

# **Dendritic TiO<sub>2</sub>-Co (II) nanocomposite based on melamine catalyzed one-pot aerobic photocatalytic synthesis of benzimidazoles**

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## **1. Experimental**

### **1.1. General remarks**

All chemicals were purchased from Merck and Fluka Chemical Companies. FT-IR spectra were recorded on a Nicolet-Impact 400D spectrometer in the range of 400-4000 cm<sup>-1</sup>. Thermogravimetric analysis (TGA) of powders carried out on Shimadzu 50 under air flow at a uniform heating rate of 10 °Cmin<sup>-1</sup> in the range of 30-800°C. Transmission electron microscopy (TEM) measurements were obtained by a 906 E instrument (Zeiss, Jena, Germany). Samples for TEM experiment were prepared by dispersion in ethanol, sonicating for 30 min, and evaporating one drop of solution onto a 200 mesh formbar-coated copper grid. The X-ray photoelectron spectroscopy (XPS) measurements were performed using a BESTEC GMBH (10<sup>-10</sup> mw) analyzer with an Al (K $\alpha$  = 1486.6 eV) X-ray source. The Co content of the catalyst was measured by an inductively coupled plasma optical emission spectrometry (ICP-OES), using a VISTA-PRO ICP analyzer. Progresses of the reactions were monitored by TLC using silica-gel SIL G/UV 254 Plates. <sup>1</sup>H and <sup>13</sup>CNMR (400 and 100 MHz) spectra were recorded on a Bruker Avance DPX 400 spectrometer. FESEM and EDX performed by TESCAN MIRA III. NMR spectra were recorded on a Bruker Avance DPX 400 MHz.

UV-C (T8) lamp of Philips model ( $\lambda$  = 200-290 nm, P= 15 W ). Visible light lamp (TL-D / ACTINIC BL) Philips model ( $\lambda$  = 366-400 nm, P= 15 W), LED lamp (AC86) of the Z.FR model ( $\lambda$  = 505 nm, P= 12 W ), Reptillight (LT) lamp NARVA model (sun light, P= 18 W), Fluorescent lamp (room light lamps,  $\lambda$  = 400-650 nm, P= 40 W)

### **1.2. Fabrication of TiO<sub>2</sub> nanoparticles**

To a solution of  $\text{TiCl}_3$  (0.05 mol) in a mixture of double-distilled water and absolute ethanol (1:1) was added citric acid (0.15 mol) and ethylene glycol (0.15 mol) subsequently. The resulting mixture was dissolved at 45 °C under ultrasound for 15 min to give a clear violet solution. The solution was refluxed at 120 °C for 8 h which turned into a metal- citrate homogeneous complex with a little color change from clear violet to black-violet. After cooling down, in order to bring about the required chemical reactions for the development of polymerization and evaporation of the solvent, the sol was further slowly heated at 90 °C for 6 h in an open bath until a beige wet gel was obtained. During continuous heating at this temperature, the polymerization between citric acid, ethylene glycol and complexes is developed and ultimately sol became more viscous as a wet gel. In the final step of sol-gel process, the wet gel was fully dried by direct heating on the hot plate at 150 °C for 6 h leading to a black powder. Then the calcination was done at 600 °C for 3 h with heating rate 5 °C  $\text{min}^{-1}$ . Finally,  $\text{TiO}_2$  nanoparticles with a white color were obtained.<sup>21</sup>

### **1.3. Preparation of aminopropylated nanotitanium dioxide (AP- $\text{TiO}_2$ )**

For the preparation of AP- $\text{TiO}_2$ , the nano-titanium dioxide was fabricated according to literature procedure.<sup>22</sup> To a 3.0 g  $\text{TiO}_2$  nanoparticles in the 50 mL anhydrous toluene was added 8 mL 3-aminopropyltrimethoxysilane (APTS) at room temperature under ultrasonic agitation for 1 h, then was stirred under reflux conditions for 8 h. Afterward, the reaction mixture was centrifuged and washed with toluene and dried in a vacuum oven at 110 °C.

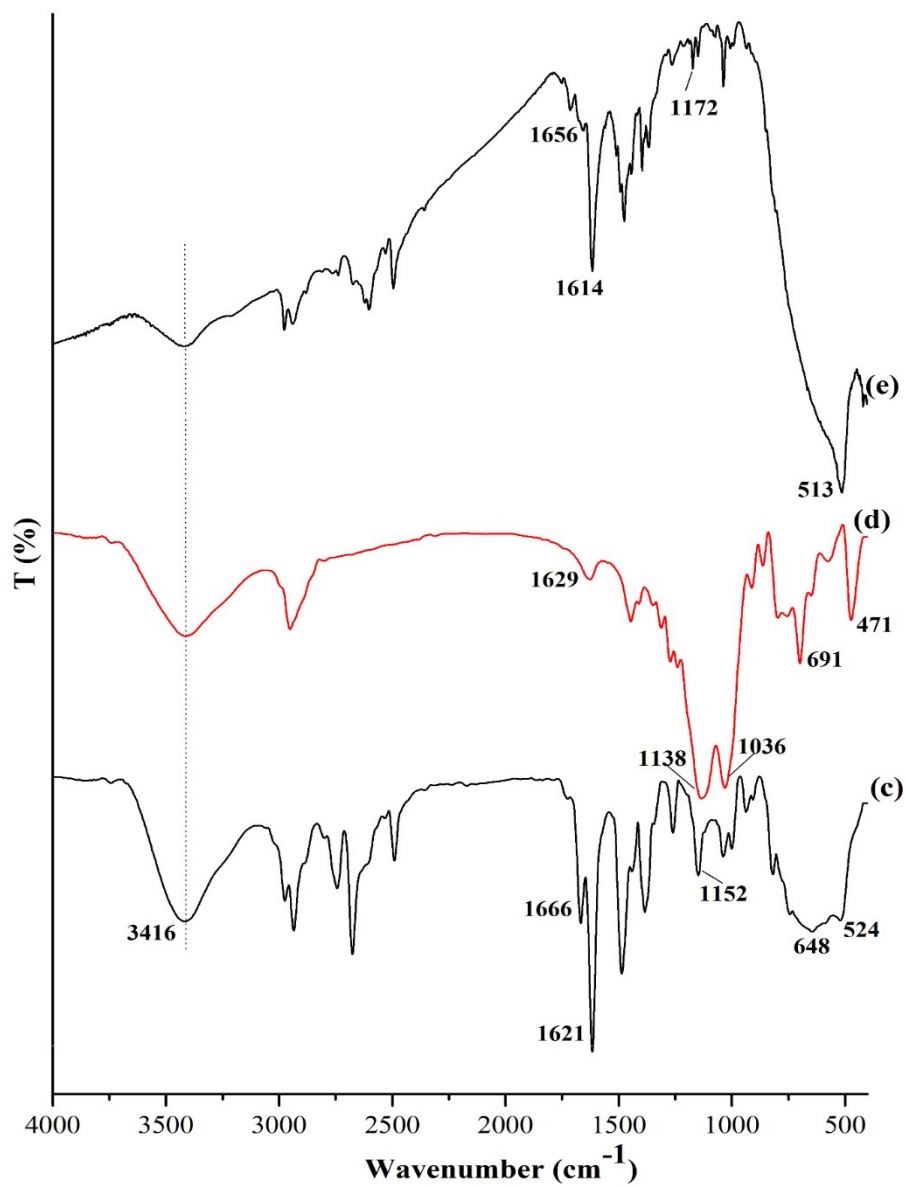
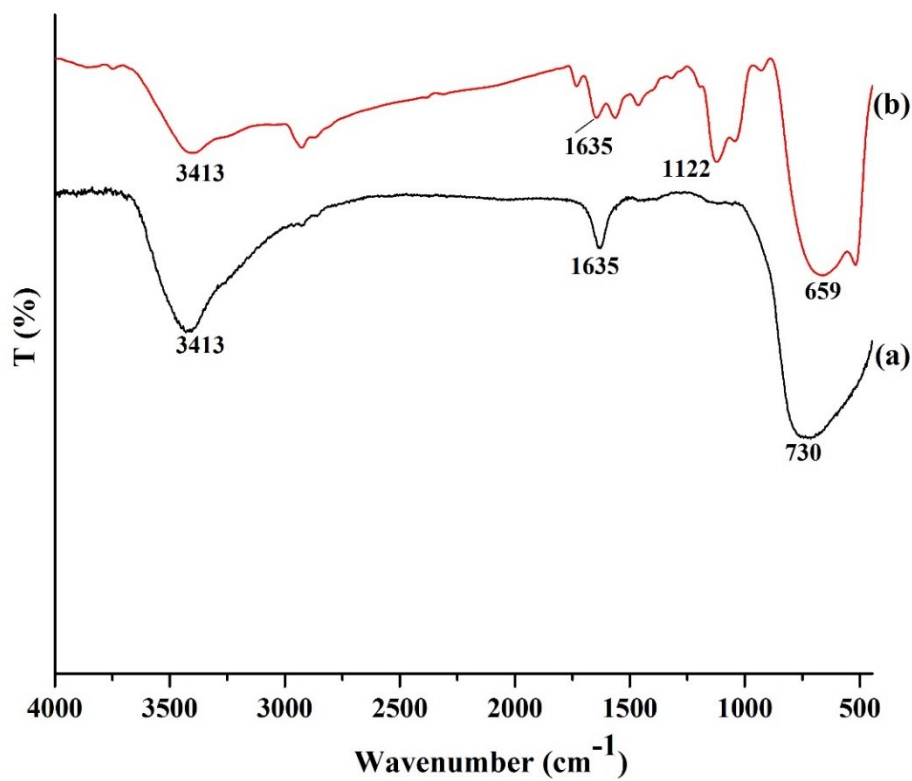
### **1.4. Preparation of triazine-based dendrimer supported on nanotitanium dioxide (G2 or TD@ $\text{TiO}_2$ )**

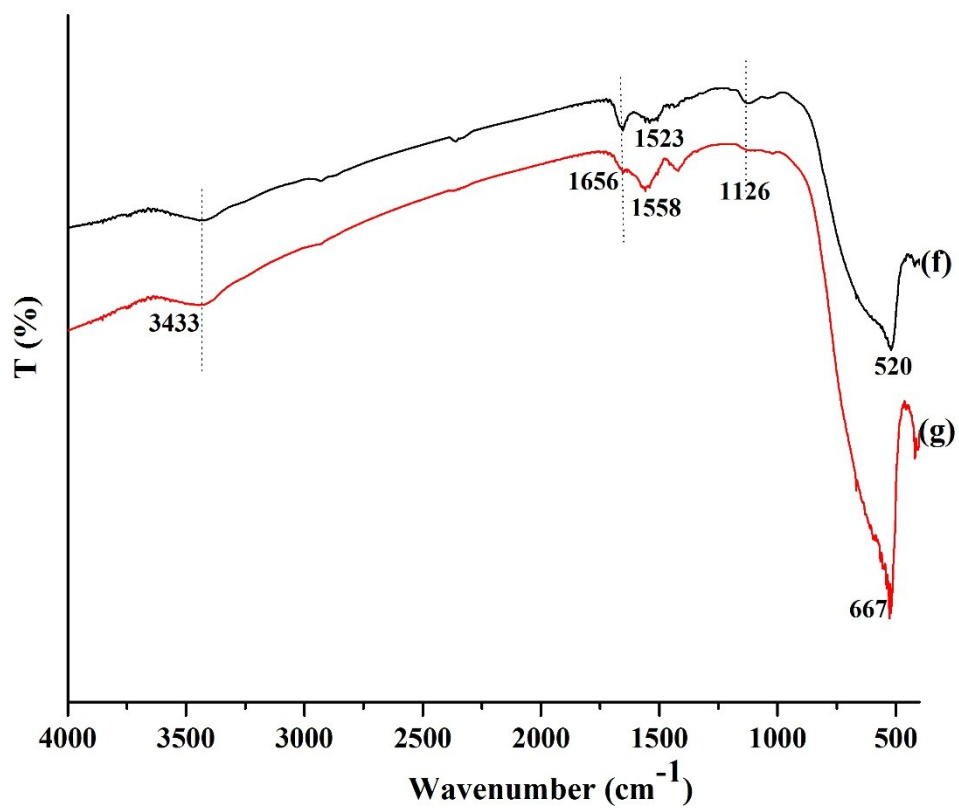
A mixture of AP-n $\text{TiO}_2$  (2g, 0.99 mmol/g), cyanuric chloride (CC) (1.85 g, 10 mmol) and triethylamine ( $\text{Et}_3\text{N}$ ) (10 mmol, 1.7 mL) in the THF (10 mL) was dispersed under ultrasound at room temperature for 1 h, then was shaken overnight at room temperature. The solid white material (CC1- $\text{TiO}_2$ ) was separated by centrifuge, washed with THF and dried in a vacuum oven at 50 °C. Then, to a solution of CC1-n $\text{TiO}_2$  (1 g) in DMF (12 mL) was added bis (3-aminopropyl) amine ( 8.11 mmol, 1 mL) and  $\text{Et}_3\text{N}$  (8.11 mmol, 1.4 mL). The reaction mixture was dispersed under ultrasound at room temperature for 1 h, then stirred under reflux condition at 80 °C for 16 h. The product first generation (G1) was centrifuged and washed with ethanol, then dried in a vacuum oven at 50 °C.

The second generation TD@ TiO<sub>2</sub> (G<sub>2</sub>) was prepared following the above procedure for the preparation of G<sub>1</sub>. A mixture of G<sub>1</sub> (1 g, 0.45 mmol), cyanuric chloride (CC) (1.66 g, 9 mmol) and Et<sub>3</sub>N (9 mmol, 1.56 mL) in THF (20 mL) was treated at room temperature under ultrasonic agitation for 1 h. Then, the reaction mixture was shaken at room temperature for 16 h. Afterward, the product was separated by centrifuge, washed with THF and dried in a vacuum oven at 50 °C. The resulting solid white material (CC2-TiO<sub>2</sub>) was obtained. Then, to a solution of CC2-TiO<sub>2</sub> (1 g) in DMF (20 mL) was added bis(3-aminopropyl)amine (9.36 mmol, 1.14 mL) and Et<sub>3</sub>N (9.36 mmol, 1.61 mL). The reaction mixture was treated at room temperature under ultrasonic agitation for 1 h, then stirred under reflux condition at 80 °C for 16 h. The resulting second generation of nano-titanium dioxide supported dendrimer (G<sub>2</sub> or TD@ TiO<sub>2</sub>) was centrifuged and washed with ethanol, then dried in a vacuum oven at 50 °C.

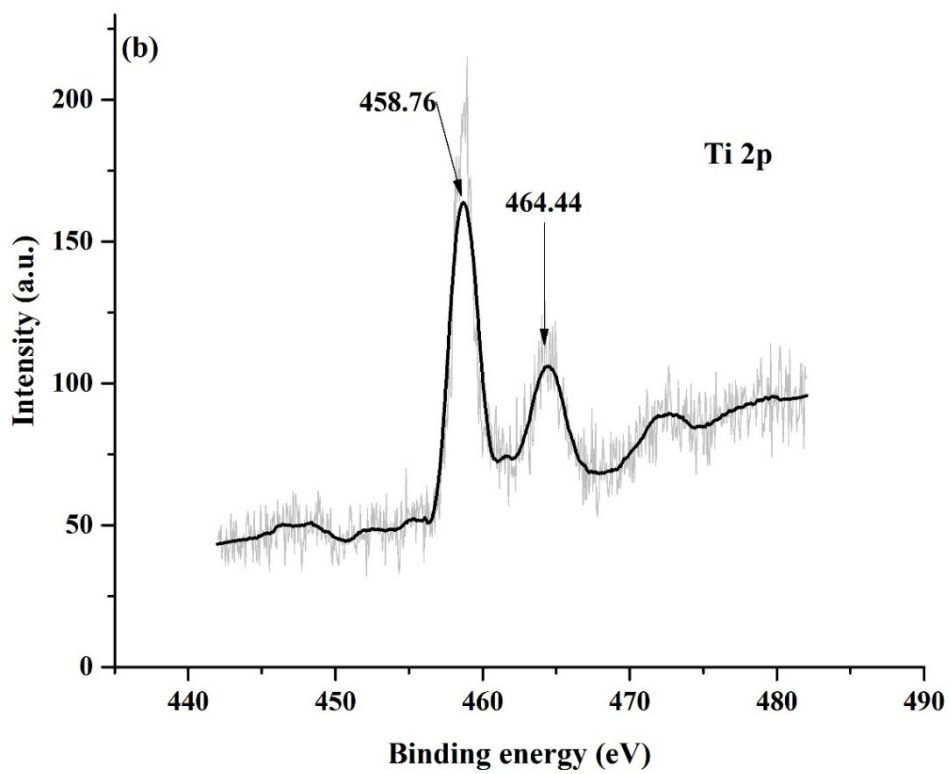
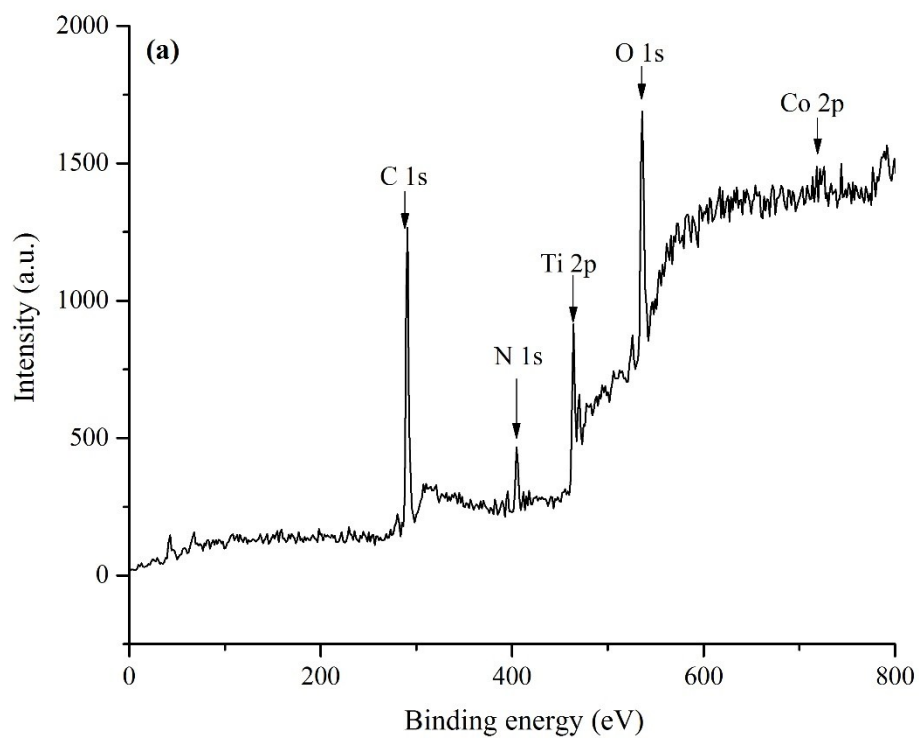
### **1.5. Preparation of Co(II) containing nanotitanium dioxide triazine dendrimer (Co(II)-TD@TiO<sub>2</sub>)**

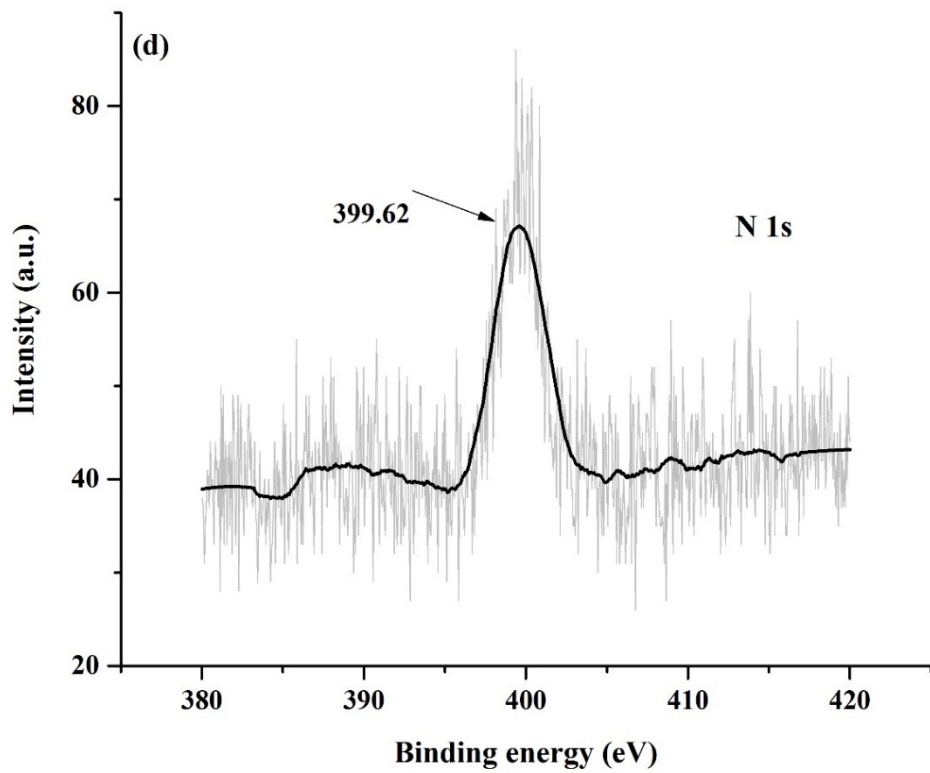
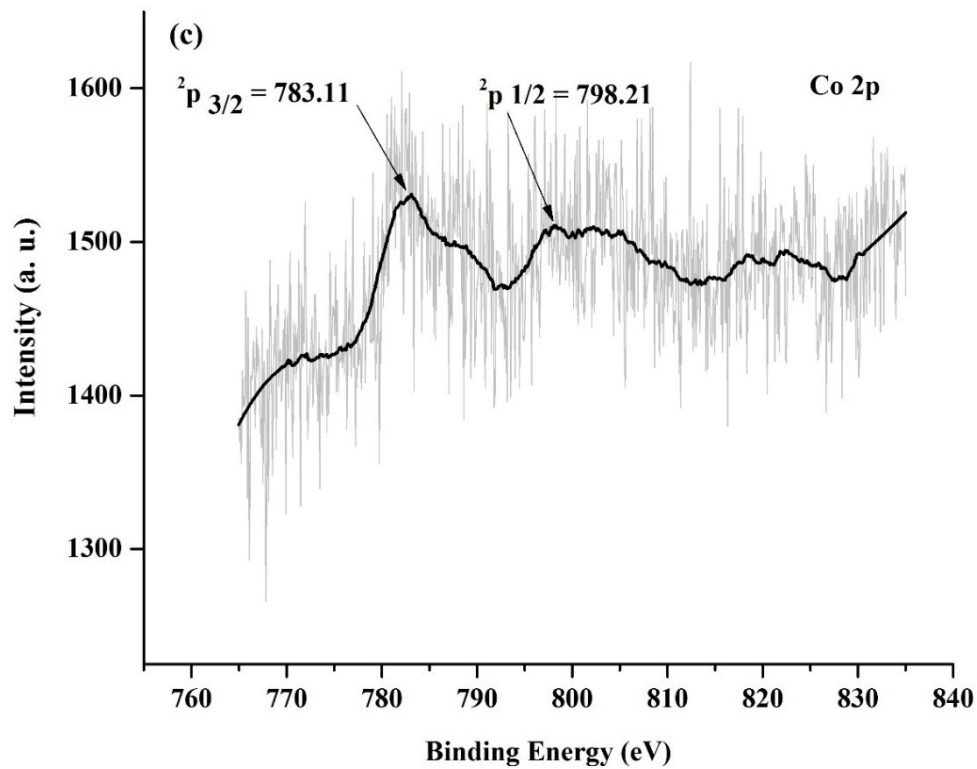
To a mixture of TiO<sub>2</sub> nanoparticles supported dendrimer (G<sub>2</sub>) (0.5 g) was gradually added Co(OAc)<sub>2</sub> (0.5 mmol) dissolved in DMF over a period 30 min at room temperature under ultrasonic agitation. Then, the as-obtained mixture was stirred at room temperature for 10 h. Afterward, the product was centrifuged and washed by ethanol. Finally, Co(II)-TD@TiO<sub>2</sub> catalyst was obtained after drying in a vacuum oven at 70 °C.

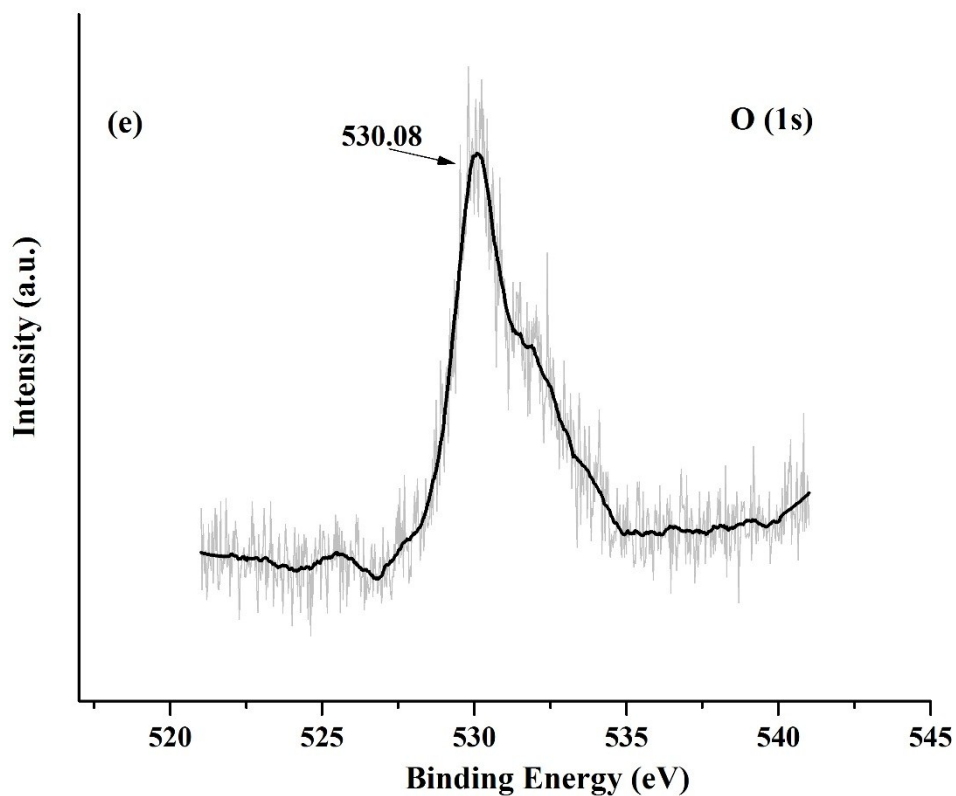




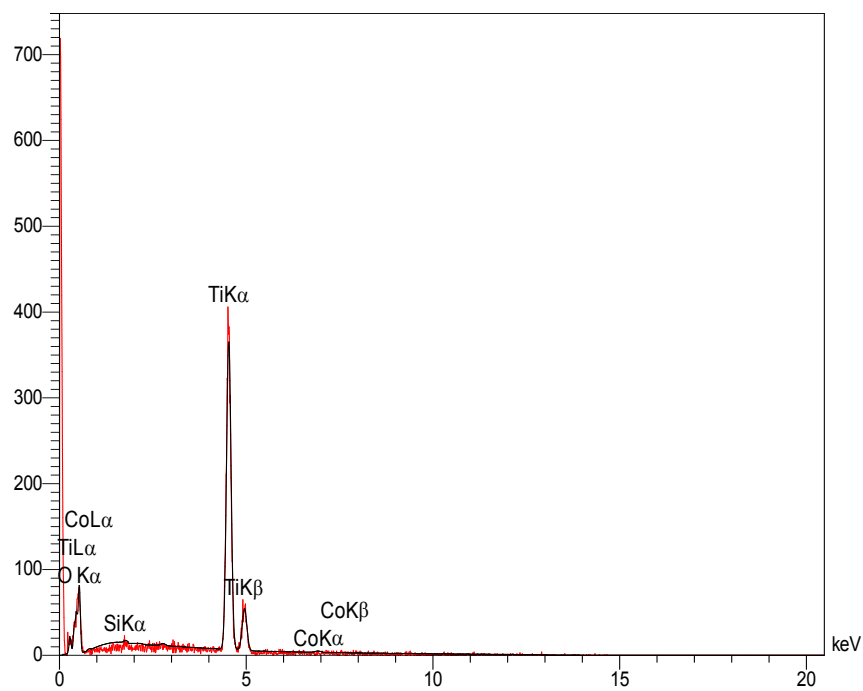
**Fig S1.** FT-IR spectra of (a)  $\text{TiO}_2$  (b) AP-n- $\text{TiO}_2$ , (c) CC1, (d) G1, (e) CC2, (f) G2 and (g) Co(II)-TD@ $\text{TiO}_2$





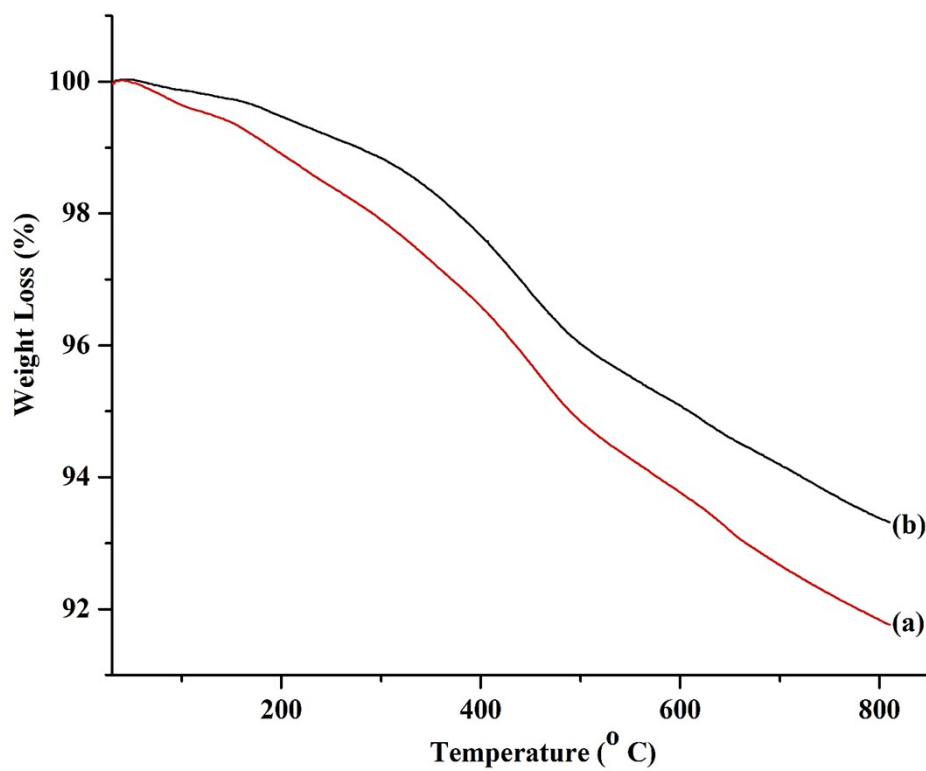


**Fig S2.** XPS spectra of Co(II)-TD@TiO<sub>2</sub> nanocatalyst (a) wide scan, (b) Ti 2p, (c) Co 2p, (d) N 1s (e)

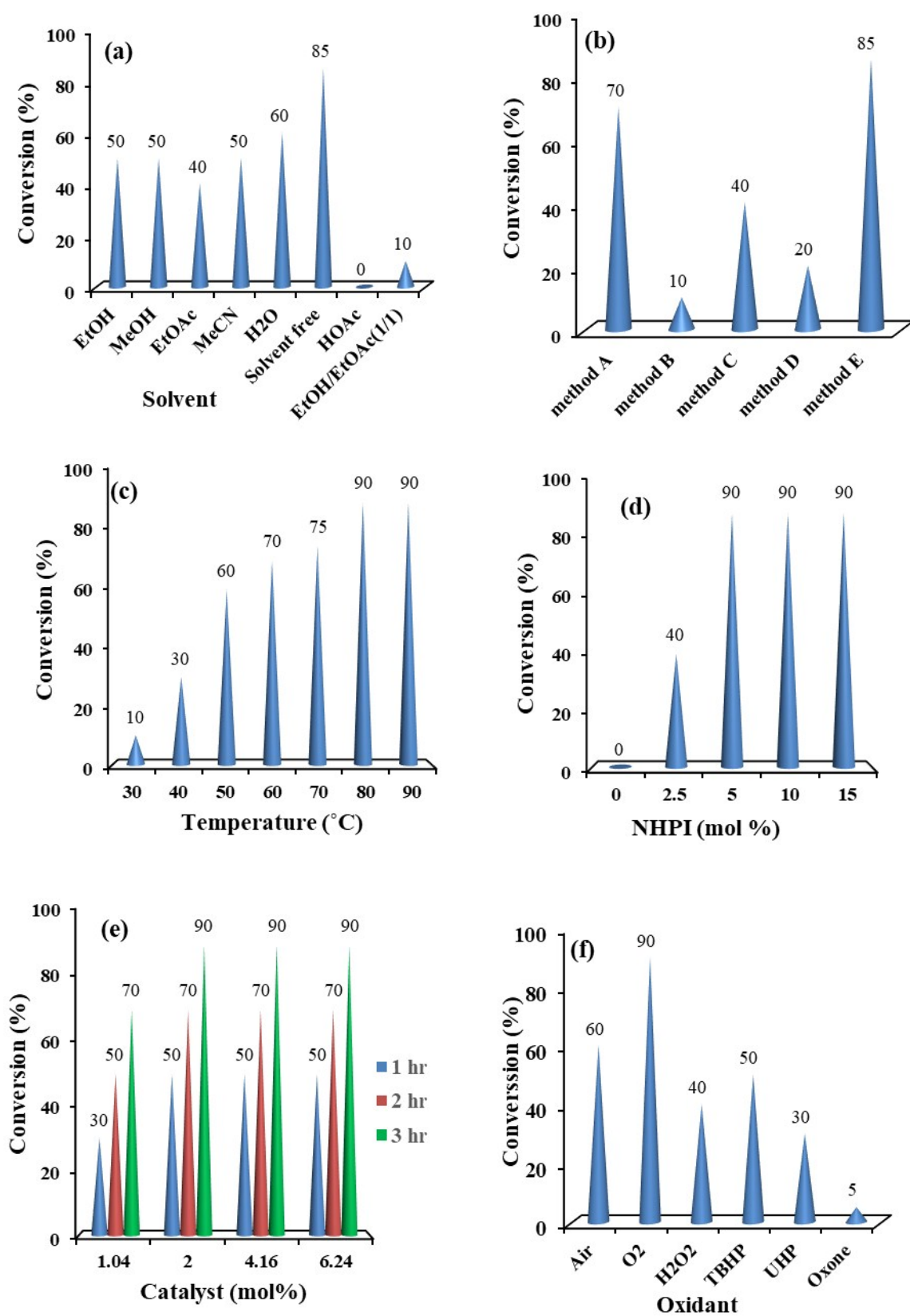


**Fig. S3.** EDX analysis of Co(II)-TD@ TiO<sub>2</sub> nanocatalyst





**Fig. S4.** The TGA of (a) G<sub>2</sub>, (b) Co(II)-TD@ TiO<sub>2</sub> nanocatalyst



**Fig S5.** The influence of reaction conditions for synthesis of benzimidazole from benzyl alcohol (1mmol) and 1,2-phenyldiamine (1.2 mmol) catalyzed by Co(II)-TD@n-TiO<sub>2</sub> after 3 h. Methods: ( A ) No cap/ 70 °C/Air/ Heater, ( B ) With cap/ 70 °C/Air/ Heater. ( C ) No cap/ 70 °C/ Air/ US, ( D ) With cap/ 70 °C/ Air/ US, ( E ) under bubbling O<sub>2</sub>/ 70 °C.

## Spectra data:

### 2-Phenyl-1*H*-benzimidazole (3a)

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ = 12.92 (br, s, 1 H), 8.19–8.16 (m, 2 H), 7.60–7.46 (m, 5 H), 7.21–7.18 (m, 2 H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>): δ = 151.6, 130.6, 130.3, 129.4, 126.9, 122.5 ppm. MS: *m/z* = 194.08 [*M*<sup>+</sup>].

### 2-(4-Chlorophenyl)-1*H*-benzimidazole (3b)

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ = 13.00 (s, 1H), 8.20 (dd, *J*<sub>1</sub> = 6.6 Hz, *J*<sub>2</sub> = 1.8 Hz, 2H), 7.65–7.63 (m, 4H), 7.23 (d, *J* = 3.0 Hz, 2H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ = 150.63, 134.96, 129.53, 128.61, 123.20, 122.29, 119.44, 111.88 ppm. MS: *m/z* = 228.05 [*M*<sup>+</sup>].

### 2-(2-Chlorophenyl)-1*H*-benzimidazole (3c)

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ = 12.73 (s, 1H), 7.92 (dd, *J*<sub>1</sub> = 7.8 Hz, *J*<sub>2</sub> = 1.8 Hz, 1H), 7.67 (dd, *J*<sub>1</sub> = 8.4 Hz, *J*<sub>2</sub> = 1.2 Hz, 2H), 7.57–7.52 (m, 3H), 7.25 (s, 2H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ 149.57, 132.56, 132.11, 131.67, 130.82, 130.45, 127.91 ppm. MS: *m/z* = 229.05 [*M*<sup>+</sup>].

### 2-(4-Methoxyphenyl)-1*H*-benzimidazole (3e)

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ = 12.76 (s, 1H), 8.13 (d, *J* = 3.0 Hz, 2H), 7.56 (s, 2H), 7.18 (dd, *J*<sub>1</sub> = 5.4 Hz, *J*<sub>2</sub> = 3.0 Hz, 2H), 7.13 (d, *J* = 2.4 Hz, 2H), 3.85 (s, 3H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ = 161.07, 151.82, 128.48, 123.18, 122.21, 114.83, 55.79 ppm. MS: *m/z* = 224.10 [*M*<sup>+</sup>].

### 2-[4-Methylthiophenyl]-1*H*-benzimidazole (3f)[unknown product]

Pale yellow solid, 30%; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ = 12.5 (s, 1 H), 8.1 (m, 2 H), 7.7–7.6 (m, 2 H), 7.4 (m, 2 H), 7.3 (m, 1 H), 7.3–7.2 (m, 1 H), 2.7 (s, 3 H) ppm. <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>): δ = 152.7, 138.0, 130.6, 129.1, 126.8, 123.4, 115.0, 20.7 ppm. MS: *m/z* = 240.08 [*M*<sup>+</sup>].

### 2-(4-Methylphenyl)-1*H*-benzimidazole (3g)

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 12.83 (s, 1H), 8.08 (d, *J* = 8.4 Hz, 2H), 7.58 (s, 2H), 7.37 (d, *J* = 7.8 Hz, 2H), 7.20 (dd, *J*<sub>1</sub> = 6.0 Hz, *J*<sub>2</sub> = 3.0 Hz, 2H), 2.39 (s, 3H) ppm. <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ = 151.84, 140.04, 129.98, 127.90, 126.87, 122.43, 21.44 ppm. MS: *m/z* = 209.10 [*M*<sup>+</sup>].

**2-(2-Methylphenyl)-1H-benzo[d]imidazole (3h)**

$^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  12.66 (s, 1H), 7.73 (d,  $J = 7.4$  Hz, 1H), 7.69 (d,  $J = 7.8$  Hz, 1H), 7.53 (d,  $J = 7.6$  Hz, 1H), 7.42 – 7.35 (m, 3H), 7.26 – 7.17 (m, 2H), 2.60 (s, 3H) ppm.  $^{13}\text{C}$  NMR (100 MHz, DMSO)  $\delta = 152.4, 144.1, 137.5, 134.8, 131.8, 130.5, 129.9, 129.8, 126.5, 122.9, 121.9, 119.4, 111.7, 21.5$ . MS:  $m/z = 208.10$  [ $\text{M}^+$ ].