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Nitrogen-doped graphene stabilized copper nanoparticles for Huisgen [3+2] cycloaddition "click" chemistry

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Nitrogen-doped reduced graphene oxide (NRGO) stabilized copper nanoparticles are designed to assist Cu(I)-catalyzed Huisgen [3+2] cycloaddition "click" chemistry (CuAAC). This study demonstrates a robust route for the synthesis of vastly dispersed heterogeneous catalyst (NRGO/Cu₂O), achieving CuAAC at low temperature without any external additive (oxidizing/reducing agent) with high stability and recyclability. Underlying mechanisms are analysed using DFT calculations, confirming the experimental results.

Cu(I)-catalysed Huisgen [3+2] cycloaddition reaction between alkynes and azides "click" reaction (CuAAC)¹⁻⁵ has become a valuable tool owing to its ability to be employed in broad range of applications, in particular in materials, bioorganic, and organic science.^{6–17} The click reactions are regioselective, functional-group-tolerant, and can be performed under different reaction conditions using wide range of solvents.^{8,18} However, after completion of reaction, the removal of copper catalyst as well as used oxidizing/reducing agent remains a challenge and thus hampering its utilization, in particular in electronics and biological applications.¹⁹ The separation of catalyst from the reaction mixture was strongly facilitated by on synthesizing the heterogeneous copper catalyst commercially available scaffolds, including resins, linear and crosslinked polymers,^{20,21} charcoal, graphene,²²⁻²⁵ or othersolid supports.^{26–29} The support materials are also helpful to reduce the agglomeration as well as to achieve a uniform distribution of particles over a large area. However, catalyst recyclability and the necessity of an external ligand/base often limits their applicability.



Scheme 1 Schematic illustration of click chemistry promoted by nitrogen doped graphene supported copper nanoparticles.

Owing to their attractive properties such as high stability, electrical conductivity, porosity, and their performance for electron capture and transport, graphene supported metal nanoparticles/catalysts present outstanding catalytic activity compared to other carbon/polymer supported catalysts. ^{30,31} To tune the intrinsic reactivity of the metal particles, the doping of heteroatom effectively alters the nature of the designed catalytic systems. N-doping of graphene oxide (GO) is cooperative, leading to a stronger interaction of metal particles and thus preventing the agglomeration of nanoparticles.³² Further, the N-doping is not only helpful to reduce the surface energy but also helpful to enhance the electrical conductivity as well as generating active sites, thus demonstrating a promising catalyst with improved catalytic performance.^{33,34} Only a few articles report use of N-doped carbon nanomaterials supported catalyst and their relevance in different applications,^{35,36} however, according to our knowledge the NRGO-Cu(I) (N-doped reduced graphene oxide) catalysed "click" chemistry has not been explored yet.

Here we explore a robust approach to improve the dispersion, stability, and recyclability of copper catalyst *via*

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immobilization of copper nanoparticles Cu(I) on N-doped reduced graphene oxide nanosheets. The synthesized heterogeneous catalyst (NRGO-Cu(I)) is used to perform click reaction at room temperature without addition of any co-catalyst (oxidizing/reducing agent).

Hummer's method was applied for the preparation of graphene oxide (GO).³⁷ GO (100 mg) was dispersed in water (30 mL) by ultrasonication. Subsequently, Copper acetate(II) (20 mg, 0,11 mmol) was added and the mixture was vigorously sonicated for 5 min, the mixture was stirred at room temperature overnight. After several washings with water and acetone the Cu²⁺-GO was dried in vacuum oven at 40 degree C. 100 mg Cu2+-GO was sonicated in ethanol resulting a uniform suspension (thick suspension). 200 mg of Melamine (2:1 ratio of N precursor to GO) is added to the above suspension and sonicated (~ 15 minute) further to obtain a uniform suspension. Ethanol from the resulting suspension was evaporated slowly at room temperature under constant stirring to obtain a powder residue. Residue has to be grinded and then dried. The dried powder is heat treated in a tubular furnace under Ar atmosphere. The temperature of the furnace was raised from room temperature to 600 °C with a heating rate of 20 °C/minute, followed by holding the temperature at 600 °C for 10 minutes. The furnace is cooled down to room temperature under Ar atmosphere. The resulting samples was washed with DI water and dried. (see Supporting Information). For studying the impact of N-doping on click reaction, pure thermally reduced GO (TRGO/Cu(I)) based conjugates were also prepared as per our earlier reported method.³⁸ X-ray photoelectron spectroscopy (XPS), Transmission electron microscopy (TEM), Elemental analysis, Flame atomic absorption spectroscopy (FAAS) were performed to investigate the chemical composition, oxidation state, and morphology of the prepared nanoconjugates.



Fig. 1 (a,b) TEM images of the NRGO/Cu(I) catalyst. (c) Copper particle size and distribution. (d) XPS of Cu element.

Figure 1 a-b shows the TEM image of NRGO/Cu(I), displaying uniformly dispersed copper nanoparticles onto the surface of N-doped reduced graphene oxide. The TEM images were also found helpful to observe the average copper nanoparticles size (~20 nm for

NRGO-Cu), where a histogram shows the particle size distribution for the NRGO-Cu particles (Figure 1c). A similar oparticles size owas observed for the TRGO/Cu(I). (for TEM image, see Fig. S1) A 7.35 x 10⁻⁷ and 7.16 x 10⁻⁷ mol mg⁻¹ loading of Cu content for NRGO-Cu(I) and TRGO-Cu(I), respectively, was determined via FAAS analysis. Elemental analysis was also made for the prepared catalysts (Table S1). XPS technique was performed to further evidence of the chemical composition of the nanoconjugates including the oxidation state of copper as well as copper interaction with doped nitrogen (Fig. S2-4). The XPS peaks correspond to C 1s (285.1 eV), O 1s (531.6 eV) and Cu 2p were observed, where the high resolution XPS (Fig. 1d) reveals the peak energy of Cu(I), confirmed by the presence of peak satellites at 932.3 eV and 952.3 eV.³⁹ Furthermore, the data confirms the absence of Cu(II), as no peak satellites at 942 eV and 962 eV was observed. A small associated peak observed at 932.7 eV (higher by 0.3 eV than that for N-free carbon; ((NRGO/Cu(I), Figure S4), could be attributed to a stronger interaction of the Cu(I) with N-doped RGO.36

After confirming the present form of copper (CuI) and immobilized amount, the catalytic activity of the NRGO/Cu and TRGO/Cu was investigated through a click model reaction between phenyl acetylene and benzyl azide (Table 1). A 100% reaction yield was achieved for the NTRGO-Cu(I) catalyst with only 2 mol% catalyst loading in THF, whereas with similar amount loading only 70% conversion was obtained for the TRGO-Cu(I) catalyst after 48 h at room temperature. As a reference, click reaction was also performed in presence of commercially available copper catalyst Cu_2O powder and Cu on charcoal (Cu/C), and in that case only very little conversion was observed (Table 1).

Table 1: Performance of different Cu-catalysts: phenyl acetylene and benzylazide in THF at room temperature

Entry Conditions		Yield (%)
1	Cu ₂ O (2 mol%) in THF, 48 h, r.t.	0
2	Copper on charcoal (2 mol%), in THF, 48 h, r.t.	0
3	TRGO without copper, in THF, 48h, r.t.	0
4	TRGO/Cu (I) (2 mol%), in THF, 12h, r.t.	3
5	TRGO/Cu (I) (2 mol%), in THF, 48h, r.t.	70
6	NRGO/Cu (I) (2 mol%), in THF, 12h, r.t.	17
7	NRGO/Cu (I) (2 mol%), in THF, 48h, r.t.	100

As shown in Table 1, compared to TRGO/Cu(I) a higher reaction rate was observed for NRGO/Cu(I) (after 12 h; Table 1, 17% and 3 % for NRGO/Cu(I) and TRGO/Cu(I), respectively). The initially obtained higher efficiency for NRGO/Cu(I) may be attributed to the formation of coordination of N-doped rGO with Cu⁺ ions,⁴⁰ including a high binding energy of the Cu nanoparticles to N-doping carbon support,^{32,35,41} The N-doping is also helpful to reduce the surface energy as well as generating active sites, enhancing the catalytic performance.^{33,34,42} Surprisingly, 70% and 100% reaction yield was obtained after 48 h for TRGO/Cu(I) and NRGO/Cu(I), respectively. The enhancement in catalytic activity with time could be due to formation of N-ligands (triazole) as a source of autocatalysis, as discussed earlier.^{17,43}

The recyclability and reusability testing for the synthesized catalyst (NRGO-Cu(I)) was carried out using the azide/alkyne click model reaction under the optimized conditions. The NRGO-Cu(I) catalyst was reused ten times and observed around 90% yield after 10th cycle, whereas washing and recyclability of catalyst was performed under open air environment, which strongly supports the stability and recyclability for the synthesized N-doped heterogeneous catalysts. However, almost 40% reduction was observed for the nitrogen free

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TRGO-Cu(I) catalyst. TEM images were observed to check the morphology of the recycled catalyst.

been investigated for copper ion (Cu⁺) adsorption on three different sites: bridge (B), at the top of a carbon atom (Ω), and 3bot (M). 57H



Fig. 2 (a,b) catalyst recycling within ten reaction cycles for NRGO/Cu(I) and TRGO/Cu(I), respectively. (c,d) TEM image of Cu particles after 10 cycles for NRGO/Cu(I) and TRGO/Cu(I), respectively.

A unchanged morphology of NRGO-Cu(I) was observed after 10 cycles (Fig. 2c), whereas agglomeration of Cu particles was observed for TRGO-Cu(I) (Fig. 2d), which might be the key factor for the reduction of catalytic activity for the synthesized catalyst (TRGO/Cu(I)).³⁸ Again, the high binding energy of Cu particles to N-doping graphene might be the reason to prevent the agglomeration of copper nanoparticles for nitrogen doped graphene oxide sheets. Metal leaching for reaction product (after 5, and 10 cycles) was studied by FAAS measurements including hot filtration; however, the detectable amount of copper was too low for accurate detection.

To evaluate the performance of synthesized catalysts, bulk click chemistry was also evaluated by differential scanning calorimetry (DSC) (Fig. 3). For the formation of a covalent network, sufficient molecular mobility is required. In order to keep diffusion high, PDMS based liquid components (bivalent azide and alkyne with high mobility; low molecular weights) were prepared (for NMR, Fig. S5-6). DSC thermograms at 5 °C/min for different catalysts are plotted in Fig. 3 (1 mol% of catalyst per functional group). Thermal click crosslinking (W/O catalyst) happened at a high temperature with a T_{onset} at 110 °C and a T_p at 173 °C, whereas, a lower T_{onset} (at 45 °C) was observed for homogeneous commercial catalyst (Cu(PPh₃)₃F), however, crosslinking reaction was not completed at a certain temperature, which might be related to the inhomogeneous dispersion of catalyst in PDMS matrix. The TRGO/Cu(I) catalyst reduced the reaction temperatures to 50 ^{o}C (T_{onset}) and 65 ^{o}C (T_p), respectively, whereas, a room temperature T_{onset} and 59 ^oC (T_p) was observed for NRGO/Cu(I) catalyst. The DSC data again confirms the better catalytic activity of NRGO/Cu(I) catalyst.

To further analyse the effect of N-doping on the click reaction, Density Functional Theory (DFT) based calculations were performed using Synopsis Atomistix Toolkit (ATK) virtual nanolab (VNL).^{44–46} The aim was to quantify the interaction of Cu⁺ ion with the pristine RGO as well as NRGO, and also to observe the impact of Cu⁺ ion cluster size **on the N**RGO for CuAAC reaction. A 5x5 optimized graphene has



Fig. 3 DSC measurements for the bulk click reaction with different catalysts at 5 $^{\rm o}\text{C}/\text{min}$ heating rate.

The computed adsorption energies are -8.545eV, -8.537eV, and -8.427 eV for B, C and H site respectively which indicates that the bridge site is energetically the most favorable adsorption site on the graphene sheet (Fig. 4(a,b), Fig. S7). It has been observed that on interaction with Cu⁺ ion, fermi level shifts into conduction band (Fig. 4c) and peaks appeared at the fermi level in TDOS profile (Fig. S8) which inferred that Cu⁺ ion adsorbed sheet is electron rich and may act as a catalyst in CuAAC reaction as reported in earlier studies,⁴⁷ whereas, Cu⁺ ion is adsorbed on NRGO with adsorption energy -8.77 eV which infer strong interaction between NRGO and Cu⁺ ions (Fig. 4b), validates our experimental studies. On adsorption of Cu⁺ ion, a bond of length 2Å has been formed between carbon and the ion. The analysis found that by doping with nitrogen, Fermi level shifts into the conduction band which is in good agreement with earlier studies;⁴⁴ on adsorption of Cu⁺ ion an indirect band gap of ~0.29 eV has been introduced (Fig. 4d; Fig. S9). In order to understand the high reaction rate that was experimentally obtained, Mulliken charge population has been calculated, showing that the charge transfer of 0.073 e takes place on N after adsorption of Cu⁺ ion; this could explain the high reaction rate.

Further studies have been carried out to evaluate the interaction of cluster containing 3 Cu⁺ ions (CU-3) and 5 Cu⁺ ions (CU-5) (Fig. 4e,f). On adsorption of CU-3, the cluster shows physisorption with adsorption energy -31.07 eV and binding distance 2.76 Å while for adsorption of CU-5, physisorption with adsorption energy and binding distance -59.31 eV and 2.79 Å respectively is found. Further, the band structure and density of states have also been explored in Fig. S10. It has been found that the band gap has reduced when increasing the size of the cluster given in Table S2. Similar results have been observed from density of state profile of the system as well. Mulliken population has been calculated to understand the reaction rate for CU-3 and CU-5, and it is found that .156 e and .094e charge has been transferred on nitrogen respectively showing high reaction rates.

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Fig. 4 (a, b) Cu⁺ adsorption on TRGO and NRGO, respectively. (c, d) Band structure of Cu⁺ adsorption on TRGO and NRGO, respectively. (e, f) NRGO with a cluster of 3 and 5 Cu⁺ ions, respectively.

In summary, we have developed a highly stable and recyclable heterogeneous catalyst (NRGO/Cu(I)), which performs click reaction under both solvent and bulk conditions. Due to an increase in electron density on the nitrogen atom doping including the formation of coordination of N-doped rGO with Cu⁺ ions, nitrogen doped graphene supported copper particles demonstrate a higher reaction yield at room temperature without adding any external ligand/base. The incorporation of graphene based catalyst can also be advantageous to enhance the physical, mechanical and conductive properties of the cross-linked materials.

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Conflicts of interest

There are no conflicts to declare.

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