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Cu@U-g-C$_3$N$_4$ Catalyzed Cyclization of *o*-Phenylenediamines for the Synthesis of Benzimidazoles by Using CO$_2$ and Dimethylamine Borane as a Hydrogen Source

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Abstract

This work reports a green and sustainable route for the synthesis of benzimidazoles via C–N bond formation using carbon dioxide (CO$_2$) as a C$_1$ carbon source. In this work, Cu@U-g-C$_3$N$_4$ catalyst was prepared from urea derived porous graphitic carbon nitride (U-g-C$_3$N$_4$) and CuCl$_2$ and characterized by FT-IR, XRD, XPS, SEM, TPD etc. The Cu@U-g-C$_3$N$_4$ as a heterogeneous recyclable catalyst has been employed first time for the cyclization of *o*-phenylenediamines (OPD) with CO$_2$ to benzimidazoles using dimethylamine borane (DMAB). The proposed protocol becomes sustainable and efficient due to the use of propylene carbonate/water as a suitable biodegradable, economical and environmentally benign solvent system. The proposed catalytic system showed a wide range of substrate scope for the synthesis of benzimidazoles in good to excellent yields.

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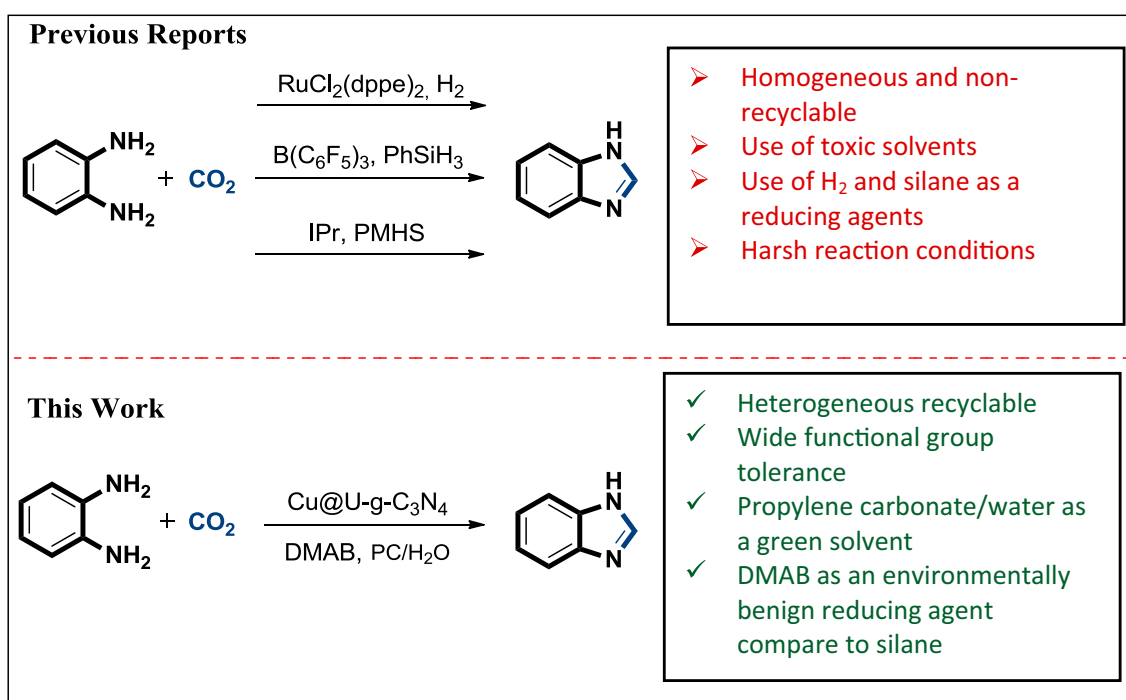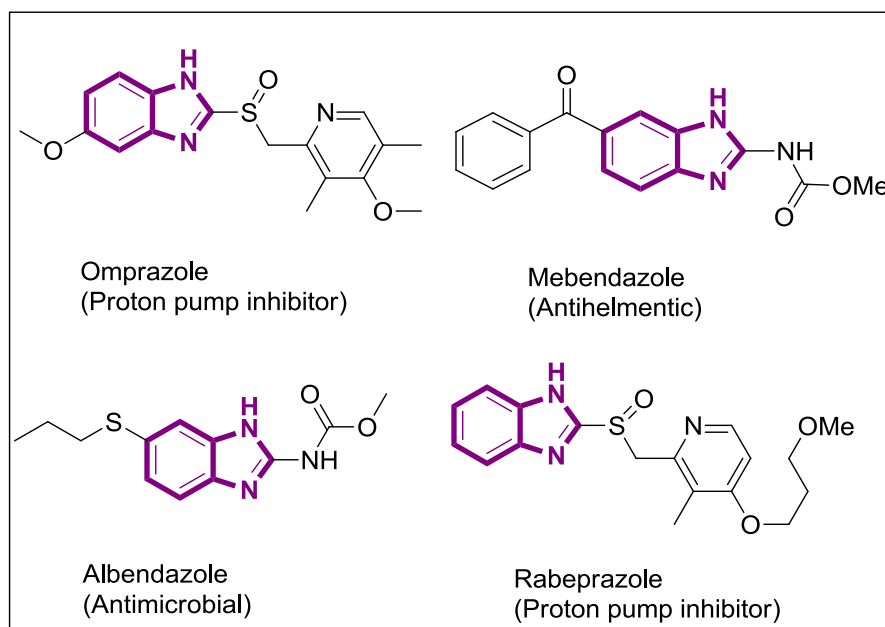
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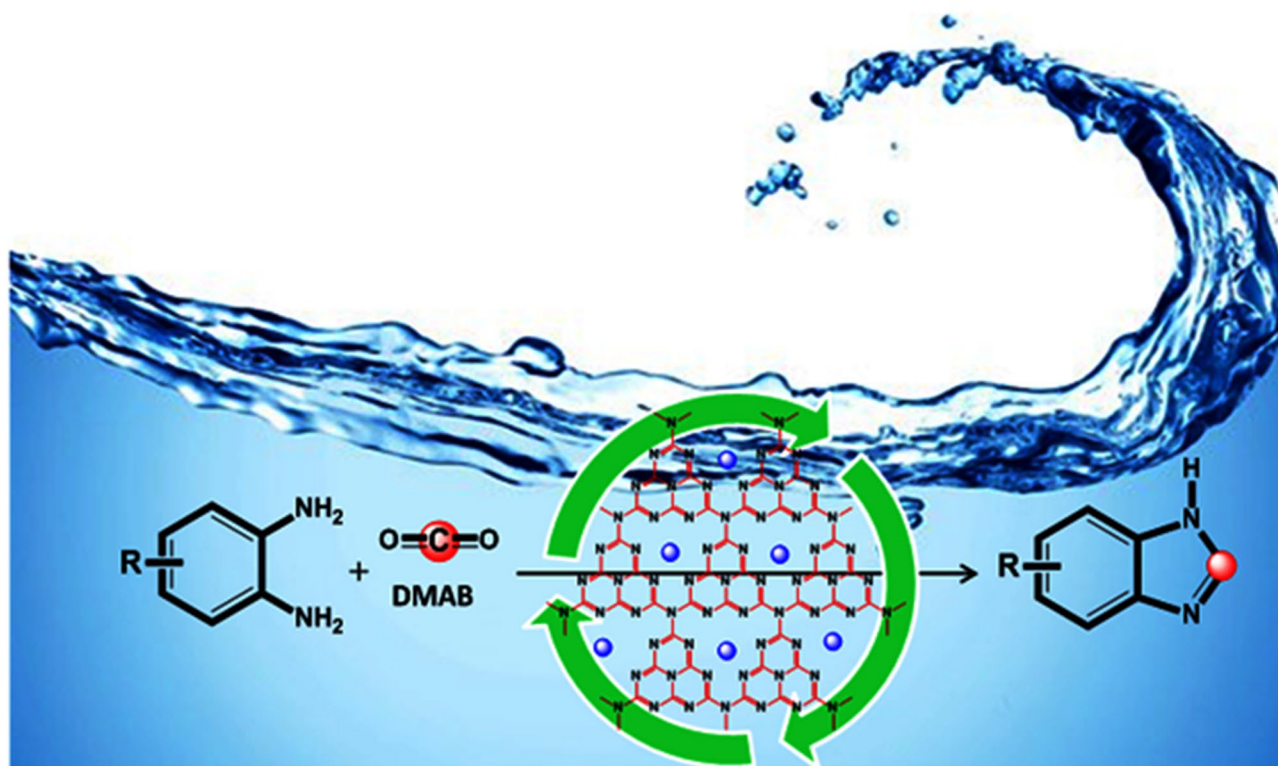
1 Introduction

The carbon dioxide utilization has become one of the important area of research as it is considered as the most responsible gas for global warming. Therefore, the capture and utilization of CO$_2$ is a straightforward solution to restrain its detrimental effect on the environment [1–3]. In recent years, the chemical synthesis involving CO$_2$ fixation has attracted much attention to the chemist. Additionally, the CO$_2$ is non-flammable and economical, easily available carbon feedstock [4] for the production of valuable chemicals such as benzimidazoles, formamides [5], carbonates [6, 7], carbamates [8], oxazolidinones [9], urea [10], methanol [11], formic acid [12], quinazoline-2,4(1H,3H)-diones [13, 14] etc. However, considering thermodynamic stability and kinetic inertness of CO$_2$, it is very difficult to activate and to convert it into value added-chemicals [15]. Most of the reported studies focused on the use of a strong nucleophilic substrate or demands the harsh reaction conditions to activate CO$_2$. Hence, cooperative activation of CO$_2$ with suitable catalyst and substrate is important. Generally, CO$_2$ is

used for the formation of C–N, C–C, C–O, and C–H bonds, which offers an environmental friendly route to synthesize the value-added chemicals.

The C–N bond forming reactions between the compounds having nitrogen groups and CO$_2$ are imperative in the industry as well as academia [16]. Benzimidazoles and its derivatives are one of the most important constituents of biologically active compounds. For example, they are used as intermediate in various important drug molecules such as Omeprazole, Rabeprazole, Mebendazole and Albendazole etc (Fig. 1) [17–20]. The traditional reports utilizes carbon monoxide, formic acid [21], DMF derivatives [22, 23], esters [24], aldehydes [25, 26], nitro methane [27], methanol [28] for the synthesis of benzimidazoles. Notably, these reported methods have certain drawbacks such as toxicity, harsh reaction conditions such as need of high reaction temperature, strongly acidic or basic conditions etc.

The strategies to use CO$_2$ as a C$_1$ source towards the synthesis of benzimidazoles from o-phenylenediamine had few reports in the literature. The Au/TiO$_2$ [30] catalyst was utilized for the conversion of o-nitroanilines

Fig. 1 Representative structures of drug molecules having benzimidazole as a constituent

Omprazole
(Proton pump inhibitor)

Mebendazole
(Antihelmentic)

Albendazole
(Antimicrobial)

Rabeprazole
(Proton pump inhibitor)

Previous Reports

RuCl$_2$(dppe)$_2$, H$_2$

B(C$_6$F$_5$)$_3$, PhSiH$_3$

IPr, PMHS

➤ Homogeneous and non-recyclable
➤ Use of toxic solvents
➤ Use of H$_2$ and silane as a reducing agents
➤ Harsh reaction conditions

This Work

Cu@U-g-C$_3$N$_4$

DMAB, PC/H$_2$O

✓ Heterogeneous recyclable
✓ Wide functional group tolerance
✓ Propylene carbonate/water as a green solvent
✓ DMAB as an environmentally benign reducing agent compare to silane

Scheme 1 Comparisons of previous reports for the synthesis of benzimidazoles from OPD in presence of a various catalyst

into benzimidazoles under CO$_2$ and H$_2$ atmosphere. Liu and co-worker developed RuCl$_2$(dppe)$_2$ [29] catalyst for synthesis of benzimidazole in presence of CO$_2$ and H$_2$ atmosphere but it require very high CO$_2$ and H$_2$ pressure and non-recyclable catalyst was used. Alternatively, Cantat and co-worker developed N-heterocyclic carbene (IPR) catalyzed synthesis of benzimidazole from OPD

with CO$_2$ in presence of silane as a hydrogen source at mild reaction condition [31]. This report used expensive ligands, non-recyclable catalyst etc. Recently, Frustrated Lewis Pair (FLP) B(C$_6$H$_5$)$_3$ catalyzed benzimidazole formation starting from OPD and CO$_2$ in the presence of PhSiH$_3$ was reported by Sun et al. [32]. This reports

require high temperature, high pressure and catalyst is non-recyclable (Scheme 1).

The selection of solvents plays very crucial role in the fixation of carbon dioxide into valuable chemicals. Traditionally organic solvents such as DMF, DCM, THF, DMSO etc have been utilized. However, toxicity, flammability, environmentally hazardous nature of these solvents imposes their applicability. From a green and sustainable chemistry point of view, replacement of these solvents by greener one will be a great achievement. The use of propylene carbonate as a solvent is an example which can overcome the limitations associated with the traditional organic solvents. The employment of propylene carbonate as a solvent has a number of advantages such as non-toxicity, aprotic, odorless, high boiling point, biodegradable [33]. Based on these benefits propylene carbonate is considered as green, environmental friendly and safe solvent. Moreover, the propylene carbonate score good to excellent in the GlaxoSmithKline (GSK) solvent selection guide [34, 35]. This showing that there is no concern of using propylene carbonate as a solvent at all criteria. Furthermore, on combustion propylene carbonate does not produce oxides of nitrogen and sulfur as it having only carbon, hydrogen and oxygen. Therefore propylene carbonate is a sustainable alternative solvent to DMF, DMSO and DCM.

Recently, g-C_3N_4 attracted much attention in the last few years due to its high thermal stability, basic property, easy recyclability, low cost, biocompatibility etc. Furthermore, the g-C_3N_4 is commonly used as a photocatalyst and active support for various metal catalysts. The advantage of these materials (simple recovery and recyclability) as compared to homogeneous catalyst can lead to environmental friendly chemical process. The advantageously, the g-C_3N_4 has van-der-waals interaction between the single layer of g-C_3N_4 like graphite which makes it insoluble in number of solvents like DMF, water, toluene, diethyl ether, THF etc [38–40]. Therefore g-C_3N_4 has wide potential in designing of high performance and environmentally benign catalyst. Therefore, our approach is to support less precious metal copper on the U-g-C_3N_4 to increase its activity towards the synthesis of benzimidazole. As copper nanoparticles (Cu NPs) have advantages such as easy preparation, inexpensive, heterogeneous, high catalytic activity etc, it has enormous application in catalysis as well as in synthesis.

Notwithstanding, previous reports have one or more disadvantages such as the use of expensive catalysts, non-recyclability of catalysts, the need for high reaction temperature and difficult catalyst preparation methods etc. Herein, we report the synthesis, characterization and application of Cu@U-g-C_3N_4 as an efficient and recyclable catalyst for the synthesis of benzimidazoles by using of OPD, CO_2 and

DMAB as a reducing agent at 100 °C in propylene carbonate/water as a green solvent medium.

2 Experimental

2.1 Materials and Methods

All chemicals were purchased from Sigma Aldrich, Alfa Aesar and used without further purification. The progress of the reaction was monitored by the thin layer chromatography (silica gel 60 F-254 plates) and the yields for the products were confirmed by gas chromatography (GC) of PerkinElmer Clarus 400 with a flame ionization detector and a capillary column (30 m × 0.25 mm × 0.25 μm) and. All of the products were identified by GC-MS (Shimadzu QP 2010 ultra, Rtx-17, 30 m × 25 mm ID), column flow 3 mL min^{-1}, 70 °C to 220 °C at 10 °C min^{-1} rise. Products were purified by column chromatography on 100–200 mesh silica gel. NMR spectra were recorded with an Agilent Technologies (^{1}H NMR at 400 MHz, ^{13}C NMR at 100 MHz) spectrometer. The U-g-C_3N_4 was prepared by pyrolysis of easily available urea [41] and Cu@U-g-C_3N_4 was prepared by precipitation method with slight modification in previously reported work [42]. We prepared three copper catalyst on the basis of copper loading (Cu@U-g-C_3N_4-1 = 3% Cu, Cu@U-g-C_3N_4-2 = 6% Cu, Cu@U-g-C_3N_4-3 = 10% Cu). The SEM images of these catalysts are shown in supporting information (Fig. S4). The detailed procedure of catalyst preparation is shown in supporting information.

2.2 Experimental Procedure for the Synthesis of Benzimidazoles

Synthesis of benzimidazole from *o*-phenylenediamine by CO_2 and DMAB in presence of Cu@U-g-C_3N_4 was carried out in high pressure reactor equipped with an overhead stirrer. In a general experiment for the synthesis of benzimidazole, *o*-phenylenediamine (1.00 mmol), DMAB (3 mmol), PC:H_2O (3 mL:1.5 mL), Cu@U-g-C_3N_4 (20 mg) were loaded into the reactor at room temperature, reactor was sealed, flushed three times with CO_2 and 2.5 MPa CO_2 pressure was loaded in to reactor, heated to required temperature with stirring (600 rpm). After completion of the reaction, the reactor was cooled to room temperature and the pressure was slowly released. The catalyst was separated by filtration, washed with ethyl acetate and water. The combined mixture was concentrated in vacuo and the products were purified by the column chromatography with silica gel of 100–200 mesh size and petroleum ether-ethyl acetate used as an eluent to afford pure products

[36, 37]. The spectroscopic data of all the products were matching with those reported in the literature. All of the products were confirmed by GCMS.

3 Results and Discussion

3.1 Characterization of Catalyst

3.1.1 FT-IR

Fourier Transform Infrared spectra (FT-IR) used for the investigation of various functional groups present in the synthesized catalyst. In our study, we measured the FT-IR spectra of U-g-C₃N₄ and Cu@U-g-C₃N₄-2 and shown in Fig. S1 (supporting information). IR spectrum of U-g-C₃N₄ and Cu@U-g-C₃N₄-2 is well resolved and the sharp peak at 809 cm^{-1} shows the presence of out of plane bending vibration characteristic of triazinecycle. The intense bands came at 1242, 1320, 1412 and 1550 cm^{-1} were due to the presence of C–N stretching of tri-s-triazine. The peak at 1635 cm^{-1} was assigned for C=N stretching vibration mode. The broad band peak begins from 2800 to 3500 cm^{-1} and shows the presence of N-H stretching vibration of the terminal amino group was observed in U-g-C₃N₄. When we loaded Cu on U-g-C₃N₄, there is no significant change in the FT-IR spectrum. This shows that Cu NPs and U-g-C₃N₄ were not forming covalent-bond interaction after loading of Cu on U-g-C₃N₄.

3.1.2 SEM

Scanning electron micrographs of U-g-C₃N₄ and Cu@U-g-C₃N₄-2 are shown in Fig. 2. The SEM images shows stacked layered like structure having the porous morphology of U-g-C₃N₄ (Fig. 2a, d). It is apparent that the morphology of U-g-C₃N₄ was not disturbed by the introduction of Cu NPs, this shows that Cu NPs were homogeneously dispersed on the surface of U-g-C₃N₄ as shown in Fig. 2b. After recycling there was a slight change in the morphology of Cu@U-g-C₃N₄-2 (Fig. 2c). The TEM images of Cu@U-g-C₃N₄-2 and reused Cu@U-g-C₃N₄-2 are shown in Fig. 2e and f respectively. The Fig. 2e and f confirms the formation of porous stacked layered morphology of U-g-C₃N₄ sheet. The Fig. 2e shows the presences of Cu NPs were dispersed on the surface of the U-g-C₃N₄, which having average particle size 38.74 nm. Moreover, there was no change in morphology of Cu@U-g-C₃N₄-2 after fourth recycle which shows that the prepared Cu@U-g-C₃N₄-2 catalyst was stable (Fig. 2f).

3.1.3 XRD

The XRD pattern confirms the presence two characteristic peaks that are assigned the presence of U-g-C₃N₄ polymer such as a graphitic stacking structure and match well with the previous report (Fig. 3) [40]. The intense and strong peak at 27.5° is proved that presence of (002) reflection of graphitic interlayer stacking structure of U-g-C₃N₄. The weak diffraction peak at 13.1° is ascribed to the (100) plane of in planar repeating motifs in U-g-C₃N₄. After loading Cu, the intensity of the peaks is slightly decreased due to the dilution effect. The new peaks of Cu appeared in the XRD pattern of Cu@U-g-C₃N₄-2, which can be ascribed to a dispersion of Cu NPs on the U-g-C₃N₄. The peaks at 42.1, 51.2 and 73.5° shows the presence of face centered cubic structure of Cu having (111), (200), (220) planes.

3.1.4 XPS Analysis

The X-ray photoelectron spectroscopy (XPS) spectrum of Cu@U-g-C₃N₄-2 was measured and shown in Fig. 4. The survey spectrum shows that there is the existence of C, N, O and Cu elements in the Cu@U-g-C₃N₄ − 2 catalyst (Fig. 4a). The C 1 s spectrum in Fig. 4c shows two peaks at 284.8 and 288.4 eV. The main peak at 288.4 eV is assigned to sp^2 bonded carbon (C=N−C) where as other peak at 284.8 eV corresponding to sp^2 carbon (C=C). From Fig. 4b the three N 1 s peaks were attributed at 398.8, 400.1 and 401.3 eV. The major peak at 398.8 eV shows the presence of sp^2-hybridized nitrogen attached to a carbon atom (C=N−C), other two peaks at 400.1 and 401.3 eV corresponding to the sp^3-hybridized tertiary nitrogen attached to carbon (N-(C)₃) and sp^3 hybridized nitrogen bonded to one hydrogen atom (C − N−H) respectively. The two major peaks at 932.7 and 952.7 eV shows that there is a shift in the binding energy of Cu 2p$_{3/2}$ and Cu 2p$_{1/2}$ respectively, suggesting that Cu(0) (metallic copper) was formed and it indicates that Cu(0) formed in the majority (Fig. 4d). The Peaks at 935 and 955 corresponding to Cu^{2+} species 2p$_{3/2}$ and 2p$_{1/2}$ and also two shake-up lines at 944.1 and 963.0 eV suggesting that Cu^{2+} present in a paramagnetic chemical shift.

3.1.5 Surface Area Measurement

The surface area measurement of U-g-C₃N₄ and Cu@U-g-C₃N₄-2 catalyst were measured by using the SMART SORB 93 instrument. The surface area of U-g-C₃N₄ and Cu@U-g-C₃N₄-2 was calculated as 29.6 m^2/g and 31.1 m^2/g respectively. From these result, it clearly
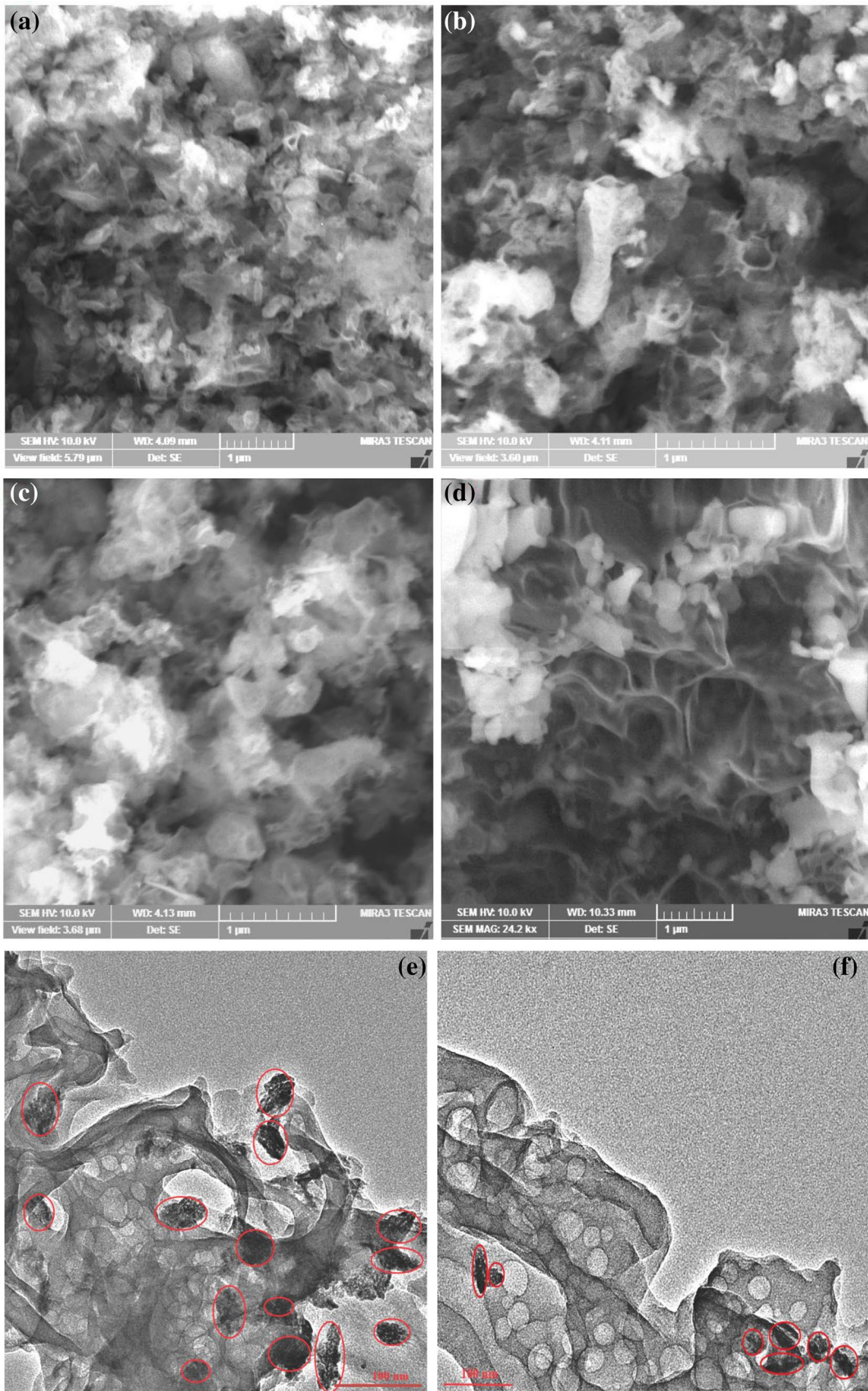
◄**Fig. 2** SEM images of **a** U-g-C₃N₄**b** fresh Cu@U-g-C₃N₄-2 and **c** reused Cu@U-g-C₃N₄-2 (after 4th recycle) **d** U-g-C₃N₄. TEM images of **e** fresh Cu@U-g-C₃N₄-2 and **f** reused Cu@U-g-C₃N₄ − 2 (after 4th recycle)

indicates that there was a small increase in surface area of Cu@U-g-C₃N₄-2, because of the exfoliation of U-g-C₃N₄ due to the sonication of U-g-C₃N₄ during the preparation of the catalyst. This shows that Cu NPs did not change the plane structure of U-g-C₃N₄, which is dispersed on the surface of U-g-C₃N₄.

3.1.6 TPD Analysis

The basic nature of U-g-C₃N₄ and Cu@U-g-C₃N₄-2 were determined by temperature programmed desorption (TPD) analysis. Before analysis, the prepared catalyst was undergone pretreatment with helium gas from 25 °C to 400 °C for 1.5 h to remove the adsorbed moisture and impurities. Then, the sample was cooled to room temperature and then CO_2 was passed at 50 °C to saturate the catalyst surface and desorption of CO_2 was carried out from 25 to 900 °C temperature with rise of 10°C/min using helium as an inert gas at a flow rate of 20 cm³/min. The CO_2 TPD was utilized to determine the basicity of the U-g-C₃N₄ and Cu@U-g-C₃N₄-2. The CO_2 TPD of U-g-C₃N₄ shows the peak at 720 °C is due to the desorption of CO_2 (Fig. S2), while in the CO_2 TPD of Cu@U-g-C₃N₄-2 shows the broad peak at 680 °C (Fig. S3).

3.2 Reaction Optimization

Initially, the reaction was carried out using OPD (1.0 mmol) as a model substrates in the presence of Cu@U-g-C₃N₄-2 catalyst (20 mg) and DMAB (3.0 mmol) under a CO_2 atmosphere (3.0 MPa) at 100 °C for 24 h, provided 70% yield of benzimidazole (1b) (Table 1, entry 1). No formation of

Fig. 3 XRD Spectra of U-g-C₃N₄ and Cu@U-g-C₃N₄-2

the desired product 1b was noted in the absence of catalyst (Cu@U-g-C₃N₄-2), this indicates that catalyst is necessary for the desired transformation (Table 1, entry 2). Various solvents used in this reaction have a remarkable effect on the yield of product 1b (Table 1, entries 1–7). The use of non-polar solvent such as toluene gave only 10% yield of 1b (Table 1, entry 3) and the polar solvent such as 1,4-dioxane and acetonitrile (ACN) furnished 40% and 55% yields of 1b, respectively (Table 1, entries 4 and 5). When reaction was carried out in propylene carbonate as a green solvent, 74% yield of 1b was observed (Table 1, entry 6). Considering the fact that DMAB is more soluble in H_2O, next, a mixture of propylene carbonate and water was employed in the ratio of 2:1. As per our expectation, this reaction progressed smoothly, furnishing 89% yields of 1b (Table 1, entry 7). After solvent study we screen different Cu@U-g-C₃N₄-2 catalyst on the basis of Cu loading (Cu@U-g-C₃N₄-1 = 3%, Cu@U-g-C₃N₄-2 = 6%, Cu@U-g-C₃N₄-3 = 10%). Out of these catalysts Cu@U-g-C₃N₄-2, Cu@U-g-C₃N₄-3 gave the good to excellent yield as compare to Cu@U-g-C₃N₄-1 catalyst (Table 1, entries 8, 9 and 10). In the next set of experiments, the effect of the temperature on the reaction system was examined. A slight increase in the yield of the desired product 1b was found when reaction temperature was raised from 100 to 110 °C (Table 1, entries 12). Lowering the temperature to 90 °C from 100 °C, furnished 68% yield of 1b (Table 1, entry 11). Therefore, the optimum temperature for the efficient conversion of 1a is 100 °C. The time studies suggest that 24 h is the ideal reaction duration. Performing the reaction for longer duration has no effect on the yield of 1b (Table 1, entry 14). A significant decrease in the yield of 1b was observed, when reaction were performed for lesser duration (Table 1, entry 13). Next, effect of the CO_2 pressure on reaction system was studied. Reducing CO_2 pressure to 2.5 MPa form 3.0 MPa led to no change in the yield of 1b (Table 1, entry 15). A further reduction in CO_2 pressure to 2.0 MPa resulted into decreased in the yield of 1b (Table 1, entry 16). The other commercial heterogeneous catalyst such as CuO was also screened for this reaction and it produced very poor yield of 1b (Table 1, entry 19). When the reaction was conducted with 2 mmol of DMAB, a decreased in the yield of the 1b was noted (Table 1, entry 18).

No benzimidazole was formed when the reaction was performed in the absence of CO_2, this confirms that the propylene carbonate does not act as a CO_2 source (Table 1, entry 20). Furthermore, the reaction was optimized with only U-g-C₃N₄ approached to 32% yield of 1b and it shows that Cu is necessary for the reaction (Table 1, entry 21). The optimized reaction conditions are OPD (1 mmol), CO_2 (2.5 MPa), DMAB (3 mmol), Cu@U-g-C₃N₄-2 (20 mg), Solvent–PC:H_2O (3 mL:1.5 mL), at 100 °C for 24 h.
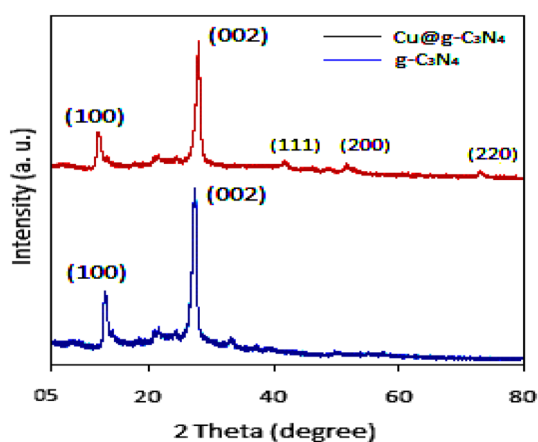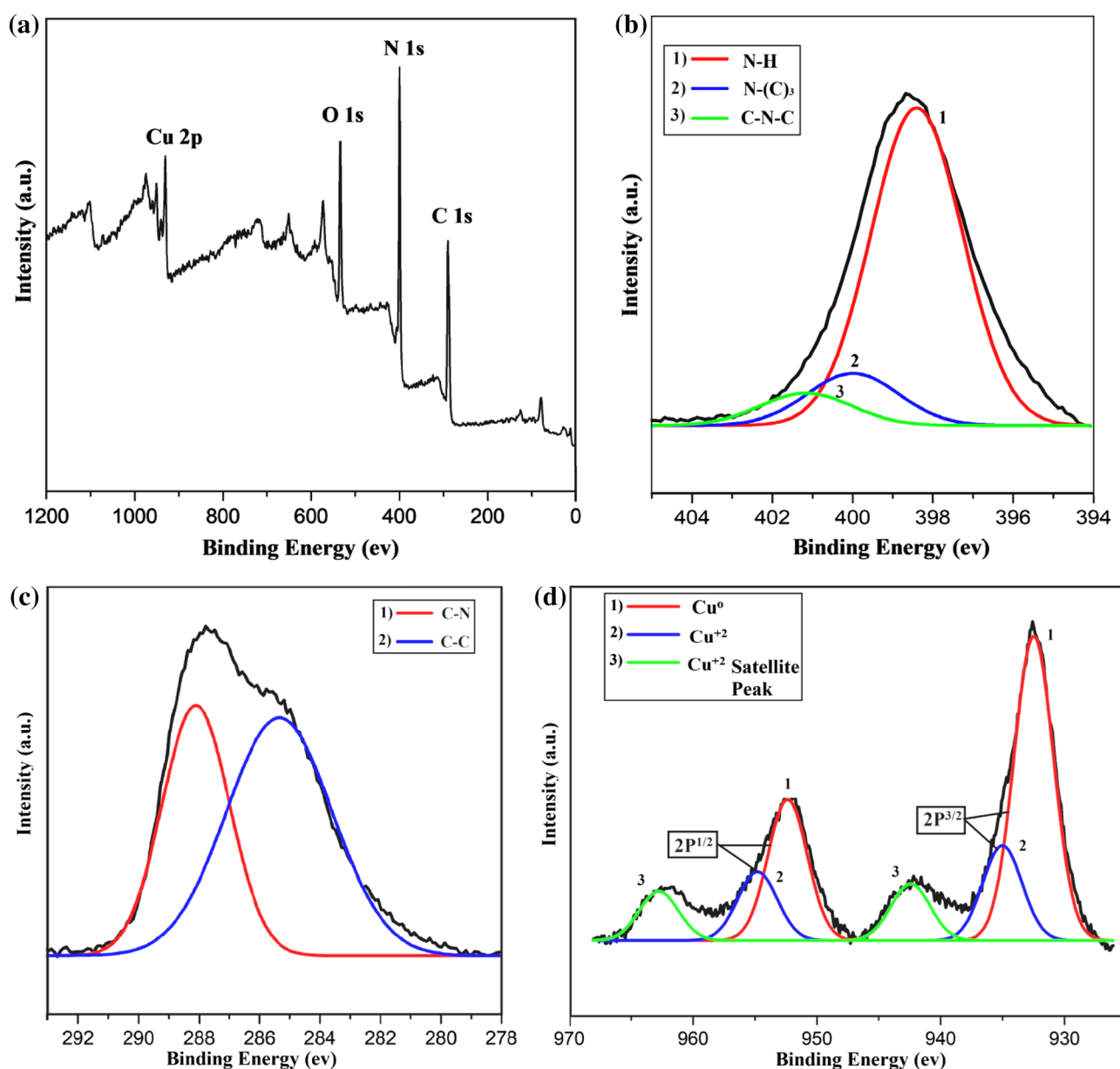
Fig. 4 XPS Spectra of Cu@U-g-C$_3$N$_4$-2: **a** survey **b** N 1 s **c** C 1 s **d** Cu 2p

3.3 Substrate Study

After optimization of reaction conditions, attempts were made to explore the substrates scope of *o*phenylenediamines to give a series of benzimidazoles as shown in Table 2. The electron donating and withdrawing substrates were well tolerated under the optimized reaction conditions furnishing the corresponding products in moderate to good yield. The 4-methyl and 4-methoxy substituted 1,2-diamine gave 90% and 78% yield of corresponding benzimidazoles 2b and 3b respectively (Table 2, entries 2 and 3). *N*-methyl-1,2-diamine provided the *N*-methylbenzimidazole (4b) in excellent yield (Table 2, entry 4). Unfortunately, no formation

of product was noted when reaction was performed with 2,3-diaminophenol (5a) (Table 2, entry 5). *O*-phenylenediamine having mono substituted weak electron withdrawing groups such as 4-chloro and 4-fluoro substituted 1,2-diamine provided 85% and 82% yield of 6b and 7b (Table 2, entries 6 and 7). The dichloro deactivate the o-phenylenediamine furnished lower yield of 5,6-dichloro-1H-benzimidazole (8b). Moreover, strong electrron withdrawing nitro group containing substrates such as 3-nitro-1,2-phenylenediamine resulted in 78% yield of 4-nitro-1H-benzimidazole (Table 2, entry 11). The nitrogen heterocyclic substrates 9a and 10a were employed for this reaction and they provided the 80% and 68% yield of corresponding benzimidazole respectively

Table 1 Optimization of reaction parameters
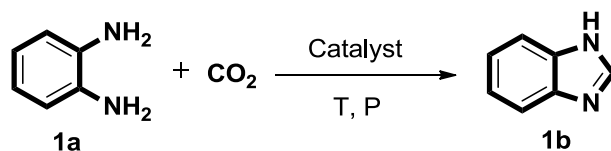
Entry	Solvent	DMAB (mmol)	Catalyst	CO_2 (MPa)	Temperature (°C)	Time (h)	Yield[a] (%)
Effect of solvent							
1	DMF	3	Cu@U-g-C₃N₄	3	100	24	70
2	DMF	3	–	3	100	24	–
3	Toluene	3	Cu@U-g-C₃N₄	3	100	24	10
4	1,4-dioxane	3	Cu@U-g-C₃N₄	3	100	24	40
5	CH₃CN	3	Cu@U-g-C₃N₄	3	100	24	55
6	PC	3	Cu@U-g-C₃N₄	3	100	24	74
7	PC:H₂O	3	Cu@U-g-C₃N₄	3	100	24	89
Effect of Cu loading							
8	PC:H₂O	3	Cu@U-g-C₃N₄-1	3	100	24	57
9	PC:H₂O	3	Cu@U-g-C₃N₄-2	3	100	24	89
10	PC:H₂O	3	Cu@U-g-C₃N₄-3	3	100	24	92
Effect of temperature							
11	PC:H₂O	3	Cu@U-g-C₃N₄-2	3	90	24	75
12	PC:H₂O	3	Cu@U-g-C₃N₄-2	3	110	24	92
Effect of time							
13	PC:H₂O	3	Cu@U-g-C₃N₄-2	3	100	18	63
14	PC:H₂O	3	Cu@U-g-C₃N₄-2	3	100	30	92
Effect of CO₂ pressure							
15	PC:H₂O	3	Cu@U-g-C₃N₄-2	2.5	100	24	88
16	PC:H₂O	3	Cu@U-g-C₃N₄-2	2.0	100	24	62
Effect of DMAB							
17	PC:H₂O	1	Cu@U-g-C₃N₄-2	2.5	100	24	45
18	PC:H₂O	2	Cu@U-g-C₃N₄-2	2.5	100	24	72
Effect of other parameters							
19	PC:H₂O	3	CuO	2.5	100	24	20
20	PC:H₂O	3	Cu@U-g-C₃N₄-2	–	100	24	–
21	PC:H₂O	3	U-g-C₃N₄	2.5	100	24	32

Reaction condition—substrate (1.0 mmol), DMAB (3.0 mmol), Cu@U-g-C₃N₄-2 (20 mg), Solvent—PC:H₂O (3.0 mL:1.5 mL) at 100 °C for 24 h

[a]Yield based on GC-GC/MS analysis. The yield was calculated by using external standard method using 1*H*-benzimidazole

(Table 2, entries 9 and 10). Next, the reaction of anthranilamide was performed which having less nucleophilic amide group. 4-quinazolinone (12b) was successfully achieved from anthranilamide and CO₂ with optimized reaction condition to get 56% yield (Table 2, entry 12).

The successful synthesis of benzimidazole and their derivatives by cyclization of diamine with CO₂ encouraged us to extend the scope of our protocol to study the reactivity of other less nucleophilic substrates such as 2-aminobenzylamine (13a). At first, 2-aminobenzylamine was employed

and it resulted into the formation of 3,4-dihydroquinazoline (13b) and quinazoline (13c) as a side product with overall 80% yield (Scheme 2).

After this, the formylation aniline and its derivatives were carried out using CO₂ and DMAB to obtain good yield of corresponding formanilide by the optimized reaction (Scheme 3).

Furthermore, a tentative reaction mechanism for the synthesis of benzimidazole has been developed on the basis of previous reported method [43, 44]. The Cu@U-g-C₃N₄
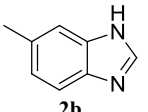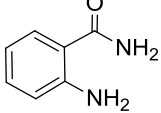
Table 2 Substrate study
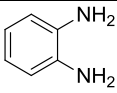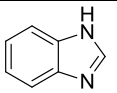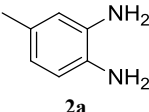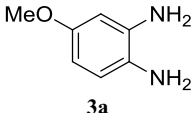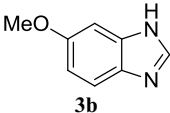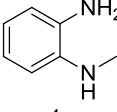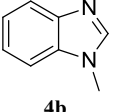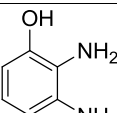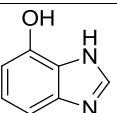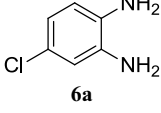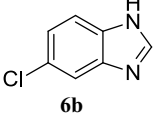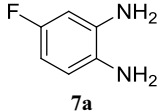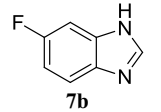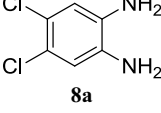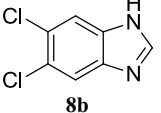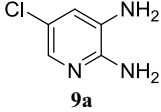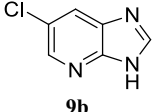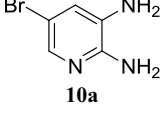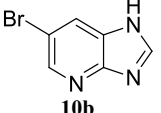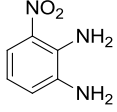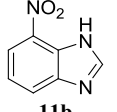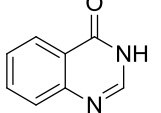
Entry	Substrate	Product	Yield[a] (%)
1	1a	1b	92
2	2a	2b	90
3	3a	3b	78
4	4a	4b	94
5	5a	5b	NC[b]
6	6a	6b	82
7	7a	7b	85
8	8a	8b	62
9	9a	9b	80
10	10a	10b	68
11	11a	11b	78
12	12a	12b	68

Scheme 2 Synthesis of 3,4-dihydroquinazoline from 2-aminobenzylamine reacting with CO_2

Scheme 3 Synthesis of formanilide from aniline reacting with CO_2

14a - R₁=R₂=R₃=H

15a - R₁=Me, R₂=R₃=H

16a - R₂=Meo, R₁=R₃=H

17a - R₁=H, R₂=R₃=Meo

14b = 78%

15b = 84%

16b = 86%

17b = 90%
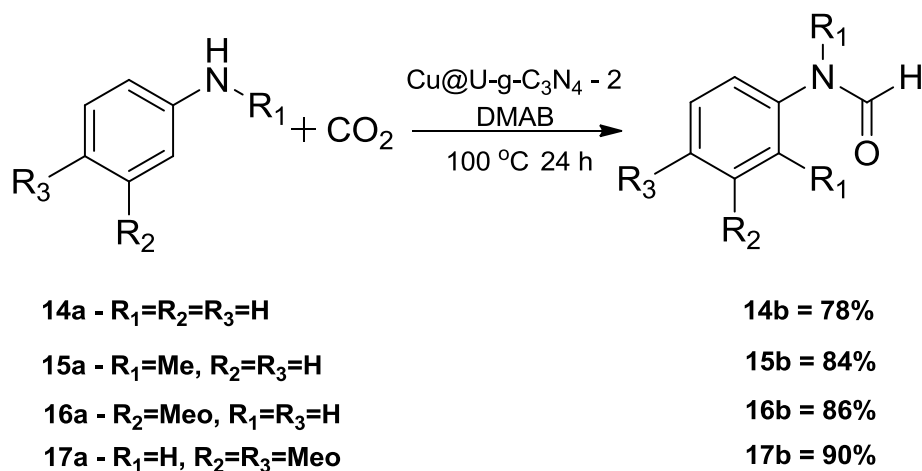
catalyst activates the DMAB to form intermediate 2 and catalyzed the insertion of CO_2 into B–H bond to form intermediate 3. Then intermediate 3 reacted with diamine to form formamide intermediate 4. Next, the intermediate 4 provide desired product (1a) by cyclization followed by dehydration (Scheme 4).

4 Recyclability Study

The recyclability of any heterogeneous catalysts is very important to determine the suitability of the developed catalysts. The recyclability of the Cu@U-g-C₄N₄-2 was also studied by using *o*-phenylenediamine as a model substrate under optimized reaction condition. The catalyst was easily separated from the reaction mixture by simple filtration or centrifugation. After separation wash with water and ethyl acetate to remove organic and inorganic impurity, then dried to 70 °C after each cycle before applying it in the next

reaction. This catalyst could be recovered and reused at least four times, without any obvious decrease in catalytic activity (Fig. 5).

5 Conclusion

In summary, we have synthesized and characterized U-g-C₃N₄ and Cu@U-g-C₃N₄ catalysts by pyrolysis of urea and facile precipitation method respectively. We have developed heterogeneous recyclable catalyst for the synthesis of benzimidazole from *o*-phenylenediamine by using CO_2 and DMAB as a hydrogen source. High stability and excellent catalytic activity, broad substrate scope, recyclability, use of green solvent makes this protocol an attractive alternative route for the synthesis of benzimidazoles. The developed protocol becomes sustainable due to the use propylene carbonate/water as a green solvent. Furthermore, the developed catalyst recovered easily by simple filtration method and

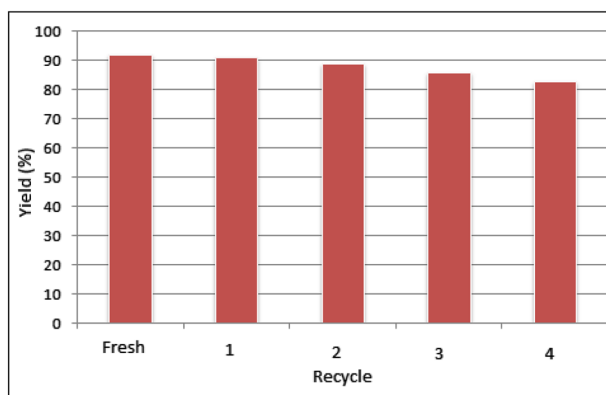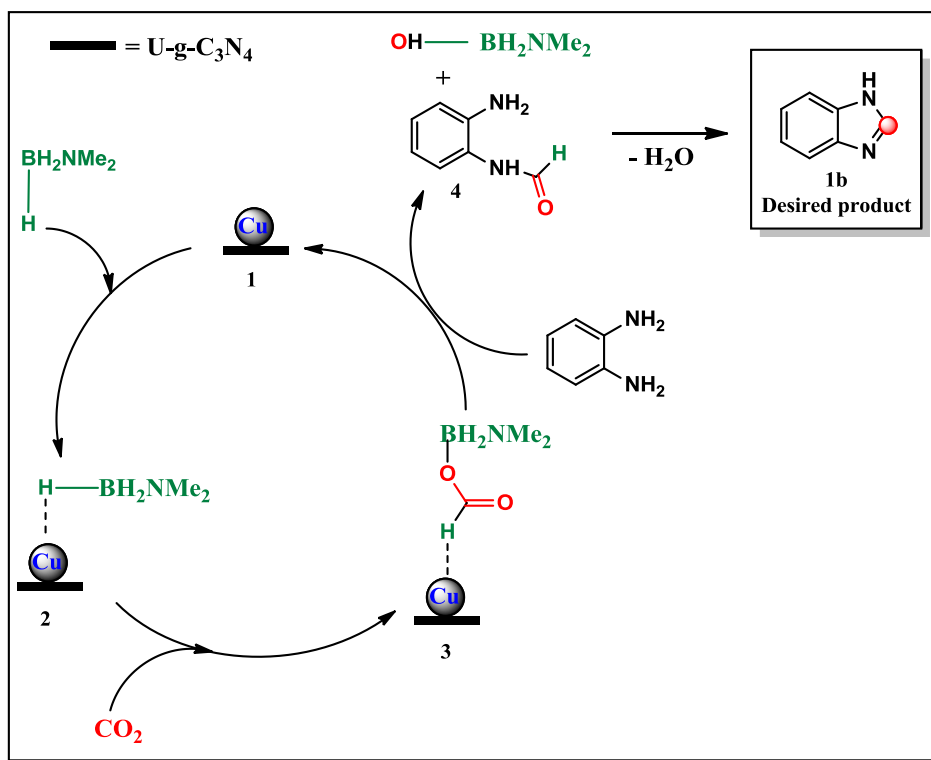**Scheme 4** Proposed reaction mechanism for synthesis of benzimidazole from OPD and DMAB in presence of CO_2

Fig. 5 Recyclability of the Cu@U-g-C$_3$N$_4$-2 for the synthesis of benzimidazole from OPD with CO_2 and DMAB

showed good recyclability up to four recycle runs without loss of its catalytic activity.

Compliance with Ethical Standards

Conflict of interest No conflict of interest, for each contributing author.

References

1. Bhanage BM, Arai M (2014) Transformation and utilization of carbon dioxide. Springer, Berlin, Heidelberg
2. He M, Sun Y, Han B (2013) Angew Chemie Int Ed 52:9620–9633
3. Liu Q, Wu L, Jackstell R, Beller M (2015) Nat Commun 6:5933
4. Aresta M (2006) Carbon dioxide reduction and uses as a chemical feedstock. In: Activation of small molecules. Wiley, Weinheim, pp 1–41
5. Nale D, Bhanage B (2016) Synlett 27:1413–1417
6. Saptal VB, Sasaki T, Harada K, Nishio-Hamane D, Bhanage BM (2016) ChemSusChem 9:644–650
7. Saptal VB, Bhanage BM (2016) ChemCatChem 8:244–250
8. Nale DB, Rana S, Parida K, Bhanage BM (2014) Appl Catal A Gen 469:340–349
9. Fontana F, Chen CC, Aggarwal VK (2011) Org Lett 13:3454–3457
10. Jiang T, Ma X, Zhou Y, Liang S, Zhang J, Han B (2008) Green Chem 10:465
11. Wesselbaum S, vom Stein T, Klankermayer J, Leitner W (2012) Angew Chemie Int Ed 51:7499–7502
12. Moret S, Dyson PJ, Laurenczy G (2014) Nat Commun 5:4017
13. Saptal VB, Bhanage BM (2017) ChemSusChem 10:1145–1151
14. Nale DB, Saigaonkar SD, Bhanage BM (2014) J CO2 Util 8:67–73
15. Wang W-H, Feng X, Bao M (2018) Transformation of carbon dioxide to formic acid and methanol. Springer Singapore
16. Li Y, Cui X, Dong K et al (2017) ACS Catal 7:1077–1086
17. Vojčić N, Bregović N, Cindro N et al (2017) ChemistrySelect 2:4899–4905
18. Keri RS, Hiremathad A, Budagumpi S, Nagaraja BM (2015) Chem Biol Drug Des 86:19–65
19. Zhang J, Wang J-L, Zhou Z-M et al (2012) Bioorg Med Chem 20:4208–4216
20. Zhou R, Skibo EB (1996) J Med Chem 39:4321–4331

21. Azizi N, Edrisi M, Abbasi F (2018) Appl Organomet Chem 32:e3901
22. Nale D, Bhanage B (2015) Synlett 26:2835–2842
23. Kattimani PP, Kamble RR, Meti GY (2015) RSC Adv 5:29447–29455
24. Fu R, Yang Y, Ma Y et al (2015) Tetrahedron Lett 56:4527–4531
25. Mann J, Baron A, Opoku-Boahen Y et al (2001) J Med Chem 44:138–144
26. Lin S, Yang L (2005) Tetrahedron Lett 46:4315–4319
27. Aksenov AV, Smirnov AN, Aksenov NA et al (2015) Org Biomol Chem 13:4289–4295
28. Feng F, Ye J, Cheng Z et al (2016) RSC Adv 6:72750–72755
29. Yu B, Zhang H, Zhao Y et al (2013) Green Chem 15:95–99
30. Hao L, Zhao Y, Yu B et al (2014) Green Chem 16:3039
31. Jacquet O, Das Neves Gomes C, Ephritikhine M, Cantat T (2013) ChemCatChem 5:117–120
32. Zhang Z, Sun Q, Xia C, Sun W (2016) Org Lett 18:6316–6319
33. Shaikh A-AG, Sivaram S (1996) Organic carbonates. Chem Rev 96:951–976
34. Adeleye AI, Patel D, Niyogi D, Saha B (2014) Ind Eng Chem Res 53:18647–18657
35. Alder CM, Hayler JD, Henderson RK et al (2016) Green Chem 18:3879–3890
36. Gautam P, Kathe P, Bhanage BM (2017) Green Chem 19:823–830
37. Parker HL, Sherwood J, Hunt AJ, Clark JH (2014) ACS Sustain Chem Eng 2:1739–1742
38. Dong G, Zhang Y, Pan Q, Qiu J (2014) J Photochem Photobiol C Photochem Rev 20:33–50
39. Gillan EG (2000) Chem Mater 12:3906–3912
40. Wang Y, Wang X, Antonietti M (2012) Angew Chemie Int Ed 51:68–89
41. Fang H-B, Luo Y, Zheng Y-Z, Ma W, Tao X (2016) Ind Eng Chem Res 55:4506–4514
42. Huang S, Zhao Y, Tang R (2016) RSC Adv 6:90887–90896
43. Zhang S, Mei Q, Liu H et al (2016) RSC Adv 6:32370–32373
44. Saptal VB, Juneja G, Bhanage BM (2018) New J Chem