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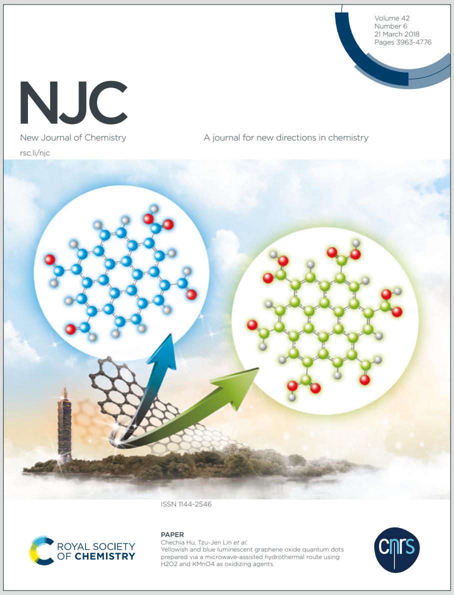
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PAPER
Chechia Hu, Tzu-Jen Lin *et al.*
Yellowish and blue luminescent graphene oxide quantum dots prepared via a microwave-assisted hydrothermal route using H2O2 and KMnO4 as oxidizing agents

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ARTICLE

Selective C-C coupling of terminal alkynes under air condition without base over Cu-Nx-C catalyst

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Fabrication of silk fibroin-driven porous, in-situ nitrogenated carbon skeleton with highly dispersed Cu–Nx–C active sites via sol-gel and pyrolysis treatment was demonstrated. Cu–Nx–C was used to catalyze oxidative homo-coupling of terminal alkynes with excellent functional group tolerance and high yields under air condition without base and no additive. The small amount of catalyst (2 mol%) and proper recyclability further demonstrated its good activity and stability. The excellent activity of the Cu–Nx–C catalyst can be ascribed to its high surface area, porous structure, small size of highly dispersed Cu–Nx–C active sites and graphitic N. Possible mechanism was deduced according to the structural and surface valance analysis of the sample before and after reaction. The report aims to demonstrate that such a nature-based sustainable catalyst can provide new insights into design of coupling reaction catalysts with outstanding catalytic C-C coupling performance.

Introduction

Trantional metal and nitrogen co-doped carbon materials(M-N-C, M: Fe, Co, Ni, Cu, Mn, etc) have aroused great interest as heterogeneous catalysts in photocatalytic degradation,[1] electrocatalytic water hydrolysis,[2-5] oxygen reduction,[6]electrocatalytic CO_2 reduction, [7] , electrochemical sensor, [8] and batteries[9-10] due to its encouraging activity and stability. Various methods have been developed to fabricate M-N-C materials, among which self-template is important for facile design 3D nitrogen and carbon precursor combining with active metal sites. [11]Compared with simple pyrolysis mixture of carbon support, nitrogen-rich molecule and metal salt, the self-template method using MOF or polymer as precursor facilitates uniform dispersion, enhanced surface area, high porosity, good conductivity, and high density of active sites. Zhu et al. prepared different M-N-C(M=Co, Fe, Mn) catalysts by heating *meso*-tetra phenyl porphyrins (*i.e.* CoTPP, FeTPPCl, MnTPPCl) precursors and applied in ethylbenzene oxidation.[12] Hou et al. further developed single metal atom bonded by N atoms anchored on carbon(M=Fe, Co, Ni, Cu) via *in situ* pyrolysis of metalloporphyrin molecules.[13] Peng et al. synthesized Fe-N-C catalyst via confining $[Fe(CN)_6]^{3-}$ in zeolitic imidazolate framework-8(ZIF-8) crystals under calcination.[14] The above reported synthetic strategy open new opportunities for exploring excellent M-N-C catalysts, yet still limited by the expensive or scarce precursors.

Biomass is rich in carbon and heteroatoms (N, P, S), the latter of which are evenly distributed in the natural materials. Biomass pyrolysis is considered to be a simple, convenient and green method to prepare porous C-N materials.[15] After pyrolysis, heteroatoms(N, S, P) uniformly distributed in the carbon skeleton thus enabled the preparation of promising natural-doped carbon material. Among them, silkworm calluses made of amino acids containing amino, carbonyl, and hydroxyl groups, etc can confine metal ions forming metal complex, and metal ions were *in situ* reduced after pyrolysis, forming M-N-C catalyst.[16-17] The present method shed light on the simple, convenient and green method to prepare M-N-C materials.

Glaser-Hay coupling is known as one of the most efficient and practical methods for the construction of conjugated 1, 3-diynes, which have been present in numerous natural products[18-23] and advanced materials.[24-25] Since the pioneering work reported by Glaser and Hay, [26-27] much efforts has been devoted to optimize the process with concern on catalyst efficiency, substrate generality and environmental friendly oxidant etc. [28] Copper(0) nanoparticles were demonstrated capable to promote Glaser-Hay coupling, although high catalyst loading and base addition were required. [29] Recently, the heterogeneous copper nanoparticles, with advantage in recyclability and stability comparing with their homogeneous counterparts, received great interests in catalyzing alkyne homo-coupling reaction. Alonso and Yus reported the copper nanoparticles on titania as more effective catalyst in alkyne homo-coupling in the presence of base. [30] Cu/C_3N_4 composite was utilized as catalyst by Zhu and Yao to achieve homo- and cross-coupling of terminal alkynes very recently, wherein additional KOH is necessary to facilitate the formation of copper acetylides intermediates.[31] In another work, amine

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replacing hydroxide worked as base, solvent and coordination ligand towards oxidative homo-coupling of terminal alkynes, and exhibited high activity. [32] As exemplified by the key contributions, it is still of challenge to achieve “green” processes (avoid additional base or particular oxidant like O_2) with consideration on the high efficiency of heterogeneous catalysts. Green approach or methodology has been developed. The mesoporous Cu/MnO_x was reported with superior activity and stability towards aerobic oxidative coupling of terminal alkynes via synergistic effect without base. [33] Cu-N_2 sites on biochar-driven porous carbon were reported high activity and selectivity towards coupling of terminal alkynes under mild conditions.[34]

Herein, nitrogenated porpous carbon with highly dispersed Cu-N_X-C active sites was fabricated with cocoon as biomass. The procedure included degum of cocoon, silk fibroin dialysis, gel under CO_2 condition, freeze-drying, pyrolysis to get final product and then application for homo-coupling of terminal alkynes. Several significant aspects should be concerned: (1) the hydrophobic and hydrophilic segments in the silk fibroin chain can be self-assembled in the solution forming a two-dimensional nano-sheet structure and further converted into a nitrogen-doped carbon nano-sheet during the pyrolysis process; (2) the CO_2 gas was constantly purged into the silk fibroin solution, changing the pH from 6-7 to 3.8-4.0 and thus reducing the gelation time from days to hours; (3) the strong interaction between the copper ions and the amino groups facilitated the formation of the highly dispersed Cu-N_X-C in the two-dimensional carbon skeleton after pyrolysis. Furthermore, the *in situ* reduction of copper during the pyrolysis process can promote the graphitization of the nano-carbon; (4) the composite can catalyze homo coupling reaction of terminal alkynes with high yield with small catalyst amount under air condition without base. Hence, the green synthesis and catalytic process would widen the further application of M-N-C catalyst.

Experimental

The cocoon was provided from Institute of Life Science, Jiangsu University, China. Copper nitrate trihydrate ($Cu(NO_3)_2{\cdot}3H_2O$), Sodium carbonate(Na_2CO_3), Lithium bromide(LiBr) were all purchased from Sinopharm Chemical Reagent Co. All chemical reagents were analytic grade and used without further purification. The solvents were used directly without any purification.

In a typical procedure, 5 g of silkworm cocoon was dissolved in 0.02 M Na_2CO_3 solution and boiled for 30 min to degum. The obtained silk fibroin was dissolved in 9.5 M LiBr solution at 60 ℃ for 4 hours. Then, the degummed silk was dialyzed against deionized water for 48 h using cellulose dialysis membrane (MWCO 8-14 kDa). The obtained protein solution was centrifuged and stored at 4 ℃ for further use. 1.488 g of copper nitrate was dissolved in 20 ml of water at room temperature. 15 g of silk fibroin was then added to the copper nitrate solution. The mixture was acidified by purging CO_2 (30 sccm) for about 1.5 h. After that, the obtained hydrogel underwent freeze-drying for 12 h. Finally, the silk fibroin hydrogel precursor was pyrolyzed in N_2 atmosphere at 100 ℃ for 30 min, then 225 ℃ for 2 h and finally 800 ℃ for 2 h with a heating rate of 5 ℃ min^{-1}. The final product was labelled as Cu–Nx–C. Silk fibroin-driven porous carbon (Nx–C) without copper was also prepared.

General Procedure for Glaser-Hay coupling: A mixture of alkyne 1 (0.2 mmol), catalyst powder (5 mg) (2 mol %) were taken in DMSO (0.5 mL) and the reaction mixture stirred at 70-100 ℃ for 8-27 h under air atmosphere, after completion of the reaction (monitored by TLC), reaction mixture was cooled to room temperature, and directly purified by using column chromatography. Homo-coupling of phenylacetylene was selected to optimize the experimental condition, such as the reagent, temperature, amount of catalysts, and reaction time. Further exploration was demonstrated to test the substrate scope of the reaction. Recovery experiments were also performed to test catalyst stability.

The structure and texture of the as-prepared samples were examined by X-ray diffraction (XRD), using D8 Advanced XRD (Bruker AXS Company, Germany) equipped with Cu Ka radiation (λ = 1.5406 Å). Scanning electron micrograph (SEM) images was performed with an Hitachi S-4800 II, Japan). X-ray photo-electron spectroscopy (XPS) was done using an ESCA PHI500 spectrometer. The Brunauer-Emmett-Teller (BET) specific surface area and pore size distribution of the samples were characterized by nitrogen adsorption with a Tristar II3020 Instrument. NMR spectra were recorded on a Brucker-400 MHz spectrometer. HRMS (Bio TOF Q) spectra were recorded on P-SIMS-Gly of Bruker Daltonics Inc.

Results and discussion

Morphology and structural analysis: Figure 1 is the schematic synthesis of Cu–Nx–C. The cocoon(Fig.1a) is degummed in Na_2CO_3 solution, and then stripped in LiBr solution and dialyzed to get silk fibroin(Fig.1b), which is composed with crosslinked peptide chain and β-crystallite(Fig.1c). After addition of copper nitrate, the sol was bubbled with CO_2 gas, changing the pH from 6-7 to 3.8-4.0 and thus reducing the gelation time from days to hours (Fig.1d,e). [35] The amide structure of SF coordinated with copper ions after CO_2 diffused into the stagnant solution, facilitating forming micellar assembly and quick gelation at the pH of the isoelectric point of SF(3.8-4.0). [36]After freeze-drying and pyrolysis, the highly dispersed Cu was *in-situ* reduced in the porous nitrogenated carbon frame, forming Cu–N_x–C catalyst(Fig.1 f, g).

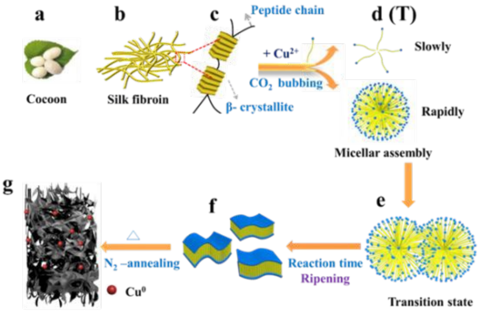

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Figure 1. Schematic procedure of synthesis of Cu–N$_x$–C catalyst

Figure 2a is photo of Cu–N$_x$–C precursor, *i.e.*, mixture of silk fibroin and copper nitrate solution after CO$_2$ bubbling. The obtained cyan fluffy sphere suggested that Cu^{2+} was evenly dispersed and anchored in the silk fibroin framework, suggesting potential highly dispersed Cu-N$_x$-C catalyst. After freeze-drying and temperature-programmed calcination, the as-prepared Cu–N$_x$–C showed a porous structure, as demonstrated by the scanning electron microscopy (SEM) image (Fig. 2b). The porosity of the Cu–N$_x$–C was further investigated using N$_2$ adsorption-desorption and Barrett–Joyner–Halenda (BJH) pore size distribution curves analysis (Fig.S1). The result indicated that it had large specific surface area of about 746.54 m ^{2} g^{-1}, average value of pore size c.a. 2.41 nm and pore volume of about 0.45 cm^3 g^{-1}.

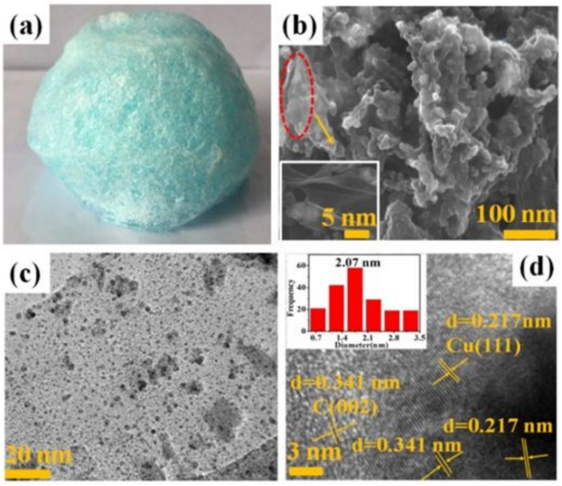

Figure 2. a) Photo of Cu–Nx–C precursor. b) SEM image of Cu–Nx-C catalyst. c) TEM images of Cu–Nx–C catalyst. d) HRTEM images of Cu–Nx–C catalyst showing the lattice fringes of Cu and graphitized carbon. The inset shows the particle size distribution.

Transmission electron microscopy (TEM) image (Fig. 2c) confirmed that Cu–N$_x$–C with particles size of c.a. 2.07 nm was evenly distributed throughout the carbon structure. HRTEM analysis (Fig. 2d) further confirmed the existence of copper with interlayer lattice distance of 0.217 nm corresponding to that of Cu (111) plane, and graphitized carbon with lattice distance of 0.341 nm. Energy-dispersive X-ray (EDX) elemental mapping of Cu–N$_x$–C also demonstrated the presence of Cu in the Cu–N$_x$–C, and C, N, and Cu elements homogeneously dispersed(Fig. 3). Inductively coupled plasma optical emission spectrometry (ICP-OES) analysis was also utilized to determine the Cu content, revealing the presence of trace amount of Cu (≈6.012 wt. %).

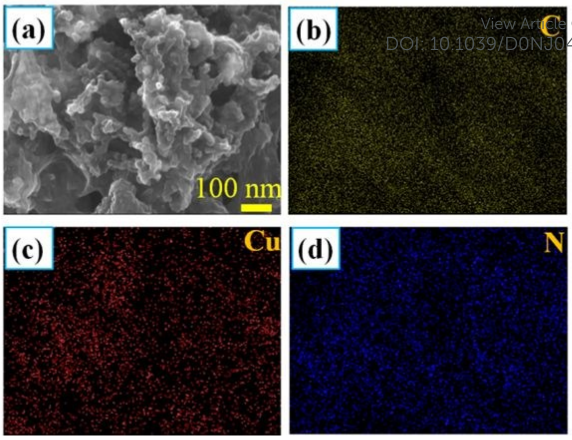

Figure 3. a) SEM image of Cu–Nx–C; EDS mapping of Cu–Nx–C with different element: b) C, c) Cu, and d) N, respectively.

X-ray diffraction pattern of Cu–Nx–C showed a keen-edged peak at 2θ values of 43.31°, 50.45°, 74.12° , which can be assigned to Cu(111), Cu(200), and Cu(220) of Cu(0)(JCPDS 85-1326), respectively (Fig.4a). The chemical state of Cu–Nx–C was characterized via X-ray photoelectron spectroscopy (XPS) and the high resolution XPS spectrum of Cu, N, and C were illustrated in Fig. 4(b-d). Cu 2p with two peaks at 952.7 eV, 932.8 eV contributed to 2p$_{1/2}$ and 2p$_{3/2}$ orbital, while peaks at 398.70 eV, 400.70 eV of N1s represented Cu-N and graphitic N, respectively, indicating that Cu was successfully anchored with carbon (Fig. 4c). The presence of Cu-N and graphitic N facilitated the deprotonation of acetylene, which was promising for efficient Glaser-Hay coupling reaction. The C 1s peaks at 284.55 eV and 285.46 eV corresponded to C=C, C-C /C-N bonds, and a partially oxidized carbon peak appeared at 287.46 eV in the XPS spectrum (Fig. 4d).

Raman spectrum showed two main characteristic vibration modes in the range of 900~2100 cm^{-1}, indicative of D-band (1360 cm^{-1}) and G-band (1586 cm^{-1}) of carbonaceous materials (Fig. S2). The value of the intensity ratio (I$_D$/I$_G$) was 0.86, indicating a higher degree of graphitization. The 2D band appeared at ≈2680 cm^{-1} indicating few layer graphene, which was consistent with the smooth surface with layered stacking graphene structure of the enlarged part in Fig.2b.

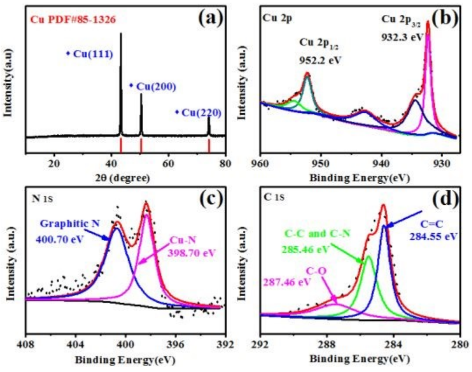

Figure 4. XRD patterns of Cu–Nx–C (a), and high-resolution XPS spectrum of Cu2p (b), N1s (c) and C1s (d), respectively.

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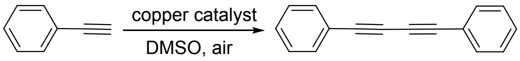
With the Cu–Nx–C composite in hand, initial investigation commenced with homo-coupling of phenylacetylene in the presence of 2 mol% Cu–Nx–C in DMSO without any additives. 1, 3-diyne (2a) was obtained in low yield after 7h at 50 ℃ (Table 1, entry 1). To our delight, when conducted at higher temperature, dramatically increased yield was observed (Table 1, entry 2). Further extending reaction time to 23 h at 70 ℃ led to excellent yield up to 95%. The employment of other polar solvents like MeOH or EtOH resulted in decreased yield as shown in entries 4-5. In contrast with copper nanoparticles, apparently, copper powder was found less efficient even in 10-fold enhancements of catalyst loading (Table 1, entry 3 vs. 6). Interestingly, the catalyst loading could be further reduced to 1 mol% when conducted at 100 ℃ (entry 7), while other copper salts was verified to be inferior to Cu-Nx-C (entry 7 vs. 8-9).

Table 1. Optimization of reaction conditions[a]



1a 2a

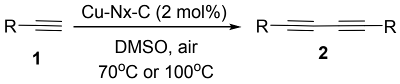
Entry	Catalyst	Loading (mol%)	Temp. (℃)	T (h)	Yield (%)[b]
1	Cu–Nx–C	2	50	7	15
2	Cu–Nx–C	2	70	7	52
3	Cu–Nx–C	2	70	23	95
4 [c]	Cu–Nx–C	2	60	15	15
5 [d]	Cu–Nx–C	2	80	22	35
6	Cu powder	20	70	23	45
7	Cu–Nx–C	1	100	12	98
8	CuI	1	100	12	42
9	Cu(OAc)$_2$	1	100	12	40

[a] The reaction of 1a (0.20 mmol) and catalyst was carried out in DMSO (0.5 mL) under air unless otherwise noted. [b] Isolated yield. [c] In MeOH. [d] In EtOH.

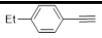
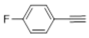
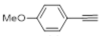
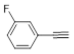
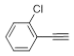
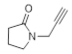
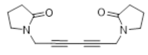
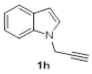
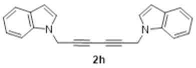
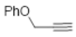
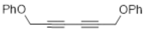
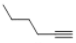
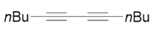
Under the optimum conditions, we next surveyed the substrate scope of this homo-coupling reaction. A range of substituted aryl-acetylenes were examined and both electron-withdrawing or electron-donating groups could be tolerated, although high temperature was needed in some cases to provide the products with satisfactory yields ranging from 71% to 94% (Table 2, entries 1-5). Moreover, substituents on ortho-, meta- and para-positions can well participate in the reaction without steric interference affording the 1, 3-diynes 2e-2f in 92% and 86% yields, respectively. When amide substituted alkyl-acetylene 1g was subjected to the standard conditions, 2g was generated in 63% yield. Other functionalized alkyl-acetylenes 1h-1i could also undergo the coupling reaction smoothly, leading to the desired products 2h-2i in good yields.

It was worthy to notice that 1-hexyne (1j) failed to participate in the coupling reaction even at 100 ℃ due to the small amount of catalyst. The π stacking interaction between graphene (on copper nanoparticles) and aromatic groups (on substituted aryl-substrates) might also benefit the substrate approaching to catalyst thus facilitate formation of copper acetylide intermediates.

Table 2. Homocoupling of terminal alkynes catalyzed by Cu-Nx-C.a



1 2

Entry	Substrate	T (h)	Product	Yield(%)[b]
1	 1b	27	 2b	94
2	 1c	24	 2c	71
3 [c]	 1d	10	 2d	91
4 [c]	 1e	11	 2e	92
5 [c]	 1f	11	 2f	86
6	 1g	23	 2g	63
7 [c]	 1h	9	 2h	88
8 [c]	 1i	9	 2i	72
9 [c]	 1j	10		n.r.

[a] The reaction of alkyne (0.20 mmol) and Cu-Nx-C (2 mol%) was carried out in DMSO (0.5 mL) at 70 ℃ under air unless otherwise noted. [b] Isolated yield. [c] At 100 ℃.

The structural and surface valance analysis of Cu–N$_x$–C after the coupling reaction were examined and illustrated in Fig. 5. After reaction, peaks observed at 42.32°, and 61.41° appeared in the XRD pattern (Fig. 5a), attributing to Cu$_2$O (PDF: 78-2076). Furthermore, the Cu 2p$_{3/2}$ and Cu 2p$_{1/2}$ at 932.3 and 953.12 eV were slightly red-shifted to 933.04 and 953.12 eV, which again identified the existence of a small amount Cu$_2$O

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(Fig. 5b). The XPS spectra of N1s and C1s agreed basically with that before the reaction (Fig. 5c, 5d).

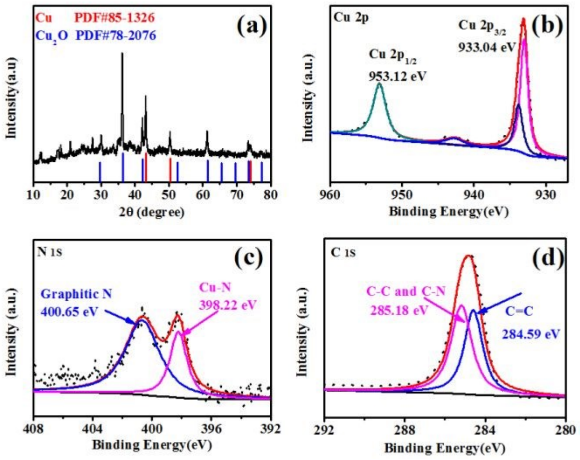
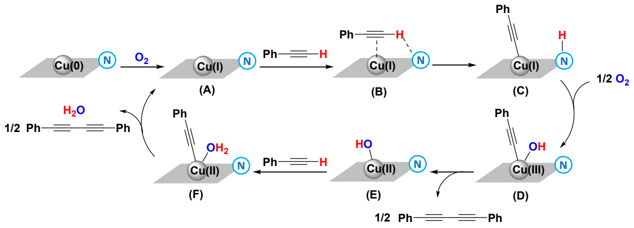


Figure 5. XRD patterns of Cu-Nx-C after reaction(a), and high-resolution XPS spectrum of Cu2p(b), N1s(c), and C1s(d) for Cu-Nx-C after reaction, respectively.

Based on preliminary results and reported mechanism studies[31-32], an individualized mechanism is illustrated in Scheme 1. Cu (0) was initially oxidized into Cu (I) by oxygen thus triggered the coordination of acetylenes to copper center. Acetylenic protons could be abstracted by nitrogen on nano-sheet to facilitate the formation of copper acetylide (C). Following oxidation would generate Cu (III) species (D) as tracked by Cyclic Voltammetry (see Fig. S3). Reductive elimination of complex D produced acetylenic coupling product 2a and Cu (II) species (E). After the capture of another acetylene, secondary reductive elimination of Cu (II) complex (F) release diacetylene and water, meanwhile regenerate intermediate (A) for the next catalytic cycle.



Scheme 1. Plausible mechanism of coupling reaction under Cu-Nx-C catalyst.

Conclusions

In summary, we have developed a novel silk fibroin-driven Cu–Nx–C composite for oxidative coupling of terminal alkynes under air condition without bases. The obtained composite with high surface area, porous pore structure, small size of highly dispersed Cu–Nx–C active sites and graphitic N exhibited high performance towards Glaser-Hay coupling reaction with excellent functional group tolerance and high yields. Furthermore, the low amount of catalyst also paves the way of sustainable development.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Graphical abstract

Selective C-C coupling of terminal alkynes under air condition without base over Cu-Nx-C catalyst

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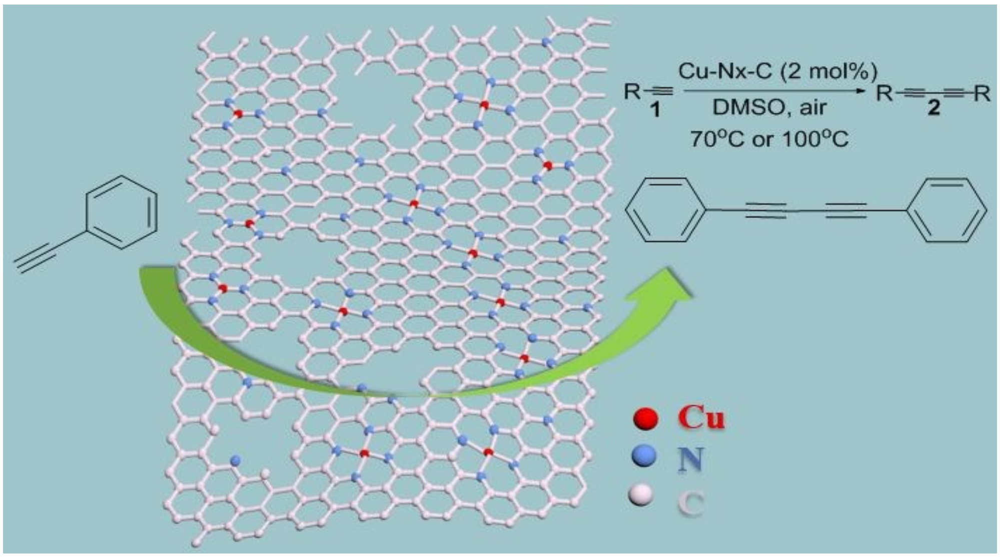

Highly dispersed copper nanoparticles supported on mesoporous nitrogenated carbon (Cu-N_X-C) were synthesized. The material exhibited superior catalytic activity towards aerobic oxidative coupling of terminal alkynes with low catalyst amount, no base, and no additive.