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Short communication

Metal-organic frameworks derived CuONPs@C nanocatalysts for synthesizing optoelectronic triarylamine molecules

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ARTICLE INFO	A B S T R A C T				
Keywords: Copper oxide nanoparticles Nanocatalysts Metal organic frameworks Luminescence Nanocomposites Carbon encapsulated nanoparticles	Carbon encapsulated copper oxide nanoparticles (CuONPs@C) fabricated using copper metal organic frame- works (Cu-MOFs) used as reusable nanocatalysts in Ullmann C—N coupling reactions for synthesizing opto- electronic triphenylamine (TPA) and carbazole (CBZ) derivatives. The formation of CuONPs in carbon matrix was confirmed by powder X-ray diffraction (PXRD), X-ray photoelectron spectroscopy (XPS) and high-resolution transmission electron microscopy (HR-TEM). The catalytic activity of CuONPs@C was performed with diphe- nylamine/carbazole with substituted aryl halides in presence of mild K ₂ CO ₃ base that produced triarylamines with 63–83% yields. Carbazole triarylamines exhibited strong solid state fluorescence ($\Phi_f = 14.54$ –36.32%) with λ_{max} between 370 and 420 nm.				

Polyaromatic amines such as triphenylamine and carbazole have been used as important core units to build molecules for optoelectronic applications such as organic light emitting diodes (OLEDs), displays, dye-sensitized solar cells, smart materials, sensors, data storage and optical switches because of their strong hole-transporting and fluorescence property [1,2]. The non-planar molecular geometry of triphenylamine can be utilized to generate strong solid state fluorescent and mechano/thermofluorochromic materials [3-5]. Palladium-catalyzed Buchwald–Hartwig coupling, [6] copper-catalyzed Ullmann reaction, [7] other transition-metal-mediated reactions primarily utilizing iron [8] or nickel-based catalysts [9] are some of the most used methods for synthesizing arylamines. However, harsh reaction conditions such as high temperature (200 °C), expensive and/or highly air-sensitive compounds such as phosphine-based ligands, catalytic sensitivity and low yields often posed great challenge [10]. Ullmann-type coupling reactions have been employed as important tool for preparing numerous biologically active natural products [11], pharmaceutical compounds and polymers [12]. Cu-catalysed arylation reactions especially using copper salts as catalysts have been explored extensively for C-C and C—N bonds (Ullmann-type couplings) formation [13]. Nevertheless, the classic Ullmann-type reactions require harsh reaction conditions, stoichiometric use of copper compounds, strong bases, and bipyridine or phosphine-type costly ligands [14-16]. Therefore, developing mild, simple and cost-efficient methods are still highly desirable.

In recent years, fabrication of heterogeneous nanocatalysts for

organic chemical transformation received significant attention since the catalysts can easily be recovered, reused and also allowed easy separation of product [17,18]. Among different solid support, porous carbon is more desirable in catalysis due to their large surface area, high thermal and mechanical stability [18]. The low cost, abundant availability, good stability and easy synthesis of copper oxide nanomaterials (CuONPs) have been used as catalysts for different organic chemical transformation including for C-N Ullmann coupling reactions [19-22]. However, most of the reaction employed strong base along with expensive ligands and mainly restricted to synthesizing diaryl amines. Metal organic frameworks (MOFs) with exciting topology offered opportunities for fabricating metal/metal oxide NPs in carbon matrix. The regularly arranged metal coordination in the MOFs can be transformed into metal/metal oxide NPs in-situ by thermolysis induced carbonization whereas the diverse organic bridging ligands tend to produce highly porous carbon matrices. The carbon matrix provides size controlling structure for nanoaprticles along with increased stability. Herein, we report the fabrication of CuONPs@C using Cu-MOFs as precursors that was generated using valine amino acid based reduced Schiff base ligand by simple calcination and utilized as nanocatalysts for synthesizing optoelectronic triphenylamine/carbazole molecules. CuONPs@C exhibited good catalytic activity in Ullmann C-N coupling reaction between diphenylamine/carbazole and aryl halides in presence of mild base that resulted in the formation of fluorescent triarylamines in good yield (63-83%).

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Fig. 1. (a) Powder X-ray diffractogram of Cu-MOFs and high resolution XPS spectra of (a) Cu2p, (b) C1s and (c) O1s orbitals.



Fig. 2. (a, b) HR-TEM images of CuONPs and (c) solid state fluorescence.

Cu-MOFs was prepared by following the reported procedure [Scheme S1, Fig. S1], [23]. CuONPs encapsulated in carbon matrix was prepared by calcination of Cu-MOFs at 330 °C for 12 h in presence of air and confirmed by PXRD [Fig. 1a]. The appearance of clear peaks in PXRD pattern indicates the formation crystalline nanoparticles with monoclinic phase (JCPDS#45-0937). XPS spectra of CuONPs@C revealed Cu²⁺ 2p_{3/2} peaks at 935.18 eV and Cu²⁺ 2p_{1/2} peak at 955.08 eV with separation of 20.0 eV that indicates the presence of oxidized state of copper [Fig. 1b], [24]. The appearance of shakeup satellites at 945.58 and 943.18 eV further established the formation of copper oxides. High resolution C1s spectra revealed peaks at 284.58 and 288.18 eV [Fig. 1c]. The O1s binding energy peaks were observed at 530.19 and

531.79 eV [Fig. 1d]. Further energy dispersive X-ray (EDX) analysis also confirmed the presence of copper in the carbon matrix (Fig. S2). The amount of copper present in the carbon matrix is 35.9%. HR-TEM image showed dispersion of 10–15 nm size of CuONPs in the carbon matrix [Fig. 2a, S3]. The magnified image clearly showed the encapsulation of crystalline CuNPs in the carbon matrix that thickness ranged between 9 and 11 nm. Raman studies of CuONPs@C did not show any characteristic peaks for graphitic carbon and hence amorphous normal carbon matrix has been formed by decomposition of Cu-MOF (Fig. S4).

The catalytic reaction was performed by mixing aryl halides and diphenylamine/carbazole in presence of mild K_2CO_3 base and CuONPs@C nanocatalysts in dichlorobenzene solvent under N_2

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Table 1

Synthesising different triarylamine derivatives using CuONPs nanocatalysts.

Entry	Aryl halide			Time (hr)	Yield (%) ^e
	R ₁	R ₂	R ₃		
TPA-1	OCH ₃	Н	Н	12	68
TPA-2	Н	OCH ₃	Н	12	63
TPA-3	Н	Н	OCH ₃	14	65
TPA-4	Н	Н	Н	10	64
TPA-5	NO_2	Н	Н	16	66
CBZ-1	OCH ₃	Н	Н	8	72
CBZ-2	Н	OCH ₃	Н	9	74
CBZ-3 ^a	Н	Н	OCH ₃	10	73
CBZ-3 ^b	Н	Н	OCH ₃	10	72
CBZ-3 ^c	Н	Н	OCH ₃	10	70
CBZ-3 ^d	Н	Н	OCH ₃	10	68
CBZ-4	н	н	Н	6	76
CBZ-5	NO_2	Н	Н	3	83
CBZ-6	Н	Н	NO_2	4	80

^a Catalyst (I cycle).

^b Recycled catalyst (II cycle).

^c Recycled catalyst (III cycle).

^d Recycled catalyst (IV cycle).

^e Isolated yield.

atmosphere [Table 1]. The reaction mixture was refluxed for 3-16 h depending on the substrates. The triarylamines (triphenylamine/ carbazole) was isolated and purified using column chromatography that showed yield between 63 and 83% [See supporting information for reaction condition and NMR spectra]. The completion of each reaction was monitored using thin layer chromatography. Diphenylamine/ carbazole starting material was disappeared at different times for different aryl halide substrates that were taken as reaction time. Further increasing reaction did not show any increase of yield. As a representative case, the reaction time for TPA-1 was increased from 12 to 16 h but obtained the same yield (68%). The efficiency of CuONPs@C for Ullmann C-N coupling reactions has also been compared by performing similar reactions using conventional copper powder as catalysts along with 18-crown-6 ligand [Table S1]. The results indicated that CuONPs@C with lower concentration without using any ligand can produce similar yield compared to copper powder that required large amount. The increased catalytic activity compared to copper powder could be attributed to the enhanced surface area of nanocatalysts. Carbon matrix also can provide higher surface area for substrate adsorption. The catalytic activity of CuONPs@C has also been compared with CuO powder synthesized by direct calcination of copper nitrate salts. Interestingly, CuO powder also showed catalytic activity but required longer reaction time (16 h) and produced lower yield (40%). Carbazole derivatives (CBZ-1-3) exhibited intense blue solid state fluorescence [Fig. 2b]. Single crystal structural analysis of CBZ-1 and CBZ-3 showed twisted molecular conformation that inhibited close molecular packing in the solid state and lead to enhanced solid state fluorescence [Fig. S5 and S6]. The fluorescence spectra of CBZ-1 powder showed fluorescence peak (λ_{max}) at 380 nm whereas crystals of CBZ-1 showed slightly red shifted peaks (384 and 400 nm. CBZ-3 crystals showed weak fluorescence and slight breaking of crystals produced enhanced fluorescence intensity. The catalyst was filtered and reused up to four times to demonstrate the reusability.

In conclusion, we have used Cu-MOFs as precursor as well as carbon source for synthesising carbon encapsulated CuONPs by simple

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calcination. Importantly, CuONPs@C exhibited good catalytic activity for synthesizing triarylamine derivatives. The synthesized carbazole derivatives exhibited strong solid state fluorescence. Thus easily accessible CuONPs were prepared and used as catalyst for synthesising optoelectronic molecules.

CRediT authorship contribution statement

Anu Kundu: Investigation, Data curation. Vadivel Vinod Kumar: Investigation, Data curation, Writing - original draft. Savarimuthu Philip Anthony: Writing - review & editing, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

None.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.inoche.2020.108301.

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