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 Cu/Cu_xO_y NPs Architectured COF: A Recyclable Catalyst for Oxazolidinedione Synthesis via Atmospheric Cyclizative CO_2 Utilization

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The present study describes the favourable construction of the crystalline covalent organic framework (COF) with exceptional surface area, tunable pore size and huge CO₂ capture efficiency to facilitate a novel multicomponent cyclization by introducing CO₂ into extremely reactive organic skeletons. In the presence of catalytic Cu/Cu_xO_y NPs-loaded COF, several 2-bromo-3-alkylacrylic acids combined with several amine derivatives and CO₂ (0.1 MPa) are converted to the desired oxazolidinediones in excellent yields (up to 96%) under alkali-free condition and ambient temperature. Intriguingly, the reaction described above is mostly catalyzed by CuO and Cu₂O sites present in Cu@COF-BD(OH)₂.

Atmospheric climate-warming carbon dioxide (CO₂) is one of the most significant greenhouse gases and its worldwide uncontrolled emission into the environment and an alarming level of atmospheric notorious CO₂ have caused increasing global concerns.¹ It is a significant C1 building unit for the synthesis of high-value chemicals due to its low-priced, abundant, and nonpoisonous nature. It has a huge potential as polymeric systems, fuels or other compounds via the utilization of renewable energy source.² The mission to control atmospheric CO₂ (a greenhouse gas) has triggered the advancement of some novel cyclizative CO2incorporated reactions. In the previous decade, transition-metal promoted CO₂ incorporation has emerged as a feasible, sustainable and potential strategy towards the more benign synthesis of several valuable commodity compounds like carboxylic acid derivatives by activating C-H bonds in organic synthesis.³ In recent times, Yoshida et al. published that harmful CO2 could straightforwardly be introduced by conducting a three-component reaction employing imines and arynes, where produced zwitterionic species from the nucleophilic attack of imine systems to arynes captured carbon dioxide as a path to biologically and pharmaceutically active derivatized benzoxazinone derivatives.⁴ Recently, Kobayashi and coresearchers employed a comparable approach for the generation of isocoumarin derivatives through novel NHC-Cu facilitated reactions participating terminal alkynes, CO₂ and orthoarynes.⁵ Therefore, the advancement of effective strategies employing atmospheric notorious CO₂ in combination with MCR-type synthetic methodology (multicomponent reaction) for the generation of heterocycle systems like oxazolidinediones is value-added chemicals for their utilities from pharmaceuticals to polymeric systems, which could unlock a novel route to a chemical library of several high-value chemical scaffolds.

Covalent organic frameworks (COFs) are an emerging kind of π bonded, stacked and layered polymeric agents featuring excellent crystallinity, which have displayed widespread utilities in energy storage,⁶ gas adsorption,⁷ metal ions isolation and recovery,⁸ chemical sensing,⁹ and catalysis,¹⁰ etc. Compared with some exfoliated 2D nanomaterials of inorganic nature or graphene, the

stacked 2D COFs retain few reasonable advantages, like several optional monomeric units, flexible building units resulting in tunable features of the layered crystalline materials.¹¹ On the other hand, owing to the comparatively intricate growth method involving crystallization, assembly and polymerization etc., it remains a huge difficulty to generate well-organized and absolutely ordered 2D stacked COF sheets so far. Generally, the construction processes of 2D sp² carbon-conjugated COFs published can be categorized into two classes, bottom-up strategy and top-down strategy. Herein, $\mbox{Cu}/\mbox{Cu}_{x}\mbox{O}_{y}$ NPs can be stabilized by heteroatom functionalized COF pores, whereas meso/micropores of this COF permit unrestricted access to these nanoparticles-based active binding sites. This COF-nanoparticles composite catalyst, as a novel catalytic system, retain definite advantages, like scalability, reusability, easy-to-handle, and their performance can be adjusted through a "by-design" approach.12 Additionally, Oxazolidinedione is a high-value constituent of numerous molecules possessing biological activity. A series of value-added pharmaceuticals consisting of these moieties are being utilized for numerous types of functions (such as therapeutic purposes) (Scheme 3).



Scheme 2. Generation of oxazolidinediones facilitated with a potential Cu/Cu_xO_y NPs embedded COF under benign conditions.

Herein, we introduced the fruitful production of oxazolidinedione derivatives from amine derivatives and derivatized 2-bromo-3alkylacrylic acids employing CO₂ as a C1 source in the presence of a definite amount of catalytic Cu/Cu_xO_y NPs-grafted COF. According to the best of our knowledge, it will be the first report of CO2incorporated multicomponent cyclization with Cu/Cu_xO_v NPs architectured covalent organic framework, (Cu@COF-BD(OH)₂), as a potential heterogeneous catalyst under alkali-free conditions (sustainable approach). Characterizations of parent COF-BD(OH)2 and resultant Cu@COF-BD(OH)₂ are performed by analyzing thermogravimetry (TG), N₂ adsorption-desorption analysis, Fourier transform infrared (FT-IR) spectrum, elemental analysis. transmission electron microscopy (TEM), powder X-ray diffraction (PXRD), scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). The schematic illustration of the construction method involved in developing 2D COF-BD(OH)₂ is presented in Scheme 3.

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COF-BD(OH)2 * COF-BD(OH); ♦Cu₂O Intensity (a.u.) (a.u.) 3.3 (100) 100) # CuO -π stacking π stacking Interaction Intensity (110) 9.8 27.3 (001)Cu@COF-BD(OH 10 20 30 40 50 60 70 80 5 70 10 20 30 40 50 60 80 20 (degree) 0 20 (degree) Cu/Cu_xO_y NPs (100) (001)doo1=3.3 Å Coral-like morphology

Fig. 1 PXRD patterns of COF-BD(OH)₂ and Cu@COF-BD(OH)₂ composite catalyst, FE-SEM pictures of Cu@COF-BD(OH)₂ composite catalyst at several magnifications (a-c).

The powder X-ray diffraction patterns of the parent COF- $BD(OH)_2$ and Cu/Cu_xO_y NPs embedded COF is presented in Fig. 1, demonstrating that the microporous layered sheets display absolutely ordered hexagonal 2D arrangement. The PXRD pattern of the as-obtained COF-BD(OH)₂ exhibits a significant diffraction peak of high intensity, which is located at a diffraction angle (2 θ) of 3.3° corresponding to the (100) facet, demonstrating the excellent crystallinity due to lower rotational freedom of the building units (Figure 1). The resultant COF-NPs composite exhibits the main peak of elevated intensity situated at a diffraction angle (2 θ) of 3.3°. caused by the (100) facet. One minor hump-shaped peak of poor intensity, caused by the (001) facet, situated at 27.3°, and the existence of this distinct peak is ascribed to a special interaction arising from $\pi\text{-}\pi$ stacking among the aromatic rings present in the ordered layered-sheet COF, suggesting exactly ordered periodicity of the as-obtained COF-BD(OH)₂.¹³ The particle sizes (crystallite size) of Cu NPs were calculated to be within the range of 14 to 17 nm determined from the Scherrer's equation (Table S7, ESI⁺). Employing Debye-Scherer formula, the determined crystallite sizes are found to be 25.03 nm and 24.69 nm for the (002) facet (CuO) and (111) facet (CuO), respectively. The TEM results are in good accordance with the calculated values obtained from the Scherrer's equation. Employing Debye-Scherrer equation, the crystallite sizes of Cu₂O are determined to be in the range of 18.5±1.5 nm (Table S8, ESI[†]). As presented in Figure 3(h), The N₂ desorption/adsorption isotherm of the microporous π -bonded stacked Cu@COF-BD(OH)₂ displays usually the copious features of type I with few additional natures of type IV pattern. The surface area obtained from BET experiment and observed pore volume of Cu@COF-BD(OH)2 composite catalyst are 192.31 m²g⁻¹ and 0.201 ccg⁻¹, respectively.

The distribution of pore size of the COF-NPs composite determined with the help of NLDFT method employing $N_{\rm 2}$ at a definite temperature (77 K) confirmed the existence of micropores having pore dimension (ca. 1.8 nm).¹⁴ As described in Figure 1(a-c), SEM (scanning electron microscopy) pictures of this COF-NPs composite suggest that a curled irregular arrangement is made up of interconnected twisted rods inside the nanoscale range (corallike microscopic arrangement).¹⁵ As presented in Figure S11 (a-d), the TEM pictures of COF-BD(OH)₂ suggested structural morphology of interlinked twisted wires (see ESI for details). As described in Figure S11 (c-d), the clearly visible borders in mentioned TEM pictures of COF-BD(OH)₂ illustrating intensely conjugated layeredsheet arrangement exists in this highly ordered parent COF owing to the presence of aromatic $\pi-\pi$ interactions.¹⁶ COF-BD(OH)₂ displayed layered-sheet arrangement observed by TEM, which is in agreement with the SEM pictures. PXRD pattern of the parent COF agrees well with HR-TEM pictures. As described in Figure 2 and 1, TEM and SEM pictures display that the structural morphology of Cu@COF-BD(OH)₂ composite catalyst can keep the same as the morphology of COF-BD(OH)2. EDAX experiments illustrated the existence of O, N and C as displayed in Figure S13 and S14 (see ESI for details). EDX also suggested the loading of copper in the COF-NPs composite to be at 6.4 wt%, which is in agreement with the copper loading (6.8 wt %) measured from the ICP experiment. XPS experiments demonstrate the existence of Cu⁺ (Cu₂O) along with a certain amount of Cu²⁺ (CuO) in the COF-NPs composite named Cu@COF-BD(OH)₂. The XPS survey scan of Cu@COF-BD(OH)₂ is presented in Figure 3a which demonstrates the existence of oxygen, nitrogen, carbon and Cu species existing in the intensely conjugated COF-based copper material.



Figure 2. The UHR-TEM pictures of Cu@COF-BD(OH)₂ material displaying the distinct lattice fringes owing to the existence of different copper species at different scales (a) 100 nm, (b) 50 nm, (c) 20 nm, (d) 10 nm, (e) 20 nm, (f) 2 nm, (g) 5 nm and (h) SAED pattern of Cu@COF-BD(OH)₂. The inset describes the distribution of particle size determined from TEM image.

The Cu 2p XPS signal has been subjected to deconvolute (Figure 3f), which displays $2p_{3/2}$ bands with binding energies of 934.8 and 932.6 eV, which are assigned to the CuO (Cu²⁺) and Cu₂O (Cu⁺) in the Cu/Cu_xO_y NPs embedded COF, respectively.¹⁷ As described in Figure 3c, the significant Cu LMM peak appeared at 570.4 eV is ascribed to the copper species featuring lower oxidation state (Cu₂O) in addition to the Auger parameters of the copper $2p_{3/2}$. Additionally, O 1s, N 1s and C 1s narrow scan (Figure 3) demonstrate the structural morphology of Cu/Cu_xO_y NPs anchored COF.



Binding energy (eV) Elivating energy (eV) Figure 3. XPS survey scan measurement on Cu@COF-BD(OH)₂ (a), C 1s narrow scan (b), XPS Cu LMM spectra (c), N 1s narrow scan (d), O 1s narrow scan measurement (e) on Cu@COF-BD(OH)₂ composite catalyst; the XPS spectrum of Cu@COF-BD(OH)₂ illustrating the bands corresponding to metallic copper NPs and copper oxide NPs featuring different oxidation states (Cu¹⁺ and Cu²⁺) and the "#" represent the shake-up photo emission bands suggesting Cu²⁺ (f), Cu 2p_{3/2} XPS core level spectra (g), and the N₂ sorption profile of Cu@COF-BD(OH)₂ composite catalyst (h); pore size distribution of Cu@COF-BD(OH)₂ (i), calculated by using NLDFT method.

The C 1s core level peak by conducting peak deconvolution displayed that bands with binding energies of 289.2, 286.02 and 284.5 eV for Cu@COF-BD(OH)₂ are ascribed to the carbon atoms of C=O, C-O/C-N and C-C, C=C and C-H, respectively.³⁵ The N 1s signal illustrates a band with binding energy of 399.9 eV corresponding to the enamine nitrogen atoms (Figure 3d). The band located at 400.8 eV corresponds to the existence of poor Cu-N attachment due to an interaction between copper species and enamine nitrogen atoms. The prominent copper 2p XPS spectra display bands at the binding energies of 932.6, 934.8, 952.2, and 954.1 eV, which are consistent with the Cu $2p_{3/2}$ and Cu $2p_{1/2}$ levels of the copper NPs and copper featuring lower oxidation state from Cu₂O (Figure 3f and 3g).18 Furthermore, two unique satellite peaks located at 964 and 944 eV are ascribed to the copper species featuring higher oxidation state. The prominent shake-up satellite arrangements and strong Cu $2p_{3/2}$ peak were subjected to deconvolute into four distinct bands, as presented in Fig. 3g. Two clearly visible peaks located at 932.6 and 934.8 eV could be attributed to Cu (I) from Cu₂O NPs and Cu(II) from CuO phases, respectively. The XPS outcomes suggest that the catalyst is composed of CuO, Cu₂O and Cu. Cu⁰ and Cu⁺ (Cu₂O) cannot be resolved by this deconvolution because their respective binding energies are fairly close and are different by around 0.1 eV (Fig. S28, ESI^{\dagger}). Cu₂O and Cu metal are best distinguished from the x-ray-excited Cu LMM Auger spectra. Two overlapping bands at about 568.08 and 570.40 eV in the XAES spectra are related to Cu⁰ and Cu⁺, respectively, and the deconvolution outcomes of these bands are utilized to estimate the molar ratios of different copper ions ($X_{Cu+} = Cu^+/(Cu^0 + Cu^+)$) (Fig. S29, ESI[†]).¹⁹



Initially, we were inspired by the outcome published on the alkali mediated atmospheric cyclization reaction of CO2, bromoacrylic acids and amines for the generation of oxazolidinediones type bioactive drugs (Scheme 1).²⁰ We expected that these value-added compounds could be generated by catalytic Cu/Cu_xO_y NPs embedded COF under sustainable conditions (Scheme 2).²¹ To establish our present hypothesis, 2-bromo-3-phenylacrylic acid 1b and aniline 2b*are employed as model substrates for the sustainable synthesis of oxazolidinedione (3bb*) in the presence of catalytic COF-NPs composite under atmospheric CO₂ (0.1 MPa) (Scheme 4). We next tested the influences of several parameters on the advancement of the CO2-incorporated cyclization reaction including catalytic systems, amount of the investigated catalyst, reaction temperatures, solvents, bases and reaction times (Table S1, ESI^{\dagger}). The use of Cu/Cu_xO_y NPs embedded COF as a potential catalytic system provided an excellent yield in the presence of atmospheric CO₂ (0.1 MPa) under ambient temperature and alkalifree condition (Table S1, entries 22, ESI[†]). The substrate scope of CO_2 -incorporated cyclizative multicomponent reaction of some derivatized bromoacrylic acids with several amines was also investigated under the optimal conditions and the outcomes obtained are presented in Table 1. Several amine derivatives and different as-prepared 2-bromo-3-alkylacrylic acids were employed to synthesize different derivatized products under the application of the optimal conditions: 40 mg of Cu@COF-BD(OH)₂ catalyst, 10 h, 25°C, 6 ml DMF solvent.

Table 1. Copper-facilitated production of several oxazolidinedionederivativesvia CO_2 -incorporatedcyclizativemulticomponentreactions with a detailed substrate scope.^a





a Reaction conditions: 2-bromo-3-alkylacrylic acids (1.0 mmol), amines (1.2 mmol), $Cu@COF-BD(OH)_2$ catalyst (40 mg), CO_2 (0.1 MPa), DMF (6 mL). Isolated yield.

Seven kinds of bromoacrylic acids with phenyl (1b), pmethoxyphenyl (1a), p-tolyl (1c), m-tolyl (1d), p-chlorophenyl (1e), 3,5-dimethylphenyl (1f) and 4-hydroxyphenyl (1g) parts were initially generated by conducting multi steps processes (See Supporting Information for additional information). The as-obtained bromoacrylic acid derivatives were allowed to react with aromatic and aliphatic amine derivatives under identical conditions. Combination of CO₂, ammonia and derivatized bromoacrylic acids Published on 21 August 2020. Downloaded by UNIVERSITY OF BRIGHTON on 8/21/2020 3:53:39 PM

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did not provide the desired oxazolidinedione derivatives (3ed* and 3cd*) even at higher temperature (80°C) and a prolonged time of the reaction did not improve the yields. Moreover, we have tried to generate the oxazolidinediones from several aromatic amines, and relatively satisfactory to excellent yields, which grew from 36% (3ff*) to 96% (3aa* and 3bb*) as summarized in Table 1. Typically, pmethoxy substituent (electron donating capacity) on aromatic amine derivatives afforded the desired oxazolidinediones (3aa*, 3ba*, 3da*, 3ea* and 3ga*) with excellent yields in the range of 81% (3da*, 3ga*)-96% (3aa*). For effective comparison, m-Cl substituent (electron withdrawing capacity) on the aromatic amine afforded the desired oxazolidinedione (3ff*) with only 36% yield. Surprisingly, p-Cl substituent on the aromatic amine afforded the desired oxazolidinedione (3ag*) with 76% yield. Similarly, the other groups such as $p-NO_2$ (2c^{*}) and $p-CH_3$ (2e^{*}) on the amines afforded the desired oxazolidinediones with satisfactory yields of 68% (3cc*), 93% (3ee*) and 79% (3be*). On the other hand, the derivatized bromoacrylic acids featuring phenyl (1b), p-methoxyphenyl (1a), ptolyl (1c), m-tolyl (1d), p-chlorophenyl (1e), 3,5-dimethylphenyl (1f) and 4-hydroxyphenyl (1g) groups on alkene systems provided moderate to excellent yields in the range of 36% (3ff*)-96% (3aa* and 3bb*), independent of the electron-donating or electronwithdrawing capacities of the substituents on the aromatic rings.

Encouraged by previously reported works,²² we investigated DFT calculations which were employed to explore the reason underlying superior catalytic performance (Fig. 4). From DFT study, it is found that Cu@COF-BD(OH)₂ activates the bromoacrylic acid for the reaction and also stabilizes the adduct to form the intermediate and plays a vital role in the cyclization to generate the product (Fig. 51 and S2, ESI⁺). Based on DFT calculation and the literature reports,²³ we have proposed a hypothetical catalytic mechanism of the title reaction (Figure S2, ESI⁺). Absorption energy of Cu ion featuring an oxidation state of +1 is about -31.37 kcal/mol. Absorption energy of Cu ion featuring an oxidation state of +2 is -38.12 kcal/mol. It has been observed that Cu²⁺ is stabilized by the carbonyl group existing in the structure of COF while Cu¹⁺ is stabilized by Vander Waals force of interaction (Figure S1(i), ESI⁺). The overall reaction energy for the entire reaction cycle is determined to be exothermic by -1.09 eV.

To get hidden information about heterogeneous nature of Cu@COF-BD(OH)₂, we have conducted ICP-AES experiment of the resultant filtrate and recovered Cu@COF-BD(OH)₂. We did not detect any noticeable copper trace in the filtrate and resultant Cu@COF-BD(OH)₂ catalyst retains almost the same copper loading as that of fresh catalyst (\approx 6.80 wt%). All these observations undoubtedly revealed the heterogeneous nature of Cu@COF-BD(OH)₂. The AAS observation corroborates well with the ICP-AES observation because only negligible amounts of leached Cu (\approx 6 ppm) were detected in the resultant solution collected by hot filtration experiment. These outcomes obtained certainly indicated that the as-obtained Cu@COF-BD(OH)₂ catalytic system is a true heterogeneous in nature. This suggests that this COF-NPs composite is a zero-leaching catalytic system of heterogeneous nature (see ESI for details).



Reaction Coordinate

Figure 4. Energy profile diagram for different transition states and intermediates for the generation of oxazolidinediones.

In summary, we have developed a cyclizative CO₂-incoporated multicomponent reaction facilitated by Cu/Cu_xO_y NPs embedded COF catalyst for oxazolidinedione production. This cyclizative reaction employed COF-NPs composite as a potential catalytic This journal is © The Royal Society of Chemistry 20xx

system under alkali-free conditions to generate several derivatized oxazolidinediones in satisfactory-to-excellent yields. A series of aromatic amine derivatives as well as bromoacrylic acids can be converted in excellent yields to the value-added oxazolidimediones. Related experiments and DFT calculations are employed to explore the mechanistic study on copper-facilitated CO₂ capture reaction. Our findings demonstrate that COF-NPs composite can unlock a novel route for accelerating the catalytic multicomponent reactions in the field of next-generation selective CO₂ capture.

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Cu/Cu_xO_y NPs Architectured COF: A Recyclable Catalyst for Oxazolidinedione Synthesis via Atmospheric Cyclizative CO₂ Utilization

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This work emphasizes the utility of COF in establishing a heterogeneous catalytic system for the generation of value-added oxazolidinediones under alkali-free condition (sustainable approach).