ChemComm

COMMUNICATION

View Article Online
View Journal | View Issue

Open Access Article. Published on 21 October 2014. Downloaded on 10/16/2025 8:51:35 PM.
This article is licensed under a Creative Commons Attribution 3.0 Unported Licence.

Cite this: *Chem. Commun.*, 2014, **50**, 15374

Received 1st October 2014,
Accepted 20th October 2014

DOI: 10.1039/c4cc07774a

www.rsc.org/chemcomm

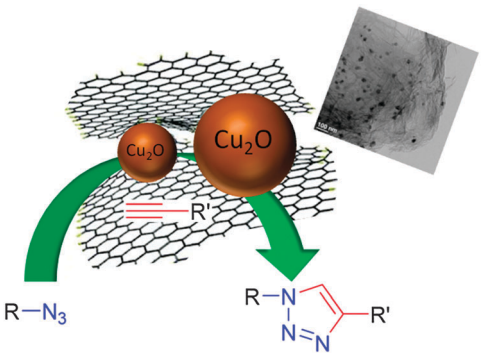
Click chemistry promoted by graphene supported copper nanomaterials†

Ali Shaygan Nia,[a] Sravendra Rana,[a] Diana Döhler,[a] Xavier Noirfalise,[b] Alice Belfiore[b] and Wolfgang H. Binder*[a]

A facile and robust approach is provided for the synthesis of highly dispersed copper nanoparticles immobilized onto graphene nanosheets, useful as a recyclable and reusable heterogeneous catalyst with excellent catalytic activity to achieve Cu(I)-catalyzed [3+2] cycloaddition 'click' chemistry.

Since its development by Sharpless[1,2] and Meldal,[3,4] the Cu(I)-catalyzed [3+2] cycloaddition reaction[5] between terminal acetylenes and azides ("click" reaction (CuAAc)) has emerged as a strategy for the rapid and efficient assembly of molecules with diverse functionality on both laboratory and production scales.[6–9] Click reactions are modular, tolerant of a wide range of functional groups, simple to perform, insensitive to reaction solvents irrespective to their polar/non-polar or protic/aprotic character.[10,11] However, in order to enhance the catalytic activity, the presence of a co-catalyst is required such as bases (mainly amines), auxiliary ligands, and oxidizing or reducing agents depending on the used Cu sources (Cu^{II}/Cu^{0}). Furthermore, the recyclability, reusability, and easy removal of the copper catalyst is often severely limited. Therefore, the development of recyclable and stable heterogeneous copper catalysts with improved catalytic activity devoid of any oxidizing/reducing agents is highly desirable.

Herein, we report a facile and robust approach for the synthesis of highly dispersible, recyclable, and reusable Cu(I) nanoparticles decorated onto graphene nanosheets, useful as a catalyst for "click" chemistry without any co-catalyst (Scheme 1). Graphene, a single layer of two-dimensional sp^2-hybridized carbon has attracted significant research interest due to its unique electrical and thermal conductivity, including exceptional mechanical, optical and chemical properties.[12–14] In contrast to single layer graphene sheets conveniently prepared by mechanical exfoliation, graphene oxide (GO) and reduced graphene oxide (rGO)[15,16] are easily available by controlled chemical reactions and can be produced on a large scale. Also due to the presence of functional groups on GO and rGO surfaces, further chemical reaction onto their surfaces is possible. On account of their large surface area, their unique interaction with metal particles,[17,18] and their performance for electron capture, transport, as well as prevention of supported nanoparticles agglomeration due to their scaffold behaviour, graphene supported catalysts have represented outstanding catalytic activity compared to other carbon supported catalysts.[19] Several reports for the preparation of different metal particles-GO heterostructures and their wide range of applications from photocatalytic hydrogen production to lithium ion batteries have been discussed.[20,21] Recently, few reports have appeared regarding the preparation of Cu–GO nanoconjugates and their relevance in hydrogen generation, supercapacitors, as well as in other applications.[22–25] However according to our knowledge their application in CuAAc catalyzed "click" chemistry has not been explored yet.



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

For the preparation of graphene oxide (GO), Hummer's method was applied,[26] whereas ion exchange with Cu^{2+} was achieved by dispersing GO in water,[27] followed by addition of copper(II) acetate under vigorous stirring for overnight. Afterwards Cu(II)–GO was reduced under Ar at 600 °C in an oven to

[a] *Institute of Chemistry, Chair of Macromolecular Chemistry, Faculty of Natural Sciences II (Chemistry, Physics and Mathematics), Martin-Luther University Halle-Wittenberg, von Danckelmann-Platz 4, Halle, 06120, Germany. E-mail: wolfgang.binder@chemie.uni-halle.de; Fax: +49 345 55 27392*
[b] *Materia Nova Research Center, 1 Avenue Nicolas Copernic, B7000 Mons, Belgium*

† Electronic supplementary information (ESI) available: Experimental details and supporting data. See DOI: 10.1039/c4cc07774a

This journal is © The Royal Society of Chemistry 2014

Open Access Article. Published on 21 October 2014. Downloaded on 10/16/2025 8:51:35 PM.
This article is licensed under a Creative Commons Attribution 3.0 Unported Licence.

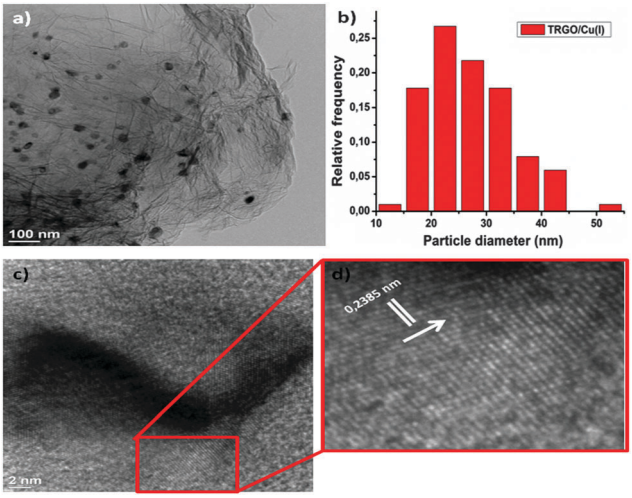


Fig. 1 (a) TEM image of the TRGO/Cu catalyst. (b) Copper particles size and distribution. (c, d) HRTEM of TRGO/Cu(I) and calculation of the lattice plane distance.

obtain TRGO/Cu(I). We first investigated the morphology and chemical composition of our nanoconjugates by TEM, EDX, XPS, and FAAS.

Fig. 1a shows the TEM image of TRGO–Cu(I) conjugates, where highly dispersed uniformly sized Cu nanoparticles on the surface of graphene nanosheets were obtained. From the TEM images the average particle size is about 25 nm for Cu particles (Fig. 1b). HRTEM was performed to measure the lattice plane distance in a single Cu nanoparticle (Fig. 1c and d), where 0.2385 ± 0.01 nm as a lattice plane distance was obtained, that could be due to the presence of CuO(110)[28] or Cu_2O(111),[29] indicative that for the TRGO–Cu conjugates the Cu is in the form of Cu(I) or Cu(II). To confirm the existing form of Cu, quantitation of nanoparticles was also achieved by STEM-EDXS (Fig. S1, ESI†) indicating that Cu and O are present in a ratio of 68.8 : 31.2 (≈2 : 1), which strongly supports that the particles consist of Cu_2O, and the valency of Cu is Cu(I) as required for their use in "click" chemistry. Further evidence of the chemical composition of the nanoconjugates was obtained by X-ray photoelectron spectroscopy (XPS) (Fig. 2a), where the peaks correspond to C 1s (285.1 eV), O 1s (531.6 eV) and Cu 2p. The high-resolution XPS (Fig. 2b) reveals that Cu $2p_{3/2}$ peaks located at 932.37 eV and 952.31 eV correspond to the peak energy of Cu(I).[30] Also there are no peak satellites at 942 eV and 962 eV and no peaks at 934.8 eV which would be related to Cu(II). The Cu content of the sample was also determined by analysis on a flame atomic absorption spectroscopy (FAAS) as 7.55×10^{-7} mol mg^{-1} loading.

The catalytic activity of the TRGO/Cu catalyst was investigated in the azide/alkyne click chemistry between benzyl azide and phenyl acetylene under different reaction conditions in high yields (up to 99%) as a model system. Also the model reaction for commercial available Cu on charcoal (Cu/C)[31] and Cu_2O powder as a reference was done, but a very low click conversion was obtained by these commercial catalysts (Table 1).

The recyclability of the catalyst was studied using the same alkyne/azide click model reactants. After four repetitions,

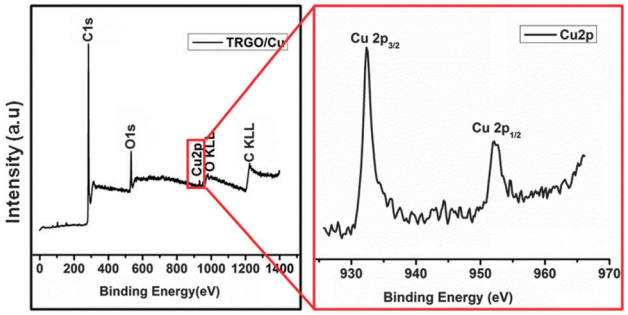


Fig. 2 (a) X-ray photoelectron spectroscopy of TRGO/Cu. (b) High resolution XPS of elemental Cu.

Table 1 Performance of various Cu-catalysts at different reaction conditions

Entry	Conditions	Conversion
1	TRGO without copper, in THF, 40 °C, 48 h	0
2	Copper on charcoal (2 mol%), in THF, 40 °C, 48 h	3
3	Cu_2O (2 mol%), in THF, 40 °C, 48 h	0
4	TRGO/Cu (2 mol%), in THF, 40 °C, 48 h	99
5	TRGO/Cu (2 mol%), in THF, room temperature, 48 h	70
6	Recycled catalyst in air (first cycle)	99
7	Recycled catalyst in air (fourth cycle)	55
8	TRGO/Cu, 1 : 1 water/methanol, room temperature, 24 h	99

a reduction (∼30%) of the reaction yield was observed (Fig. 3a), whereas the washing and recycling of the catalyst was accomplished in open air environment, supportive of the stability and recyclability of the synthesized catalyst (Table 1, Fig. 3a). The reduction of reaction yield after several repetitions could be due to agglomeration of Cu particles, as observed by TEM (Fig. 3b).

For kinetic investigation, NMR studies have been performed. Therefore aliquots were taken at intervals from the reaction, filtered to remove the catalyst and conversion of the reaction was determined by the resonance of the CH_2-moiety of benzyl azide (educt) in comparison to the CH_2-moiety of the click product (Fig. S2, ESI†). Eqn (1)[32] was used for the kinetic study and calculation yielded $k' = 1.33\ M^{-1.3}\ h^{-1}$, which was in the same range as those reported previously by Finn *et al.*[33] using $CuSO_4$ and sodium ascorbate as catalytic system.

$$\text{rate} = k'\,[\text{alkyne}]^{1.3\pm0.2}[\text{azide}]^{1\pm0.2} \quad (k' = k[\text{Cu}]^2) \qquad (1)$$

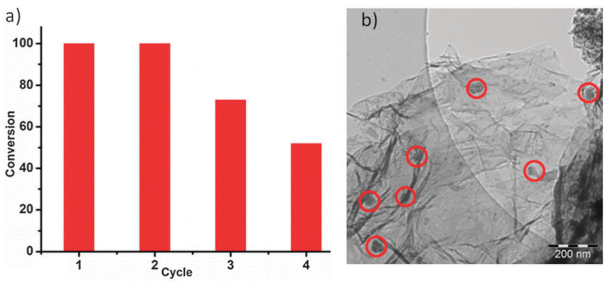
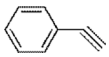
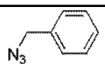
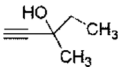
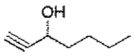
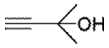
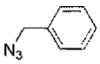


Fig. 3 (a) Catalyst recycling and stability in four cycles of click chemistry. (b) TEM image of Cu particles after the fourth run.

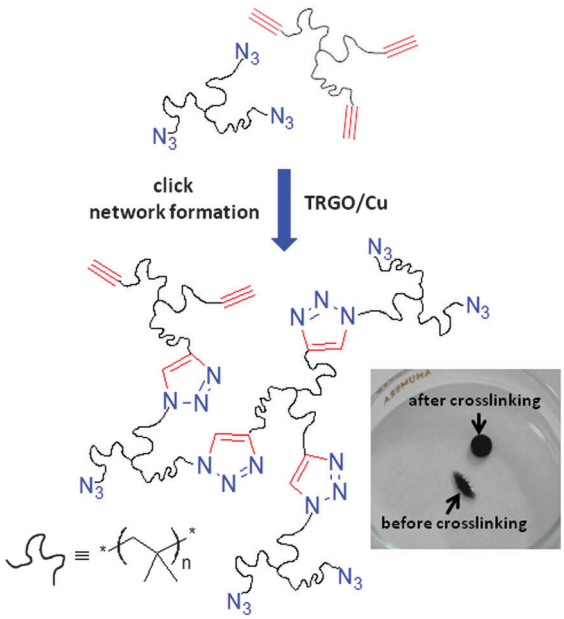
Open Access Article. Published on 21 October 2014. Downloaded on 10/16/2025 8:51:35 PM.
This article is licensed under a Creative Commons Attribution 3.0 Unported Licence.

Table 2 Click reaction of benzyl azide with different alkynes with 2 mol% TRGO/Cu at 40 °C after 48 h

Entry	Alkyne	Azide	Conversion
1			99
2			90
3			97
4			90
5			80

Furthermore Table 2 shows the different types of click reactions with different alkynes for TRGO/Cu catalyst, and even with a highly sterically hindered alkyne (entry 3) and linear hydroxy alkynes (entry 4) a high conversion was achieved.

To evaluate the performance of synthesized TRGO/Cu catalyst for bulk click chemistry including high molecular weight molecules, melt rheology was carried out for trivalent azide- and alkyne-functionalized polyisobutylenes (PIBs, M_n 5500 g mol^{-1} and 6900 g mol^{-1} respectively) (Scheme 2), suitable for crosslinking *via* "click" chemistry at room temperature, being designed for self healing materials.[9] For crosslinking experiments an azide-functionalized trivalent PIB and an alkyne-functionalized trivalent PIB were mixed with the TRGO/Cu catalyst (2 mol%, 0.7 mass%) and crosslinking was investigated on a rheometer plate. Fig. S3a† shows the rheology result of the "click" reaction of polymers at 20 °C, where at the beginning of the reaction, the sample clearly possesses liquid like character; the loss modulus is higher than the storage modulus ($G'' > G'$). After some time (520 minutes), both moduli increase and a crossover was observed (gel point), which is indicative of network formation. The structure of polymer-TRGO–Cu mixtures before and after crosslinking was investigated using FT-IR measurements (Fig. S3b, ESI†), where after crosslinking a complete disappearance of the azide peak (2097 cm^{-1}) confirms the complete crosslinking of the polymer. In contrast, in experiments with Cu/C and without catalyst no gel point was observed even after 1000 minutes, which again supports the high activity of the synthesized TRGO/Cu catalyst.



Scheme 2 Schematic illustration of the bulk click reaction of PIB-azide and PIB-alkyne with TRGO/Cu(I) at 20 °C *via* melt rheology.

In summary, we have presented a facile and robust approach for the immobilization of Cu(I) catalyst onto graphene nanosheets obtaining a highly active TRGO/Cu(I)-catalyst for the Cu(I)-catalyzed alkyne-azide "click" cycloaddition reaction. The TRGO/Cu-catalyst shows high stability at standard reaction conditions (air) with excellent recyclability and reusability. Furthermore, the TRGO/Cu catalyst shows excellent performance for bulk click reactions as proven *via* melt-rheology. Thus, Cu nanoparticles immobilized onto graphene nanosheets can function as an effective catalyst in click chemistry under both solvent and bulk conditions, including low and high molecular weight molecules.

We gratefully acknowledge the financial support from the EU-IASS project: Improving the Aircraft Safety by Self-Healing Structure and Protecting Nanofillers, European Union Seventh Framework Programme (FP7/20072013), Grant Agreement No. 313978 as well as the grant DFG-BI 1337/8-1 and DFG-BI 1337/8-2 within the SPP 1568 ("Design and Generic Principles of Self-Healing Materials).

Notes and references

1 H. C. Kolb, M. G. Finn and K. B. Sharpless, *Angew. Chem., Int. Ed.*, 2001, **40**, 2004–2021.
2 V. V. Rostovtsev, L. G. Green, V. V. Fokin and K. B. Sharpless, *Angew. Chem., Int. Ed.*, 2002, **41**, 2596–2599.
3 M. T. Meldal and C. W. Tornøe, Proceedings of the Second International and the Seventeenth American Peptide Symposium, 2001, pp. 263–264.
4 C. W. Tornøe, C. Christensen and M. Meldal, *J. Org. Chem.*, 2002, **67**, 3057–3064.
5 R. Huisgen, *Proc. Chem. Soc.*, 1961, 357–396.
6 W. H. Binder and R. Zirbs, *Encyclopedia of Polymer Science and Technology*, John Wiley & Sons, Inc., 2002.
7 W. H. Binder and R. Sachsenhofer, *Macromol. Rapid Commun.*, 2007, **28**, 15–54.
8 B. Uszczynska, T. Ratajczak, E. Frydrych, H. Maciejewski, M. Figlerowicz, W. T. Markiewicz and M. K. Chmielewski, *Lab Chip*, 2012, **12**, 1151–1156.
9 D. Döhler, P. Michael and W. H. Binder, *Macromolecules*, 2012, **45**, 3335–3345.
10 R. K. Iha, K. L. Wooley, A. M. Nyström, D. J. Burke, M. J. Kade and C. J. Hawker, *Chem. Rev.*, 2009, **109**, 5620–5686.
11 J.-F. Lutz, *Angew. Chem., Int. Ed.*, 2007, **46**, 1018–1025.
12 X. Huang, X. Qi, F. Boey and H. Zhang, *Chem. Soc. Rev.*, 2012, **41**, 666–686.
13 K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva and A. A. Firsov, *Science*, 2004, **306**, 666–669.
14 S. Yang, R. E. Bachman, X. Feng and K. Müllen, *Acc. Chem. Res.*, 2012, **46**, 116–128.
15 S. Eigler, S. Grimm, F. Hof and A. Hirsch, *J. Mater. Chem. A*, 2013, **1**, 11559–11562.
16 S. Eigler and A. Hirsch, *Angew. Chem., Int. Ed.*, 2014, **53**, 7720–7738.

 This journal is © The Royal Society of Chemistry 2014

Open Access Article. Published on 21 October 2014. Downloaded on 10/16/2025 8:51:35 PM.
This article is licensed under a Creative Commons Attribution 3.0 Unported Licence.

17 E. Yoo, T. Okata, T. Akita, M. Kohyama, J. Nakamura and I. Honma, *Nano Lett.*, 2009, **9**, 2255–2259.
18 G. M. Scheuermann, L. Rumi, P. Steurer, W. Bannwarth and R. Mülhaupt, *J. Am. Chem. Soc.*, 2009, **131**, 8262–8270.
19 Y. Li, H. Wang, L. Xie, Y. Liang, G. Hong and H. Dai, *J. Am. Chem. Soc.*, 2011, **133**, 7296–7299.
20 J. Qin, W. Lv, Z. Li, B. Li, F. Kang and Q.-H. Yang, *Chem. Commun.*, 2014, **50**, 13447–13450.
21 T. Jia, A. Kolpin, C. Ma, R. C.-T. Chan, W.-M. Kwok and S. C. E. Tsang, *Chem. Commun.*, 2014, **50**, 1185–1188.
22 P. D. Tran, S. K. Batabyal, S. S. Pramana, J. Barber, L. H. Wong and S. C. J. Loo, *Nanoscale*, 2012, **4**, 3875–3878.
23 S. K. Movahed, M. Dabiri and A. Bazgir, *Appl. Catal., A*, 2014, **481**, 79–88.
24 C. Hong, X. Jin, J. Totleben, J. Lohrman, E. Harak, B. Subramaniam, R. V. Chaudhari and S. Ren, *J. Mater. Chem. A*, 2014, **2**, 7147–7151.
25 X. Dong, K. Wang, C. Zhao, X. Qian, S. Chen, Z. Li, H. Liu and S. Dou, *J. Alloys Compd.*, 2014, **586**, 745–753.
26 W. S. Hummers and R. E. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339.
27 T. Kyotani, K.-y. Suzuki, H. Yamashita and A. Tomita, *Tanso*, 1993, **1993**, 255–265.
28 O. García-Martínez, R. M. Rojas, E. Vila and J. L. M. de Vidales, *Solid State Ionics*, 1993, **63–65**, 442–449.
29 M. L. Foo, Q. Huang, J. W. Lynn, W.-L. Lee, T. Klimczuk, I. S. Hagemann, N. P. Ong and R. J. Cava, *J. Solid State Chem.*, 2006, **179**, 563–572.
30 S. Suzuki, M. Saito, S. C. Kang, K. T. Jacob and Y. Waseda, *Mater. Trans., JIM*, 1998, **39**, 1024–1028.
31 B. H. Lipshutz and B. R. Taft, *Angew. Chem., Int. Ed.*, 2006, **45**, 8235–8238.
32 V. O. Rodionov, V. V. Fokin and M. G. Finn, *Angew. Chem.*, 2005, **117**, 2250–2255.
33 V. O. Rodionov, S. I. Presolski, S. Gardinier, Y.-H. Lim and M. G. Finn, *J. Am. Chem. Soc.*, 2007, **129**, 12696–12704.