2.2.1 General Procedure for Synthesis of Benzimidazole from Benzyl Alcohols and o-Phenylenediamines

To a mixture of benzyl alcohol (1.2 mmol), 1,2-phenylenediamine (1 mmol) and NHPI (5 mol%) in a glass test tube (10 cm tall × 1 cm diameter) was added TiO_2/AA/Co nanocatalyst (0.06 mol%) and the reaction mixture was heated at 70 °C under air, visible light and solvent free conditions. The reaction progress was monitored by TLC. After 3 h, ethanol (5 mL) was added to the mixture and then TiO_2/AA/Co nanocatalyst (solid phase) was separated by centrifuging followed by decantation (3 × 5 mL ethanol). Desired product (liquid phase) was extracted by plate chromatography eluted with n-hexane/EtOAc (10/2). Assignments of products were made by ^{1}H NMR spectral data in comparison with authentic samples.

2.2.2 General Procedure for Synthesis of Benzimidazole from Benzaldehydes and o-Phenylenediamines

To a mixture of benzaldehyde (1.2 mmol), 1,2-phenylenediamine (1 mmol) in ethanol (0.8 mL) in a glass test tube (10 cm tall × 1 cm diameter), was added TiO_2/AA/Co nanocatalyst (0.02 mol%) and the reaction mixture was heated at 60 °C under air and visible light conditions for the required time. The reaction progress was monitored by TLC. After completion of the reaction, ethanol was added to the reaction mixture (3 mL). TiO_2/AA/Co nanocatalyst (solid phase) was separated by centrifuging followed by decantation (3 × 5 mL ethanol). Desired product (liquid phase) was purified by plate chromatography eluted with *n*-hexane/EtOAc (10/2). Assignments of products were made by ^{1}H NMR spectral data in comparison with authentic samples.

3 Results and Discussion

3.1 Synthesis of Benzimidazoles using Aromatic Diamines and Benzylic Alcohols (Method A)

Initially, we tried to prepare benzimidazole derivatives using benzene-1,2-diamines and benzylic alcohols. The observations for model reaction of phenylenediamine (1 mmol) and benzyl alcohol (1.2 mmol) have been summarized in Fig. 1. It was found that to trigger the reaction, both TiO_2/AA/Co nanohybrid and NHPI should be present in the reaction in an open vessel (in air). Moreover, the reaction reached to the highest conversion under solvent-free conditions at 70 °C (Fig. 1i, ii). Raising the temperature up to 70 °C decreased the yield (Fig. 1ii). To achieve the quantitative yield of product, the reaction needs to 0.06 and 5 mol% of catalyst and NHPI, respectively. (Fig. 1iii and vi). The role of NHPI as a free radical oxidation co-catalyst in combination with cobalt complexes under aerobic conditions has been well documented (Fig. S2) [52].

Besides, when the other common oxidants such as O_2, H_2O_2, TBHP, UHP, Oxone® and tetra-*n*-butylammonium Oxone® (TBAOX) were used under optimized conditions, the yields of benzimidazole reduced (Fig. 1v).

The scope and generality of the reaction with various aryl alcohols and 1,2-diaminoarenes discovered under the above mentioned optimized conditions using air as oxidant and visible light as energy source (Table 1). According to the results summarized in Table 1, the benzimidazole derivatives were successfully produced by the visible light irradiation of aryl alcohols solutions containing *o*-arylenediamines and catalytic amount of TiO_2/AA/Co (Table 1). Inspection of the results in Table 1 revealed that the reaction rate affected by electronic demands of substrates. Benzyl alcohols bearing electron-donating groups were efficiently converted to the pertinent benzimidazole derivatives (Table 1, entries 5 and 7). Nevertheless, strong electron-withdrawing nitro group on the phenyl ring of both alcohol and amine molecules, significantly retarded the reaction (Table 1, entry 4, 10).

3.2 Synthesis of Benzimidazoles Using Aromatic Diamines and Benzaldehydes (Method B)

Next, the catalytic system was employed for condensation of benzaldehydes with *o*-phenylenediamine. Performing the condensation reaction of 4-chlorobenzaldehyde with *o*-phenylenediamine under conditions used for benzyl alcohols (Table 1) led to 60% of the pertinent benzimidazole after 3 h. To achieve a new condition for efficient condensation of benzaldehydes and *o*-phenylenediamines different factors were screened (Fig. S1). The reaction of 4-chlorobenzaldehyde (1.2 mmol) with *o*-phenylenediamine (1 mmol) in ethanol (0.8 ml) containing 0.02 mol% TiO_2/AA/Co nanohybrid proceeded quantitatively within 30 min under aerobic conditions at 60 °C with no need to NHPI.

Various aryl aldehydes were allowed to react with *o*-phenylenediamines. The corresponding benzimidazoles produced in high yields, except for electron-deficient ones which formed moderately (Table 2, entries 4, 5, 13 and 17).

3.3 Photocatalytic Activity

To evaluate the photocatalytic function of TiO_2 at the core of title nanocomposite, the model reactions under conditions used in methods **A** and **B** (aerobic oxidative condensation of phenylenediamine and benzyl alcohol as well as phenylenediamine and benzaldehyde) subjected under UV and visible light as well as in dark (Table 3). Increasing the reaction rate under light radiation particularly UV light revealed the involving of the photocatalytic activity of TiO_2 core on the catalytic efficiency of TiO_2/AA/Co nanohybride (entries 3 and 6) (see proposed mechanism in SI). A good evidence for this claim may be the smaller band-gap of 2.8 eV for TiO_2/AA/Co nanohybrid than that of bare TiO_2 nanoparticles (3.2 eV) [52].

The superior catalytic performance of TiO_2/AA/Co nanoparticles in both methods **A** and **B** was also affirmed by replacing the other nanoparticulate metal oxides such as MoO_3 [57], monoclinic ZrO_2 [58], TiO_2 as well as their nanocomposites, such as TiO_2/AA, AA/Co, γ-Fe_2O_3/AA/Co, and MoO_3/AA/Co. The product yield and selectivity reduced markedly under the same conditions (Table 4).

In continued, the dependence of the catalytic activity on the irradiation wavelength was illustrated in Fig. 2 (Method B). A series of optical low-pass filters were employed to block light below a specific cut-off wavelength. For example, the 450 nm optical filter blocks the wavelength below 450 nm and over 800 nm, in other words, the light irradiating the reactor has a wavelength range from 450 to 800 nm. Without any filters, the irradiation of the light with wavelengths ranging from 400 to 800 nm gives a 2-[4-chlorophenyl] benzimidazole yield of 96%. The yield decreases to 73, 46 and 34% when the wavelength range of the irradiation is 450–800, 550–800, and 600–800 nm, respectively. Since the yield of 2-[4-chlorophenyl] benzimidazole in the dark is 20%, the contribution of 400–450 nm light accounts for about 30% ((76–53)/76 × 100%) in the total light-induced yield. Similarly, the light in the wavelength range of 450–550, 550–600 and 600–800 nm, respectively accounts for 36, 16 and 18% of the light-induced yield (Fig. 2A). These values agree well to the UV–visible absorption

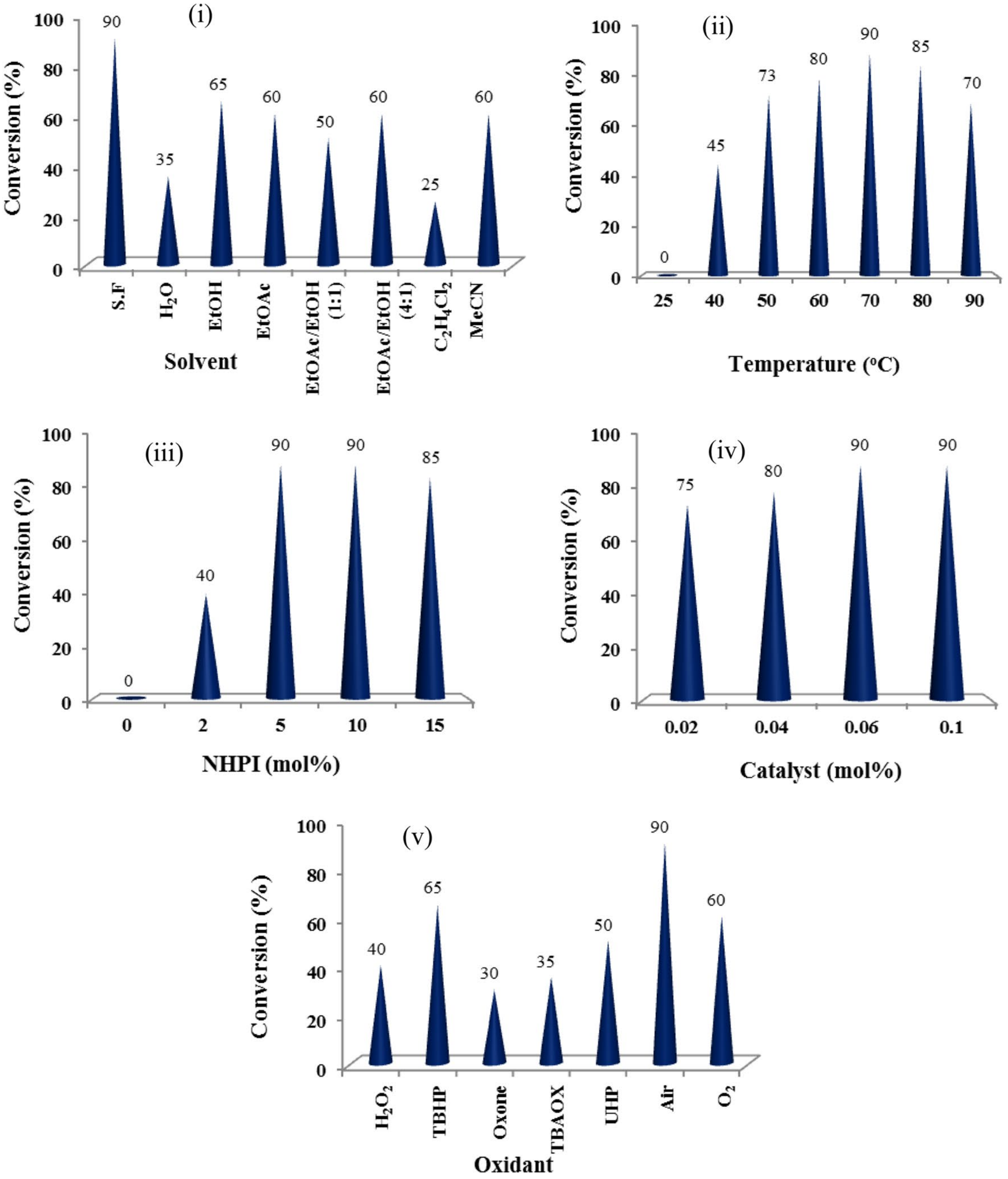
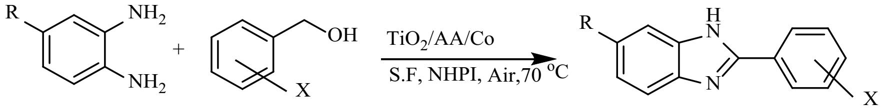


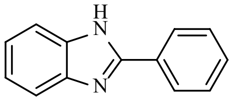
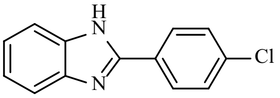
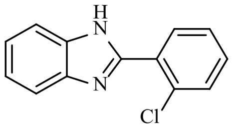
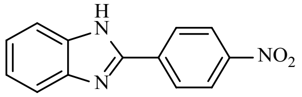
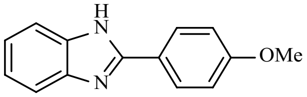
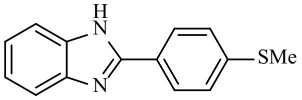
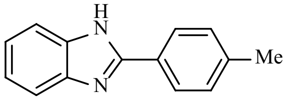
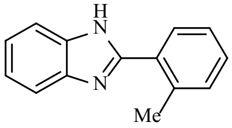
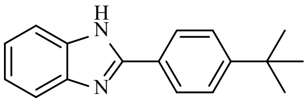
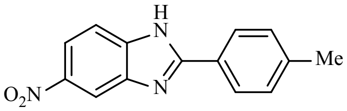
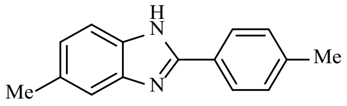
Fig. 1 The screening of the (**i**) solvent nature (**ii**) temperature (**iii**) NHPI amount (**iv**) catalyst amount (**v**) various oxidant on synthesis of benzimidazole from benzyl alcohol (1.2 mmol) and benzene-1,2-diamine (1.0 mmol) catalyzed by TiO_2/AA/Co after 3 h under air and visible light

spectrum of the TiO_2/AA/Co catalyst (Fig. 2B). Because the TiO_2/AA/Co catalyst has a strong absorption at about 493 nm, the light in the wavelength range of 450–550 nm contributions the highest light-induced conversion. This further confirms that the light absorbed by Co complex is the major driving force of the reaction.

The action spectra for synthesis of 2-[4-chlorophenyl] benzimidazole has been shown in Fig. 3. The action spectrum is a useful tool for determining whether an observed reaction occurs via a photoinduced process or a thermocatalytic process which should show one-to-one mapping between the wavelength-dependent photocatalytic rate and

Table 1 Synthesis of benzimidazole derivatives from benzyl alcohols and *o*-phenylenediamines[a]



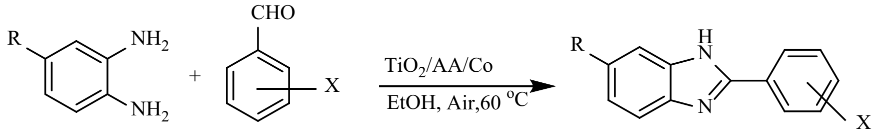
Entry	Diamine R	Alcohol X	Product[b]	Yield %[c]
1	H	H		90
2	H	4-Cl		80
3	H	2-Cl		65
4	H	4-NO_2		-
5	H	4-OMe		94
6	H	4-SMe		37
7	H	4-Me		83
8	H	2-Me		75
9	H	4-*t*-Bu		72
10	NO_2	4-Me		15
11	Me	4-Me		79

[a] *Reaction condition* 1,2-phenylene diamine (1 mmol), Benzyl alcohol (1.2 mmol), catalyst (0.06 mol%), NHPI (5 mol%) at 70 °C after 3h under air, visible light and solven free conditions

[b] The products were identified by ^{1}H NMR spectroscopy

[c] Isolated yield

Table 2 Synthesis of benzimidazole derivatives from benzaldehydes and *o*-phenylenediamines[a]



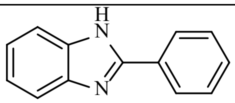
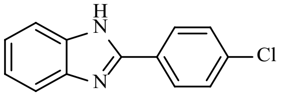
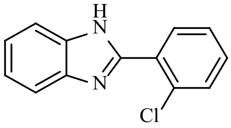
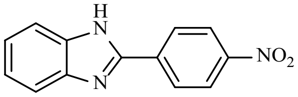
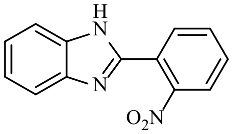
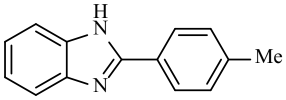
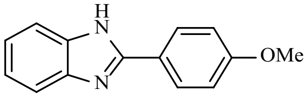
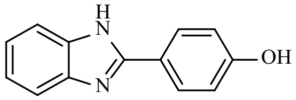
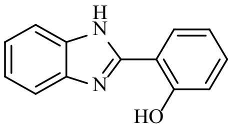
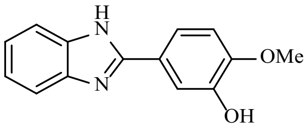
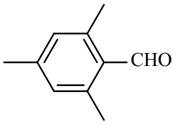
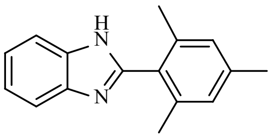
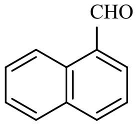
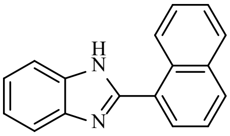
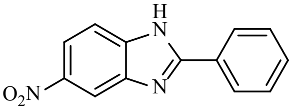
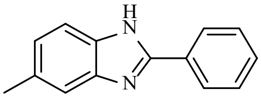
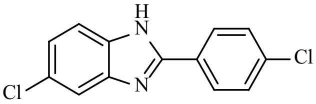
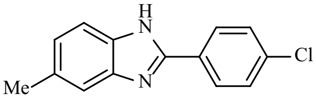
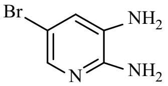
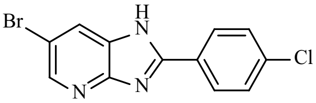
Entry	Diamine R	Aldehyde X	Product[b]	Time (min)	Yield (%)[c]
1	H	H		50	85
2	H	4-Cl		30	96
3	H	2-Cl		20	95
4	H	4-NO_2		120	46
5	H	2-NO_2		180	50
6	H	4-Me		50	95
7	H	4-OMe		65	96
8	H	4-OH		65	94
9	H	2-OH		60	90
10	H	4-OMe 3-OH		60	95
11	H			45	95

Table 2 (continued)

Entry	Diamine R	Aldehyde X	Product [b]	Time (min)	Yield (%)[c]
12	H			95	85
13	NO_2	H		180	60
14	Me	H		40	96
15	Cl	4-Cl		40	90
16	Me	4-Cl		25	95
17		4-Cl		70	42

[a] *Reaction condition* 1,2-phenylene diamine (1 mmol), Benzaldehyde (1.2 mmol), catalyst (0.02 mol%) in ethanol (0.8 ml) at 60 °C under air and visible light conditions

[b] The products were identified by ^{1}H NMR spectroscopy

[c] Isolated yield

Table 3 Screening of the photocatalytic activity of TiO_2/AA/Co

Entry	Catalyst	Condition	Method A[a] yield% (time)	Method B[b] yield% (time)
1	TiO_2	UV light[c]	20 (3 h)	30 (30 min)
2	TiO_2/AA	UV light	25 (3 h)	25 (30 min)
3	TiO_2/AA/Co	UV light	85 (2 h)	100 (15 min)
4	TiO_2	Visible light[d]	10 (3 h)	20 (30 min)
5	TiO_2/AA	Visible light	10 (3 h)	30 (30 min)
6	TiO_2/AA/Co	Visible light	90 (3 h)	100 (30 min)
7	TiO_2	Darkness	10 (3 h)	20 (30 min)
8	TiO_2/AA	Darkness	10 (3 h)	15 (30 min)
9	TiO_2/AA/Co	Darkness	20 (3 h)	20 (30 min)

[a] *Reaction condition* Method A: 1,2-phenylene diamine (1 mmol), Benzyl alcohol (1.2 mmol), catalyst (0.06 mol%), NHPI (5 mol%) at 70 °C under air and solvent free conditions

[b] Method B: 1,2-phenylene diamine (1 mmol), 4-chlorobenzaldehyde (1.2 mmol), catalyst (0.02 mol%) in ethanol (0.8 ml) at 60 °C under air

[c] $\lambda = 200–290$ nm

[d] Fluorescent lamp

the light extinction spectrum [59, 60]. In this study, the reaction rates of the synthesis of 2-[4-chlorophenyl] benzimidazole using TiO_2/AA/Co at 60 °C under irradiation with different wavelengths were determined. To obtain an action spectrum in this photocatalytic system, the AQY versus the respective wavelengths of the reaction is plotted. AQY was calculated with the following equation:

$$\mathrm{AQY}\ (\%) = \left[\left(\mathrm{Y_{vis}} - \mathrm{Y_{dark}}\right) \times 2/(\text{photon number entered into the reaction vessel})\right] \times 100$$

where $\mathrm{Y_{light}}$ and $\mathrm{Y_{dark}}$ are the amounts of products formed under light irradiation and dark conditions, respectively. As shown in Fig. 3, a good correlation is observed between AQY and the diffuse reflectance spectrum of the TiO_2/AA/Co nanohybrid which confirms that the reaction is taking place photocatalytically.

3.4 Stability and Reusability of Catalyst

Finally, recycling experiments were conducted to find out the stability and reusability of the catalysts. The catalyst was easily separated by centrifugation and reused in four consequent runs in the reaction of 1,2-phenylenediamine and benzyl alcohol (Method **A)** as well as in condensation of 1,2-phenylenediamine and 4-chlorobenzaldehyde (Method **B)** (Table 5). Slight reduction in the product yields was observed after 4th run indicating the efficiency and stability of title nanocatalyst. More evidences for this issue were observed by comparing the FT-IR and TEM image of used catalyst with fresh one (Fig. 4). The structure, size and morphology of catalyst remained intact after recycling. Further,

Table 4 The comparison of catalytic activity of TiO_2/AA/Co with other nanocomposites and nanooxometals

Entry	Catalyst	Method A[a,b] yield (%)	Method B[c] yield% (selectivity %)
1	TiO_2/AA/Co	90	96 (100)
2	TiO_2/AA	30	30 (66)
3	AA/Co	45	50 (80)
4	AA	0	0
5	TiO_2	20	20 (50)
6	ZrO_2	20	20 (50)
7	MoO_3	55	65 (69)
8	MoO_3/AA/Co	65	55 (90)
9	Fe_2O_3/AA/Co	25	25 (60)
10	Co $(OAc)_2$	60	65 (76)

[a] *Reaction condition* Method A: 1,2-phenylene diamine (1 mmol), Benzyl alcohol (1.2 mmol), catalyst (0.06 mol%), NHPI (5 mol%) at 70 °C after 3 h under air, visible light and solvent free conditions

[b] 100% selectivity

[c] Method B: 1,2-phenylene diamine (1 mmol), 4-chlorobenzaldehyde (1.2 mmol), catalyst (0.02 mol%) in ethanol (0.8 ml) at 60 °C after 30 min under air and visible light

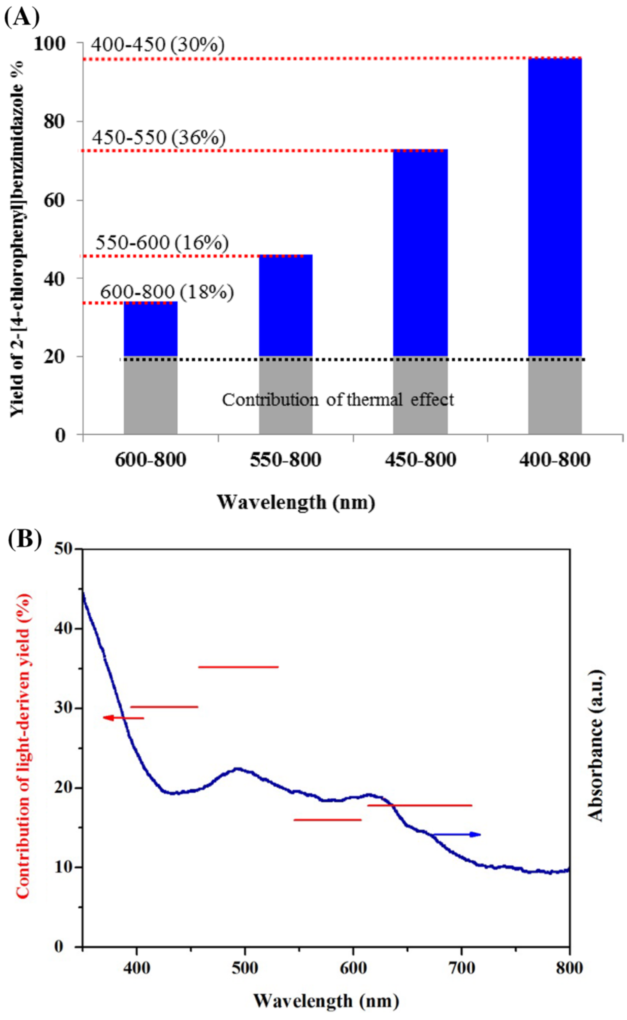


Fig. 2 Dependence of 2-[4-chlorophenyl] benzimidazole yield on the irradiation wavelength (**A**), and the action spectrum of the photocatalytic reaction, in which the light driven conversion is plotted against the irradiation wavelength (**B**)

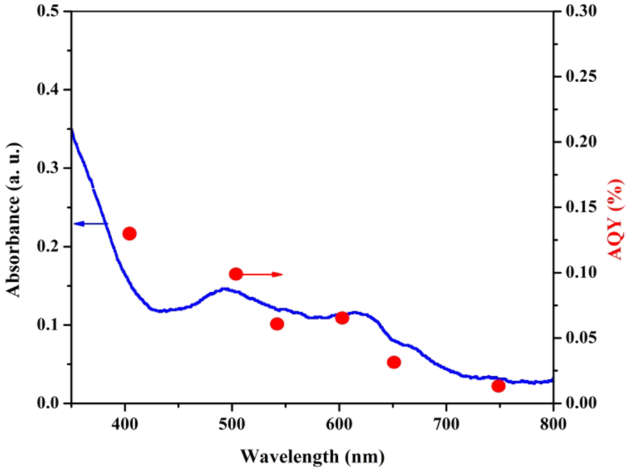


Fig. 3 Photocatalytic action spectrum for synthesis of 2-[4-chlorophenyl] benzimidazole using TiO_2/AA/Co photocatalyst. The light-absorption spectrum (left axis) is the DR−UV/vis spectra of TiO_2/AA/Co nanohybrid (blue curve)

Table 5 Recyclability of the catalytic systems in the synthesis of benzimidazoles

Reaction	Yield % (run 1)	Yield % (run 2)	Yield % (run 3)	Yield % (run 4)
Method A[a]	90	90	90	88
Method B[b]	96	96	95	94

[a] The aerobic oxidative coupling of benzyl alcohol with 1,2-phenylene diamine

[b] The aerobic oxidative coupling of 4-chloro benzaldehyde with 1,2-phenylene diamine

AAS revealed a very small amount of Co (< 2 ppm) in the filtrate using a hot filtration method.

Additional advantageou of these methodologies is the possibility of applying the scale-up conditions. When the reaction performed using 20 mmol 1,2-phenylenediamine and 24 mmol of benzyl alcohol, 86% of the corresponding benzimidazole was secured at the same time and conditions mentioned in Table 1.

4 Conclusion

In conclusion, we have developed an expedient and direct method for the synthesis of benzimidazoles by TiO_2/AA/Co nanohybrid under visible light irradiation conditions in good to excellent yields, starting directly from a variety of alcohols or aldehydes and 1,2-phenylenediamine derivatives. In case of alcohols, the protocol involves photooxidation of alcohols to aldehydes followed by cyclocondensation with 1,2-phenylenediamine to afford benzimidazoles in one-pot operation with good to excellent yield. The methods afford environmentally friendly reaction conditions. The process is also efficient even on a multi-mmole scale and provides easy product isolation. Therefore, this process has the potential to enable a more sustainable benzimidazole synthesis. The combination of photocatalytic and catalytic reactions presented here may help to develop a new strategy towards the development of photocatalysis-based organic synthesis.

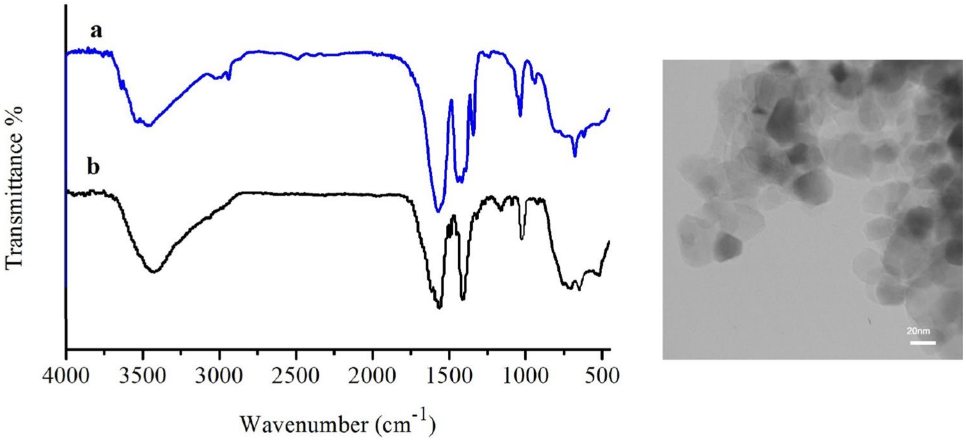


Fig. 4 (Left) FT-IR spectra of TiO_2/AA/Co itself (*a*) and after 4 times reuses. (*b*) (Right) TEM image of TiO_2/AA/Co after reuses

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Compliance with Ethical Standards

Conflict of interest The authors declare no conflict of interest.

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