

# Green Synthesis of 1,1'-Carbonyldiimidazole Using Copper Oxide Nanofiber as a Heterogeneous Catalyst

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Poly(vinyl pyrrolidone) (PVP)/copper oxide composite nanofibers were prepared by electrospinning technique using PVP and copper acetate as precursors and calcinated at high temperature to yield polymer free, phase pure copper oxide nanofibers (CuO NFs). The powder X-ray diffraction (XRD) pattern, transmission electron microscopic (TEM) images and selected area electron diffraction pattern (SAED) results showed that the calcinated CuO NFs were crystalline with 166 nm diameter and monoclinic in phase. From the catalytic application point of view, the newly prepared electrospun CuO NFs were tested for N-arylation of imidazole using aryl halides. To our surprise, 1,1'-carbonyldiimidazole (CDI) was obtained under the conditions of air and nitrogen atmosphere. Furthermore, the same product CDI was obtained from the reactions where in no aryl halide was involved but with imidazole alone as substrate. Our methodology to prepare CDI is free from the use of toxic phosgene as carbonyl source, as reported earlier. Hence, the present process possesses some advantages such as green and cost effective alternate for the existing synthesis method.

**Keywords:** Electrospinning, CuO Nanofibers, Catalyst, Carbonyldiimidazole.

## 1. INTRODUCTION

The best outcome of an intense search for simplified process to synthesis bioactive compounds is the catalytic process. Generally, a catalyst assisted process got much attention by overcoming the difficult steps of conventional, un-catalysed synthesis of organic products such as extended time duration, more E-factor, less selectivity and reactivity. From the literature, it was clear that most of the copper catalysed coupling of heterocyclic compounds with aryl halides afforded N-arylated products which are effective compounds for common chemotherapy.<sup>1</sup> Copper catalysed N-arylation are well demonstrated and appropriately understood from the classic Ullmann type reactions to Buchwald type reactions.<sup>2,3</sup> Most of the heterogeneous copper catalysed N-arylation reactions follow the mechanism of oxidative addition and reductive elimination.<sup>2,4</sup> In the recent years, copper oxide nanoparticles were utilized for N-arylation, oxidation, selenide coupling and cross coupling reactions etc.<sup>5–8</sup>

Electrospun nanofibers play a vital role as implant materials, drug delivery systems, stationary phase in chromatographic systems, super capacitors, catalysts, gas sensors

and biosensors.<sup>9–15</sup> Presence of more active sites, facile functional groups and surface coating of nanoparticles on the nanofibers prompted several researchers to utilize electrospun nanofibers as catalytic system for less time consumption and easy separation of catalyst in organic synthesis. Karvembu et al., reported that the ruthenium and silver nanoparticles functionalised cellulose acetate nanofibers showed 100% selectivity for oxidation of benzyl alcohol and aza-Michael reaction.<sup>16</sup> In 2016, a new type of heterogeneous chemical reactor was introduced by Jie Bia and co-workers. They reported that the glass-Ag supported palladium chloride-PAN nanofibers was an effective catalytic system for rapid Suzuki coupling reactions.<sup>17</sup>

1,1'-carbonyldiimidazole (CDI), a hygroscopic compound known since 1962 is widely used in pharmaceuticals and fine chemical industries. The degradation kinetics of CDI reported by Engstrom and co-workers revealed that the presence of moisture influenced the rate limiting step. Hence, relative humidity or atmospheric moisture greatly influences the stability of CDI.<sup>18</sup> Predominantly, CDI is employed for the preparation of esters, amides, isocyanides, ethers, small molecules and as peptide coupling reagents.<sup>19</sup> Recently, Badr and co-workers prepared heparin modified bacterial cellulose (HBC) using CDI as an

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activating agent. Further HBC was coated on the surface of PVC film to prepare specific ion selective electrode. As-prepared electrode material showed enhanced biocompatibility than the normal PVC sensing film.<sup>20</sup> Khalid et al., reported a simple and efficient synthesis of acyl/sulfonyl hydrazines in a single pot reaction using CDI.<sup>21</sup> The commercial synthesis of CDI from imidazole involved the use of highly toxic phosgene as carbonyl source.<sup>22</sup> The current work describes the green synthesis of CDI in high quantity starting from DMF as solvent and also as carbonyl source with less amount of copper oxide nanofibers as catalyst.

## 2. MATERIALS AND METHOD

Poly(vinyl pyrrolidone) (PVP) of different molecular weights ( $M_w = 10,000, 40,000$  and  $1,30,000$  g/mol), copper acetate and all organic substrates were purchased from Sigma Aldrich. All the solvents of reagent grade were purchased from Merck Millipore and used without further distillation. Preparation of nanofibers was carried out using Espin Nano instrument, Physics Equipment Pvt., & Ltd., India. Size and morphology of nanofibers were analysed with SEM (Quanta 200, ICON analytical) and HR-TEM. High resolution images and selected area electron diffraction (SAED) pattern of nanofibers obtained with HR-TEM. Vibrational spectra recorded using Nicolet Avatar FT-IR and crystalline nature of nanofibers obtained from XRD pattern at room temperature from PANAnalytical using Cu  $K\alpha$  radiation. Nanofiber catalysed organic products were confirmed by GC-MS of Perkin Elmer, Germany. Gas chromatography equipped with capillary column of 0.3 mm diameter and 60 m length was connected to mass analyser. Helium was used as carrier gas with 1 ml/min flow rate and the column temperature was increased from 40 °C to 280 °C with the rate of 10 °C/min. In mass spectrum, electron ionisation and mass detector was employed for the analysis. Further, melting point of all the organic products was found by Lab India Instrument.

### 2.1. Preparation of Nanofibers

A general procedure for the preparation of inorganic nanofibers was detailed by Dharmaraj et al.<sup>23</sup> The typical procedure for the preparation of copper oxide nanofibers was as follows. Precursor sol was prepared by mixing 0.1 M of copper acetate in ethanol and the viscous polymer solution was obtained by the dissolution of PVP at 8, 10, 12 and 15 weight% in dimethylformamide (DMF) with continuous stirring. The spinning solution was prepared by mixing polymeric viscous solution of different concentration with sol solution at the stirring rate of 800 rpm at room temperature (28 °C) for 5 hrs and subjected to electrospinning.

Standard electrospinning process consisted of three major steps:

- (1) Loading solution into the syringe
- (2) Applying high voltage power supply

- (3) Optimise the instrumental parameters (distance between the tip to collector, temperature and humidity).

Composite solution prepared by sol-gel method had been feed into the hypodermic syringe; one end of the high voltage power supply was connected to needle and the other end at collector (rotating drum surrounded by aluminium foil). Optimised distance between tip of the needle to the collector was 11 cm with the applied voltage of 12 kV. While reaching the high voltage, ejection of fibers started with the formation of Taylore cone. The composite nanofibers thus obtained were separated from the aluminium foil, dried and calcinated at high temperature to get phase pure copper oxide nanofibers.

### 2.2. Catalysis

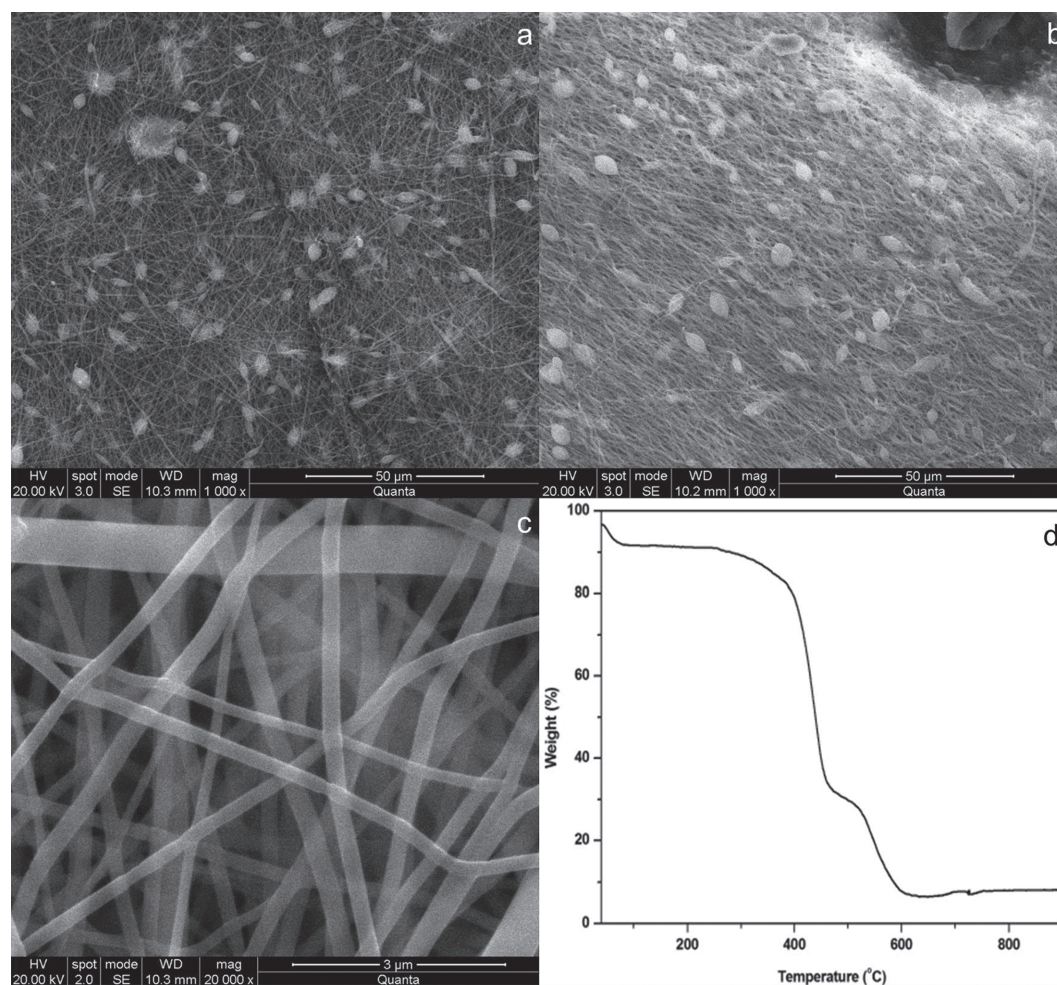
Imidazole was chosen as the model substrate for the N-arylation reaction in presence of electrospun CuO NFs as catalyst. The reaction flask was packed with 0.1 mM of CuO NFs, 5 ml of DMF followed by the charging of imidazole (1 mM) and bromobenzene (1 mM) at 110 °C with constant stirring. The progress of the reaction was monitored by thin layer chromatography (TLC). After completion, the catalyst was separated by centrifuge and washed several times with water and ethyl acetate for re-use. The product was isolated by evaporation of solvent in vacuum and purified. The obtained product was characterized with FT-IR for functional group identification and GC-MS for structural confirmation.

## 3. RESULTS AND DISCUSSION

### 3.1. Preparation and Characterization of CuO Nanofibers

Initially, various concentration of simple polymer solution was screened to produce smooth fibers with narrow diameter. Electrospinning of the pure polymer of different weight percentage resulted nanofibers of different morphology and sizes. To know the effect of concentration on the fabrication process, we prepared composite nanofibers by mixing 8, 10, 12 and 15 weight percentage (wt%) of PVP solution with copper acetate in ethanol. The as-prepared composite nanofibers from different spinning solution showed much variation on their size and morphology. The SEM images revealed that only 15 wt% of polymer solution with copper acetate sol produced smooth fibers without any beads, whereas 10 and 12 wt% solutions furnished non-continuous beaded fibers (Fig. 1). In the case of 8% weight of polymer composite solution, only spray of the solution on the aluminium foil was noticed. Thus, 1:1 weight ratio of 15 wt% polymer with copper acetate sol was chosen as the optimum solution concentration and the corresponding composite nanofibers obtained were utilized for further studies.

Temperature dependent removal of polymer from the composite nanofibers was studied by TGA analysis and showed in Figure 1(d). Initial 5% weight loss was assigned



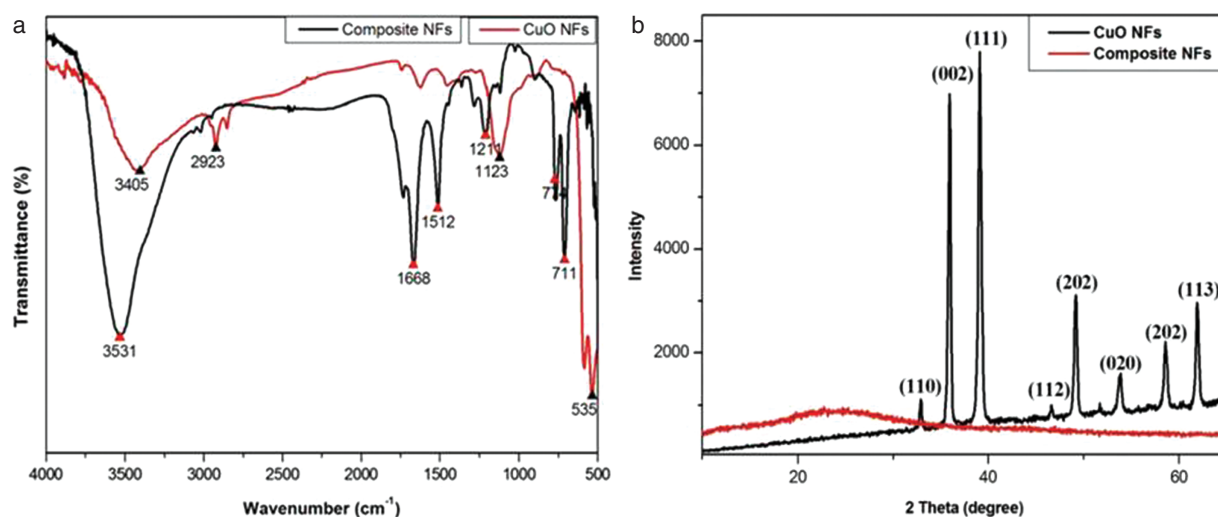
**Figure 1.** SEM images of PVP-copper acetate sol composite NFs with (a) 10 wt%, (b) 12 wt%, (c) 15 wt% of PVP and (d) TGA of 15 wt% composite NFs.

as surface water molecules and the major weight loss (83%) occurred in the range of 350 °C to 600 °C indicated the decomposition of acetate moieties and the polymer template of PVP. The residual copper oxide accounted for the 11% of the total mass of the composite nanofibers. Heating the material up to 900 °C did not show any changes in the TGA curve indicating the formation of a stable copper oxide.<sup>24</sup>

Composite NFs were calcinated at 600 °C and corresponding polymer free phase pure CuO NFs were characterized by FT-IR and X-ray analysis. Figure 2 shows the FT-IR spectrum and powder XRD pattern of composite and pure CuO nanofibers. In FT-IR, peaks corresponds to PVP at 3531 (O–H str), 1668 (C=O str) and 1123 cm<sup>-1</sup> (C–N str) were disappeared by high temperature treatment and new peak at 535 cm<sup>-1</sup> araised due to Cu–O stretching. Crystalline nature of nanofibers were obtained from powder X-ray analysis. There was no significant peaks in composite NFs owing to the amorphous nature of PVP. After calcination at 600 °C, sharp diffraction peaks at 2θ values

32.5, 35.6, 38.7, 46.3, 48.8, 53.5, 58.9 and 61.6 were observed. These diffraction peaks are in good agreement with the previous report as well as JCPDS card number 5-0661.<sup>25</sup> Hence, XRD data also confirmed the complete removal of polymer and formation of monoclinic CuO NFs.

Surface properties of calcinated CuO NFs obtained from HR-TEM images were shown in Figures 3(a) and (b). Low and high magnification of CuO NFs showed smooth fiber nature but a decrease in the size of nanofibers upon high thermal treatment. Notable decrease in size of composite NFs from 300 nm to pure NFs of 166 nm was confirmed from HR-TEM results. Removal of polymer had not significantly changed the morphology of the pure NFs as found in the high resolution image of a single copper oxide nanofiber. Appearance of bright spots rather than circles in the selected area electron diffraction (SAED) pattern of pure CuO NFs (Fig. 3(d)) proved that the nanofibers are monocrystalline. Based on the above characterization results, it is confirmed that the newly prepared CuO NFs was phase pure monoclinic crystalline fibers.

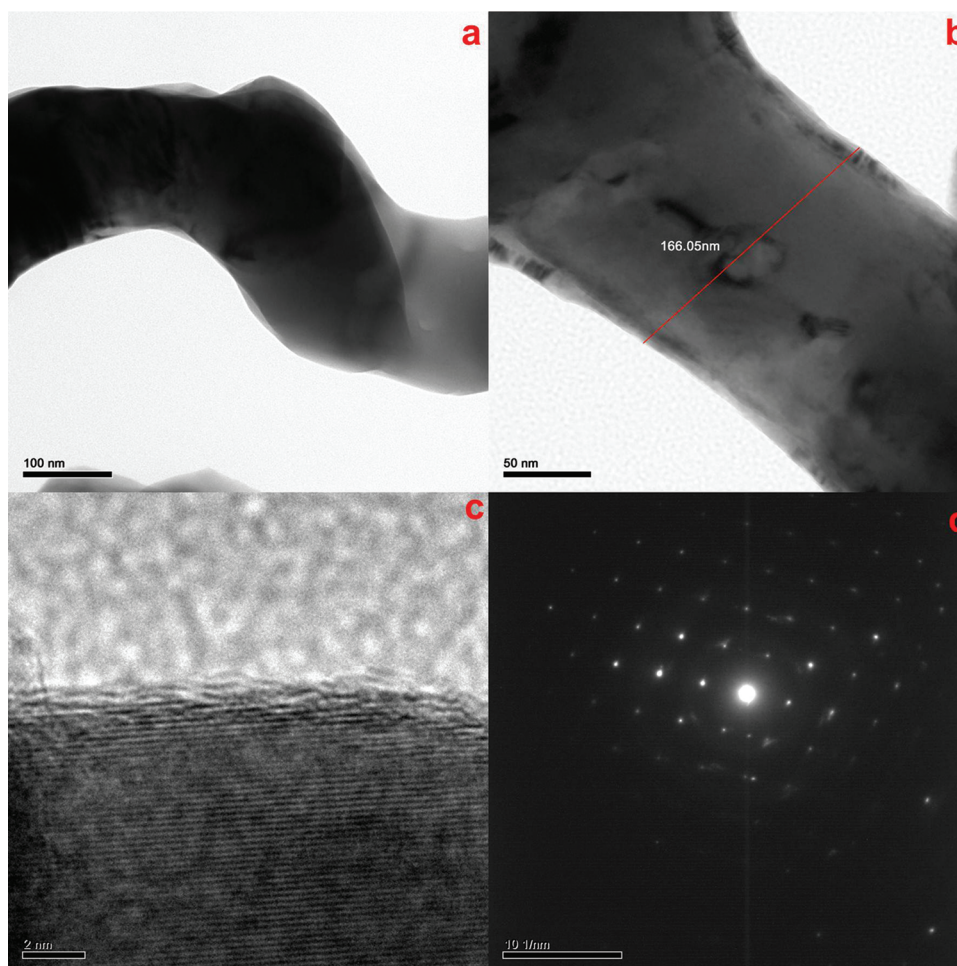


**Figure 2.** (a) FT-IR spectrum and (b) powder XRD peaks of composite and pure CuO nanofibers.

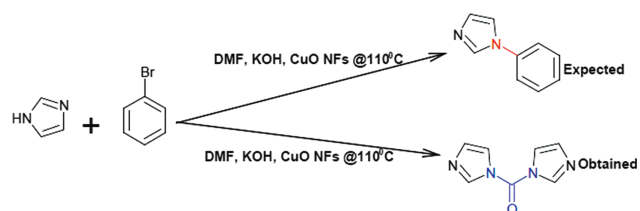
### 3.2. Optimisation of Catalysis Reaction Conditions

Electrospun nanofibers of copper oxide were utilized as catalyst for N-arylation of imidazole and benzimidazole. We have started our investigation based on the previous

publications related to copper catalysed Buchwald type reaction<sup>3</sup> with heterocyclic compounds. Initially, the reaction between imidazole and bromobenzene was carried out in presence of an inorganic base and CuO NFs as catalyst



**Figure 3.** HR-TEM images of pure CuO NFs (a) lower magnification, (b) higher magnification, (c) high resolution image and (d) SAED pattern.



**Scheme 1.** CuO NFs catalysed reaction of imidazole with bromobenzene.

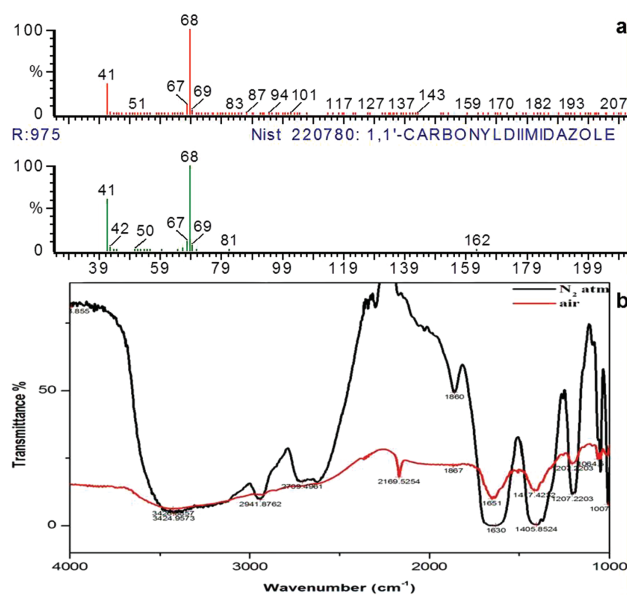
(Scheme 1) with different solvents as listed in Table I. In low boiling solvents like water and ethanol, no progress was noticed. However, upon using a mixture of low and high boiling solvents (H<sub>2</sub>O and DMF), the reaction was onset with the formation of a product (Table I, entries 1–3). But, use of DMF as an exclusive solvent had facilitated the process with higher yield of the product compared with the DMAc (entries 4, 5). Also, no product was obtained in the case of reactions performed without any base or catalyst (Table I, entries 6, 7).

Various inorganic bases were screened for better yield of the product and KOH was identified as a suitable base for this case (Table I, entries 8–10). The major drawback of classical Ullmann reactions was large catalyst loading and harsh conditions. So, we examined lower amount of catalyst (0.1 mM) for the reaction and surprisingly that resulted in an excellent yield (96%) of the product. Further decrease in the quantity of the catalyst (0.05 mM) decreased the yield (28%) drastically. The completion of the reaction was observed after 5 hours at the temperature of 110 °C. The same reaction carried out at temperatures below 110 °C didn't afford the product. The product formed in the reaction was separated and analysed with FT-IR and then confirmed with GC-MS analysis. In contrast to the IR spectrum of the expected N-arylated imidazole, the spectrum of the product showed a sharp and intense absorption at 1660 cm<sup>-1</sup> suggesting the presence

**Table I.** Condition optimisation of CuO NFs catalysed reactions.

S. no	Catalyst (mM)	Solvent	Base	Yield (%)
1	0.1	H <sub>2</sub> O	KOH	No reaction
2	0.1	Ethanol	KOH	No reaction
3	0.1	H <sub>2</sub> O + DMF	KOH	25
4	0.1	DMF	KOH	96
5	0.1	DMAc	KOH	30
6	–	DMF	KOH	No reaction
7	0.1	DMF	–	No reaction
8	0.1	DMF	NaOH	25
9	0.1	DMF	Na <sub>2</sub> CO <sub>3</sub>	28
10	0.1	DMF	K <sub>2</sub> CO <sub>3</sub>	30
11	0.05	DMF	KOH	28
12	0.01	DMF	KOH	10
13	0.1	DMF	KOH	95*
14	0.1	DMF	KOH	95**
15	0.1	DMF	KOH	95 <sup>#</sup>

Notes: \*reaction at inert atmosphere; \*\*reaction performed with 2 mM concentration of aryl halide; <sup>#</sup>with different aryl halides (ArX, X = Cl, F, I).



**Figure 4.** (a) Mass spectrum and (b) FT-IR of CDI.

of a carbonyl functional group (Fig. 4(a)). Appearance of the carbonyl absorption forced us to analyse the product with GC-MS in order to confirm the identity of it. The GC-mass spectrum of the product confirmed that the unexpected product 1,1'-carbonyldiimidazole was formed in the attempted N-arylation of imidazole. The mass spectrum of it was compared with that of the reference spectrum shown in Figure 4(b) and good agreement was observed (NIST-R: 975, 220780).

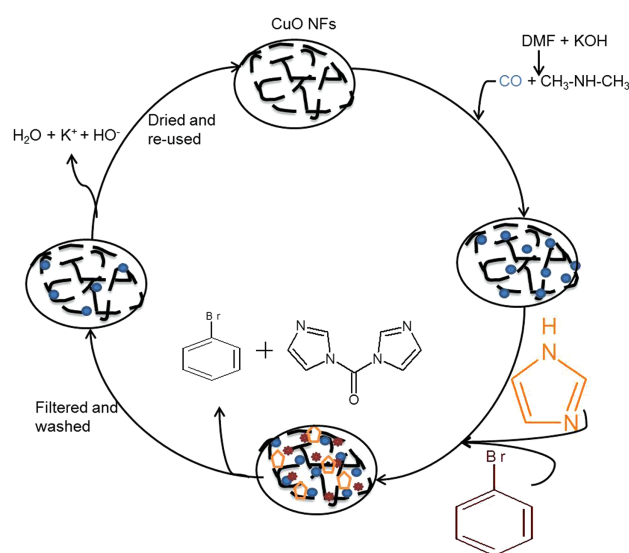
With a view to obtain the expected N-arylated imidazole, again the reaction was carried out with higher concentration of aryl halide. In this case also the same product was realised in excellent yield. To investigate the selectivity and reactivity of different aryl halides with imidazole as a substrate, the reaction was tested with three different aryl halides (ArX, X = Cl<sup>-</sup>, F<sup>-</sup> and I<sup>-</sup>). All these reactions yielded the same product irrespective of the aryl halides used and thereby indicated that the aryl halides did not take part in the reaction (entry 15). Another, control experiment was done without the addition of aryl halide but with all other reagents and catalyst. To our surprise, the same product was formed even in the absence of aryl halides and thus prompted us to investigate reaction further. Hence, the reaction was carried out in air as well as in N<sub>2</sub> atmosphere to gain some information on the mechanistic aspects of the product formed. Very interestingly, in both the cases, the product obtained was one and the same which was identified as 1,1'-carbonyl diimidazole. The data from GC-MS and melting point attested the structure of it. The melting point of the product (CDI) determined was 117 °C (literature value is 116–118 °C).

Our investigation of reaction mechanism started with the influence of solvent and the activity of the catalytic system in this reaction. To confirm heterogeneity of the

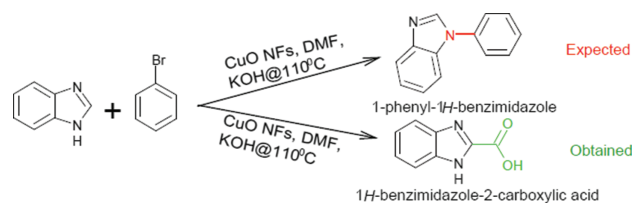
catalyst, reaction was stopped in between and the catalyst was separated and reaction was continued without catalyst. No progress was observed in the reaction after the removal of the catalyst. Therefore, catalytic process here follows pure heterogeneous conversion and no catalyst (CuO NFs) reacted with any of the substrate or leached out. Subsequently, solvent effect was studied to get an insight into the possible mechanism for the unexpected product formed in this reaction. The team of Alterman and Hallberg<sup>26(a)</sup> attempted similar type of Buchwald-Hartwig amination reactions with imidazole using strong base in presence of palladium acetate catalyst with ligands and surprised with the dimethylamide product instead of arylated product. They proposed the mechanism that in presence of strong base and high temperature, DMF fragmented as CO and Me<sub>2</sub>NH. The degraded compound was reacted with the different amines, aryl halide and produced aryl amides as product. Recently, a review by Ding and Jiao reported that the dimethylformamide served as a source of carbon monoxide, oxygen, formyl group, dimethylamine and dimethylaminocarbonyl group.<sup>26(b)</sup> Hence in this work, the CO obtained from the solvent reacted with the substrate in presence of CuO NFs catalyst and yielded CDI. The possible mechanism for this conversion was shown in Figure 5.

### 3.3. CuO NFs Catalysed Reaction of Benzimidazole with Aryl Halides

As discussed in the preceding section of the manuscript, formation of an unexpected product in the attempted N-arylation of imidazole with CuO NFs as catalyst in DMF increased our curiosity to conduct another experiment under identical conditions by involving benzimidazole as a substrate instead of imidazole. Scheme 2 explains the optimised conditions for the N-arylation of



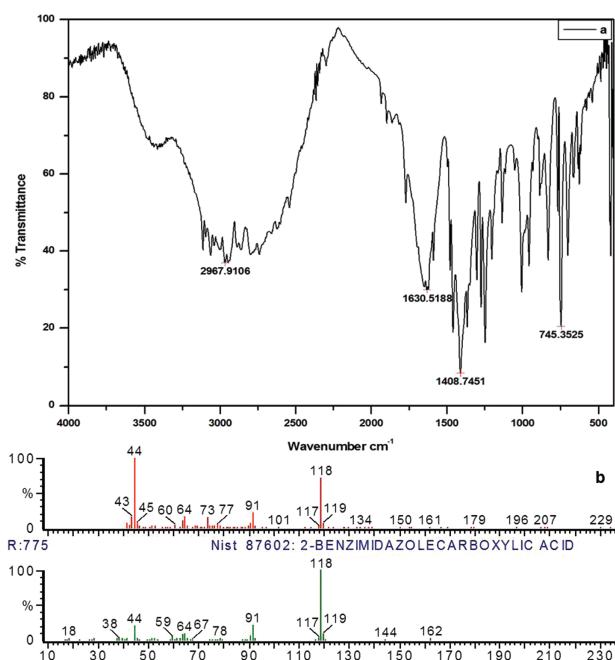
**Figure 5.** Proposed mechanism for CuO NFs catalysed synthesis of CDI.



**Scheme 2.** Synthesis of 1H-benzimidazole-2-carboxylic acid using CuO NFs.

benzimidazole with electrospun copper oxide nanofibers as catalyst.

Preliminary studies were carried out with benzimidazole and bromobenzene in presence of CuO NFs (0.1 mM) as catalyst. In consistent with the imidazole system, benzimidazole also yielded a product which was not the expected N-arylated product. The IR spectrum of the product obtained in the benzimidazole case with CuO NFs as catalyst showed the presence of carbonyl moiety in contrary to the expected N-arylated product (Fig. 6(a)). To ascertain the nature of the carbonyl group, the product was subjected into preliminary tests for aldehydes, ketones, esters and carboxylic acids. The compound did not give any positive response towards the tests for aldehydes, ketones and esters. However, up on treatment with a drop of phenolphthalein indicator, the colourless solution remains as such (no pink colouration) indicating the presence of carboxylic acid functional group. Another test was performed to confirm the carboxylated product that the solution of sodium bicarbonate was added with the dissolved product; brisk effervescence evolved immediately and ensured the presence of –COOH group in the



**Figure 6.** (a) FT-IR and (b) mass spectrum of 2-benzimidazole carboxylic acid.

product. Based on these ideas that the compound formed in the case of benzimidazole reaction with aryl halides was a carboxylic acid, the complete structure of it was analysed by GC-MS analysis. Figure 6(b) shows the GC-mass spectrum of the purified product with the  $m/z$  at 118, 44 and 91. Comparing with the NIST reference, the obtained pattern was in good agreement with that of benzimidazole-2-carboxylic acid and with the previous reports.<sup>27</sup> The observed melting point of the product was 175 °C (literature value is 176–180 °C).

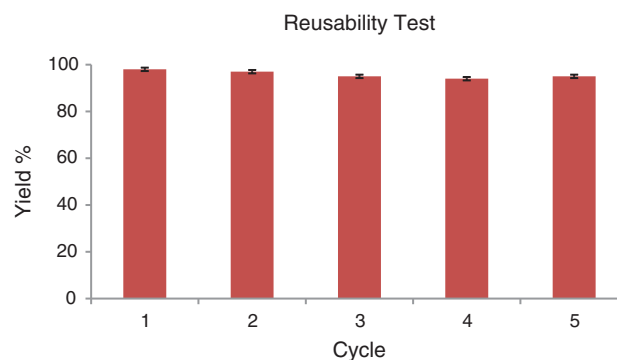
To investigate the role of aryl halides in the selected catalytic reaction, different aryl halides were screened and the obtained results are listed in Table II. Up on varying the aryl halides, the quantity of the yield was also different in all the cases (Entries 1–5). As we understand from the attempted arylation of imidazole that the reaction proceeded well even without the aryl halides, we also made a similar attempt in the case of benzimidazole. To our surprise, the reaction proceeded without the aryl halide also yielded the same product in an appreciable yield and revealed the key for this mechanism that the carboxylate group was generated only from DMF used as reaction medium for arylation of benzimidazole. An exclusive review on the role of DMF as a source for reactive species like CO, formyl and formate under different conditions published by Jacques Muzart.<sup>28</sup> He reported that the DMF could be fragmented in many ways and the products are formyl unit, formate unit, carbon monoxide,  $\text{Me}_2\text{N}$ ,  $\text{Me}_2\text{NCO}$ ,  $\text{Me}_2\text{NCH}$  and  $\text{CHOH}$ . It is also reported that the presence of sulphuric acid and copper catalyst activate the C–H bond in benzoxazole system to promote the amination at C-2 carbon of benzoxazole moiety. Therefore, we believed that our work on the copper oxide nanofibers catalysed N-arylation of benzimidazole in basic medium might have activated the C–H bond and resulted in the formation of carboxylated product by decomposition of DMF rather than the expected arylated nitrogen heterocycles.

### 3.4. Reusability Test

Major drawbacks of homogeneous catalysis such as the separation and re-use of the catalytic system are normally avoided in heterogeneous catalysis. The electrospun CuO NFs used for the first catalytic cycle was separated by simple centrifugation and washed several times with water and ethyl acetate and dried before the next cycle. The catalyst

**Table II.** CuO NFs catalysed reactions of benzimidazole.

S. no	Substrate	Ar(R or X)	Isolated yield (%)
1	Benzimidazole	Iodobenzene	50
2	Benzimidazole	Chlorobenzene	30
3	Benzimidazole	Bromobenzene	45
4	Benzimidazole	2-bromoanisole	30
5	Benzimidazole	4-bromobenzaldehyde	28
6	Benzimidazole	–	90



**Figure 7.** Reusability test of CuO NFs.

could be reused up to five times without significant loss of its activity in terms of yield (Fig. 7).

### 3.5. Advantages of Electrospun CuO NFs Catalytic Process

Thus obtained dissimilar product of CDI used as reagent in various peptide coupling process and in the synthesis of certain organic compounds.<sup>19</sup> Commercial synthesis of CDI consumes huge amount of highly toxic phosgene<sup>22</sup> which cause major environmental issues. Surprisingly, electrospun CuO NFs catalytic system had produced CDI without use of any toxic chemicals and hence equipped environmental benign method for the existing difficult and toxic process. The reaction of imidazole in presence of the electrospun CuO NFs activated the N–H bond thereby produced the stable 1,1'-carbonyldiimidazole as the product. In the case of benzimidazole, C–H bond at the second carbon was activated and the carboxylated product was obtained.

## 4. CONCLUSION

A simple and cost effective method for the preparation of 1,1'-carbonyldiimidazole (CDI) in 96% yield using DMF as a solvent as well as source of carbonyl functionality catalysed by electrospun CuO nanofibers with about 166 nm diameter was demonstrated. Advantageously, this methodology is free from the use of highly toxic chemical warfare agent phosgene for the synthesis of CDI. The CuO nanofibers were characterized by FT-IR, SEM and TEM images. The FT-IR spectrum of the copper oxide nanofibers calcinated at 600 °C confirmed the complete removal of the polymer template and the existence of Cu–O stretching vibrations of copper oxide. Powder XRD and TEM studies established the monoclinic crystalline phase of CuO nanofibers. Further, the catalyst was reusable up to five cycles without appreciable loss in its activity.

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