Supporting Information

TiO₂ nanoparticle decorated with Co-Schiff base–g-C₃N₄ as an efficient photocatalyst for one pot visible light-assisted synthesis of benzimidazoles

Narges Pourmorteza, Maasoumeh Jafarpour*, Fahimeh Feizpour, Abdolreza Rezaeifard*

^a Catalysis Research Laboratory, Department of Chemistry, Faculty of Science, University of Birjand, Birjand, 97179-414 Iran

Experimental

General remarks

All chemicals were purchased from Merck and Fluka Chemical Companies. Powder X-ray diffraction (XRD) was performed on a Bruker D8-advance X-ray diffractometer with Cu K α (λ =1.54178 Å) radiation. The FT-IR spectra were recorded on the NICOLET system. Thermogravimetric analysis (TGA) of nanopowders was performed in the air by Shimadzu 50. Diffuse reflectance UV–Vis spectra were recorded using an Avantes spectrometer (Avaspec-2048-TEC model). Scanning Electron Microscope performed by FEG-HRSEM SU8220 from HITACHI with EDX detector (Bruker) for elemental analysis. The Co content of the catalyst was determined by the OPTIMA 7300DV ICP analyzer. Progress of the reactions was monitored by TLC using silica-gel SIL G/UV 254 plates and also by GC-FID on a Shimadzu GC-16A instrument using a 25 m CBP1-S25 (0.32 mm ID, 0.5 μ m coating) capillary column. The dependence of the catalytic performance on the light wavelength was investigated by employing various optical filters to allow the transmission of specific-wavelength light. The Lamps used in this work are as: UV light (λ = 200–290 nm, 15 W), LED (λ = 505 nm, 12 W), sunlight (18 W), Actinic BL lamp (λ = 366–400 nm, 15 W) and CFL lamps (Compact Fluorescent lamp, λ =400–700 nm, 40 W).

Preparation of TiO₂ nanoparticle

In a typical hydrothermal method, a solution of $TiCl_3$ was prepared using $TiCl_3$, DI water, and citric acid (CA) at room temperature. To control the pH, NaCl was added to the solution. The molar ratio of $TiCl_3:H_2O:$ CA: NaCl was 0.024:0.500:0.183:0.059. The solution was moved to 47 mL of a Teflon-lined stainless steel autoclave and heated at 180 °C for 4 h. Subsequently cooled naturally to room temperature, collected precipitates were washed with deionized water and ethanol several times then dried at 60 °C for 2 h in a vacuum oven.

Preparation of g-C₃N₄ powder

Graphite-like C_3N_4 sheets were prepared based on a procedure reported previously. Specifically, 5.0 g of melamine was calcined at 550 °C for 4 h with a heating rate of 2 °C/min in a muffle furnace covered with a lid to maintain the calcination process in static air. The obtained yellow agglomerates were collected and ground into powder for further synthesis.

Preparation imine of C₃N₄

To a solution of $g-C_3N_4$ (0.1 g) in ethanol (10 mL) was gradually added a solution of (3-oxopropyl) trimethoxysilan (0.4 mL, 2.5 mmol) in ethanol (10 mL) at 70 °C under ultrasonic agitation. Then, the reaction mixture was kept under the same conditions. After ultrasonication for 5 h followed by drying at 70 °C to remove ethanol, the product which was precipitated was washed with ethanol to remove unreacted chemicals. The isolated product was then dried at 100 °C for 12 h in a vacuum oven.

Preparation of Co-g-C₃N₄ -imine/TiO₂ nanohybrid

First, 0.1 g of TiO₂ nanoparticles were gradually added to 0.1 g Schiff base of carbon nitride in ethanol at 60 °C under ultrasonic agitation. Then, the as-obtained mixture was refluxed for 8 h. Thus, the product was centrifuged and washed with ethanol. Finally, $g-C_3N_4$ -Imine/TiO₂ nanocomposite was obtained after drying in air. Subsequently, to load Co on the surface of g-C₃N₄-Imine/TiO₂ heterostructure, a volume of Co(OAc)₂ suspension (6 mg per mL ethanol) was added to 0.1 g of g-C₃N₄-Imine/TiO₂ dispersed in 2 mL ethanol. After sonication for 1 h, the mixture was refluxed for 3 h. The grey participants were collected by centrifuging and washing ethanol repeatedly and dried in air.

Procedure for Determining Photoefficiency (Action Spectra Analysis)

The wavelength-dependent photocatalytic performance was investigated by employing various optical filters to allow the transmission of specific-wavelength light. A full-spectrum 40 W CFL bulb was used as an irradiation source. The filters used in this work are a blue filter (Leybold Heraeus GMBH 46811) with lux = 1000 to irradiate at $\lambda \approx 450$ nm; a green filter (Leybold Heraeus GMBH 46807) with lux = 1200 to irradiate at $\lambda \approx 530$ nm; a solution mixture of Cu(OAc)₂, methyl orange, and NaNO₂ with lux=3720 to irradiate at $\lambda \approx 570$ nm; a solution mixture of Fe(EDTA), KMnO4, and Cu(OAc)₂, lux = 3300 to irradiate at $\lambda \approx 630$ nm; and a solution mixture of methylene blue, phenol red, and KMnO₄ with lux = 3200 to irradiate at $\lambda \approx 760$ nm.



Scheme S1. Synthetic route for Co- g-C₃N₄ -Imine/TiO₂ nanohybrid



Fig. S1. Elemental mapping images (a-g) and EDX analysis of Co-g-C $_3N_4$ -Imine/TiO $_2$ nanohybrid





Fig. S2. UV-DR spectra of TiO₂, C₃N₄, C₃N₄-Schiff base/TiO₂ nanohybrid



Fig. S3. TGA curve of Co-g-C₃N₄-Imine/TiO₂ nanohybrid



Fig S4. The screening of the various oxidant in the Oxidation of 4-chlorobenzyl alcohol (0.125 mmol) at 70 °C using 2 mg of catalyst, 0.012 mmol NHPI under a visible light source (CFL, 40 w).



Fig. S5. Screening of aerobic oxidation of 4-chlorobenzyl alcohol in the presence of Co- g-C₃N₄ -Imine/TiO₂ nanohybrid and starting materials and catalyst precursors



Scheme S2. Proposed mechanism for the synthesis of benzimidazoles using Co-g-C₃N₄-Imine/TiO₂ nanohybrid.

R NH2 + X O		$\xrightarrow{\text{Co-g-C}_3N_4\text{-Imine/TiO}_2}_{\text{Air, CFL lamp}} \xrightarrow{\text{R}}_{N} \xrightarrow{\text{H}}_{N} \xrightarrow{X}$		
Entry	Solvent	Temp. (^o C)	Catalyst (mg)	Yield (%) ^a
1	Solvent-free	50	2	40
2	H_2O	50	2	53
3	EtOH	50	2	80
3	EtOAc	50	2	67
4	MeCN	50	2	75
5	EtOH	60	2	97
6	EtOH	40	2	65
7	EtOH	25	2	50
8	EtOH	60	1	60
9	EtOH	60	3	95

Table S1. Synthesis of benzimidazole derivatives from benzaldehydes and 1,2-phenylenediamines ^a

^aReactions were run for 50 min in 0.5 mL of solvent containing 0.12 mmol of 4-Clbenzaldehyde, 0.15 mmol of 1,2-phenylendiamine, under visible light (CFL, 40 w), air condition



Fig. S6. Recycling of catalytic system for oxidation of 4-Cl-benzyl alcohol (green) synthesis of benzimidazoles from 4-Cl-benzyl alcohol (grey) and 4-Cl-benzaldehyde (red) using $Co-g-C_3N_4$ -Imine/TiO₂ nanohybrid according to procedures mentioned in the experimental section.



Fig. S7. (a) FT-IR spectra of fresh Co-g-C₃N₄-Imine/TiO₂ nanohybrid; recovered Co-g-C₃N₄-Imine/TiO₂ nanohybrid in (b) the oxidation of 4-Cl-benzyl alcohol; (c) synthesis of benzimidazole using 4-Cl-benzyl alcohol according to procedures mentioned in the experimental section.