Catalysis Science & Technology

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/catalysis

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

A facile and rapid route for the synthesis of Cu/Cu_2O nanoparticles and its application in Sonogashira coupling reaction of acyl chlorides with terminal alkynes

Manohar A. Bhosale,[a] Takehiko Sasaki[b] and Bhalchandra M. Bhanage[a*]

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

We have demonstrated a facile and one-step synthetic strategy for the preparation of Cu/Cu_2O nanoparticles (NPs) via microwave method. The microwave energy acts as a driving force for the synthesis of Cu/Cu_2O NPs which makes the process economical. In the current methodology, Cu/Cu_2O NPs were synthesized within three minutes using copper (II) acetate as a precursor and 1,3-propanediol as solvent. The 1,3-propanediol plays multiple role in a reaction such as solvent, reactant, promoter and capping agent and no need of any other additives. The structural and morphological study of Cu/Cu_2O NPs was carried out with the help of XRD, FEG-SEM, EDS, TEM, FT-IR, DSC-TGA and TPR techniques. This is one of the simple, faster, inexpensive and greener approach for the synthesis of nanocrystalline Cu/Cu_2O. Furthermore, the nanocrystalline Cu/Cu_2O showed excellent catalytic activity in Sonogashira coupling reaction of alkynes with acyl chlorides.

Introduction

Recently, there has been increasing interest in the synthesis of size and shape controllable nanoparticles because of their selective size and morphology along with monodispersity in crystal structure increases the catalytic activity.[1] Microwave assisted synthesis of colloidal inorganic nanomaterials is an important class of advanced nanoscience and material chemistry.[2] Cu/Cu_2O nanoparticles (NPs) are attractive material due to its physical as well as chemical properties and numerous applications. The Cu/Cu_2O NPs shows extensive applications in assorted field such as catalytic degradation of dye,[3] glucose sensor,[4] catalysis,[5] generation of hydrogen by using ammonia–borane.[6] Most of the researchers reported various methods such as solvothermal method,[4] thermal decomposition[7] and reduction method[8] for the synthesis of Cu/Cu_2O nano and microparticles with different size and morphology. However, these methods have numerous disadvantages like use of high temperature, utilization of toxic and costly reagents ($NaBH_4$ and PVP), multistep synthesis, need of capping agents and reducing agents, long reaction time and requisite of external additives like base, stabilizer and promoter during the reaction for the synthesis of Cu/Cu_2O nanoparticles.

Recently, Liu and co-workers[9] demonstrated the two-step synthesis of Cu_2O/Cu nanocomposites via solvent-thermal route using N,N-dimethylformamide as solvent in Teflon-lined stainless steel autoclave but the methodology has one or more limitations such as higher temperature (180 °C), long reaction time (26 h) and multistep synthesis. Salavati-Niasari and co-workers[10] reported the synthesis of copper and copper (I) oxide NPs by thermal decomposition. Zhang and co-workers demonstrated the interfacial hydrothermal synthesis of Cu@Cu_2O core-shell microspheres.[11] Even though they achieved nanoparticles in nano region it has one or more same drawbacks mentioned above. Therefore there is need to develop alternative method which is simple, facile, one step, economic, additive free, without the use of templates or capping agents and greener protocol for the synthesis of nanoparticles.[12]

Nowadays, the synthesis of NPs by using microwave assisted route is getting lot of attention owing to the several advantages offered by microwave irradiation.[2,13] In our recent work, we showed the advantages of microwave method and importance of synthesis of microwave assisted NPs.[14] Microwave irradiation is simple, faster, one step and greener method for synthesis of NPs. Along with this it has several advantages such as it provides volumetric heating, energy efficient, rapid reaction kinetics, homogeneity, selectivity, time economy, convenience along with compactness of equipments and better product yield.[13a,14d] Overall considering all this advantages, microwave irradiation is simple, inexpensive and economic method for synthesis of NPs than other conventional methods. The efficiency of the microwave heating is given by following equation:

$P = cE^2 f \varepsilon''$

Wherein, P is microwave power dissipation per unit volume in solvent, c is radiation velocity, E is electric field in the material, f is radiation frequency and ε'' is the dielectric loss constant. ε'' is the most significant parameter that determines the ability of the a material to heat in the microwave field. 1,3-propanediol has a high value of ε'' and it having high boiling point (217 °C).

In the present work, we have developed an effective, facile, rapid, template free, capping agent free and additive free method for the synthesis of Cu/Cu_2O NPs via microwave-assisted route under mild reaction conditions using only two reagents such as, $Cu(CH_3COO)_2$ as a starting material and 1,3-propanediol as a solvent. 1,3-propanediol plays fundamental role in a reaction to control the size and shape of NPs. This is facile technique for the synthesis of Cu/Cu_2O NPs via microwave method and it may also be further extended to the synthesis of other metal oxides. We have also showed the application of Cu/Cu_2O NPs in catalysis and it exhibited good catalytic activity for the coupling of terminal alkynes and acyl chlorides (benzoyl chlorides).

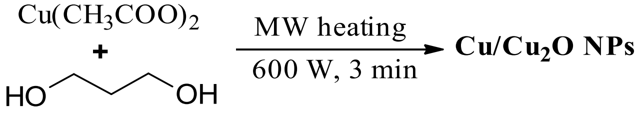
Experimental Section

Materials

A.R. grade copper acetate $[Cu(CH_3COO)_2.H_2O]$ and 1,3-propanediol were procured from S. D. Fine Chemicals Pvt. Ltd. India. All chemicals are highly pure and were used without further purification.

Synthesis of Cu/Cu_2O NPs

Cu/Cu_2O NPs was synthesized by taking mixture of 0.4 g of $Cu(CH_3COO)_2.H_2O$ in 10 mL 1,3-propanediol in 100 mL glass beaker and kept inside the domestic microwave oven (LG intellowave, operating at 100% power of 800 watt (W) and frequency of 2.45 GHz) for 3 min at electric power 600 W with on/off mode having time interval of 30 sec (Scheme 1). The reaction progress was observed by the change in colour of reaction mixture and finally it was converted blue to brick-red signifying the formation of Cu/Cu_2O (inset image in Fig. 1). The synthesized NPs were collected by decanting the reaction solvent. The separated product was then washed with distilled water and absolute ethanol for several times and dried in oven at 70 °C for 1 h. The obtained NPs were characterized by different analytical techniques.



Scheme 1 Synthesis of Cu/Cu_2O nanoparticles by microwave irradiation

Method of characterization of Cu/Cu_2O NPs

As prepared Cu/Cu_2O NPs was characterised by X-ray diffractometer (Shimadzu XRD-6100 using CuK_α radiations = 1.5405 Å) with scanning rate 2° per min and 2 theta (θ) angle ranging from 10° to 80° at current 30.0 mA and voltage 40.0 kV, The morphology of the samples was examined using field emission gun-scanning electron microscopy (FEG-SEM) analysis (Tescan MIRA 3 model) and transmission electron microscopy (TEM) using Philips CM- 200, operating voltage 200 kV. The energy dispersive X-ray spectrum (EDS) was recorded by using INCA x-act Oxford instrument (Model 51-ADD0007). X-ray photoelectron spectra (XPS) were monitored by using PHI 5000 versaprobe scanning ESCA microbe. Fourier transform infrared spectroscopy (FT-IR) measured on Brucker Perkin Elmer-100 spectrometer. Temperature programmed reduction (TPR) was recorded on Thermo scientific TPDRO 1100 and Differential scanning calorimetry-Thermogravimetric analysis (DSC-TGA) was done on Perkin Elmer STA 6000.

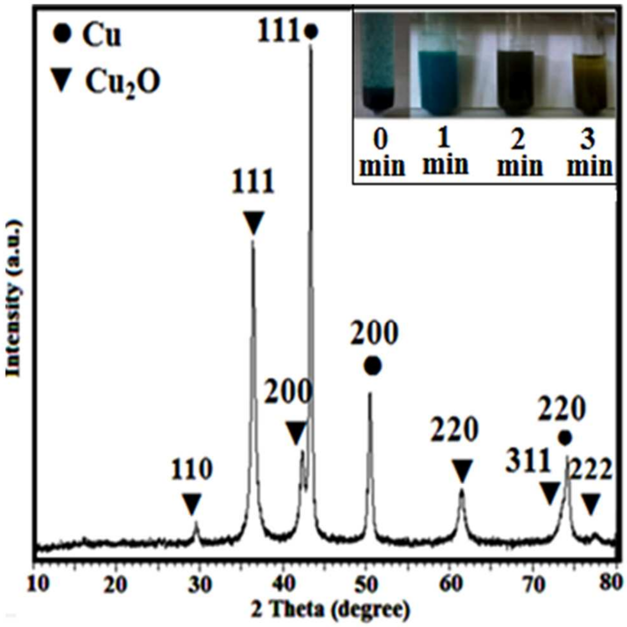


Fig. 1 XRD pattern of Cu/Cu_2O NPs with reaction progress observed by colour change (inset)

Results and Discussion

Characterization of prepared Cu/Cu_2O NPs

The general representation for synthesis of Cu/Cu_2O NPs by microwave irradiation is shown in scheme 1. The Phase identification of Cu/Cu_2O NPs was carried out by X-ray diffractometer (Fig. 1), it shows Bragg's reflections at 43.3°, 50.4°, 74.1° corresponds to (111), (200), (220) planes are of Cu whereas diffraction peaks at 29.5°, 36.4°, 42.3°, 61.3°, 73.5°, 77.3° corresponds to (110), (111), (200), (220), (311), (222) planes are of Cu_2O. The reaction progress was observed by gradual change in colour of reaction mixture during reaction (inset Fig. 1). The obtained results are in well agreement with JCPDS cards No. 04-0836 for Cu and JCPDS cards No. 05-0667 for Cu_2O.[4b,8b] The FEG-SEM images (Fig. 2) clearly indicate the size and shape of NPs and shows spherical as well as tubular morphology of the Cu/Cu_2O NPs. The morphology of Cu/Cu_2O NPs seems to be slightly irregular and it was observed that the particles are in nano region having particle size range 70 nm to 110 nm which leads to the availability of high surface area for catalytic activity (See SI Fig. S1, S2 and S3). To check the changes in morphology, the microwave irradiation time for the reaction was extended to 4 min and 6 min. But in both the cases similar morphology and nearly similar particle size was observed. (See SI Fig. S4 and S5). The particle structure and size can also be determined by TEM analysis. The TEM analysis was carried out by dispersing Cu/Cu_2O powder sample in ethanol and then it was exposed to ultrasonication bath for 10 min. A drop from this slurry was deposited on a copper grid. The TEM images Fig. 3 shows the Cu/Cu_2O NPs are in nano region and spherical as well as tubular morphology along with some aggregation. The morphology and particle size of Cu/Cu_2O NPs from TEM micrograph which is good extent similar to the result obtained by FEG-SEM (See supporting information Fig. S2). The energy-dispersive X-ray spectrum (EDS) shows peaks only for copper and oxygen elements which indicate the prepared nanomaterial which is pure and free from impurities (Fig. 4a). To check the complete reduction of precursor in to Cu NPs, the microwave irradiation time for the reaction was extended to 4 min and 6 min. But in both the cases it was observed that the presence of copper and oxygen in EDS analysis which evidence for presence of Cu_2O (See SI Fig. S4 and S5). The selected area electron diffraction (SAED) pattern of Cu/Cu_2O NPs points the product is fine crystalline in nature (Fig. 4b). Fig. 5a shows the typical survey spectrum of Cu/Cu_2O NPs, which shows the copper photoelectron peaks (Cu3p Cu3s, Cu2p and its Cu LMM Auger), the oxygen peaks (O1s) and the photoelectron peak of the carbon (C1s). The XPS survey spectrum shows the major peaks were Cu, O and C elements present on the surface of Cu/Cu_2O NPs. The carbon peak comes from the carbon tape used for XPS analysis. The corresponding high resolution XPS spectra of O1s region shown in Fig. 5b and the high resolution XPS spectra of Cu2p region shown in Fig. 5c attributed to presence of Cu_2O. The peak at 931.8 eV is assigned to $Cu2p_{3/2}$ and the peak at 951.35 eV is assigned to $Cu2p_{1/2}$. The additional peaks to the $Cu2p_{3/2}$ and $Cu2p_{1/2}$ are the two shake-up satellite peaks appearing at binding energies of 943.5 eV and 963.7 eV. These peaks are evident and diagnostic of an open $3d^9$ shell, corresponding to Cu^{+1} state. The thermal analysis was carried out by using DSC/TGA measurement of synthesized Cu/Cu_2O NPs in the inert N_2 atmosphere (20 mL/min) for the range from 30 °C to 800 ºC with a ramp rate of 10 ºC/min (Fig. 5a). The TGA curve (Fig. 5a, blue) shows a mass loss in the range of 80 ºC to 120 ºC is due to the evaporation of moisture absorbed by Cu/Cu_2O nanopowder. The DSC curve (Fig. 5a, green) shows thermal stability of Cu/Cu_2O catalyst. The DSC curve of Cu/Cu_2O exhibits endothermic peak at 217 ºC is due to the thermal decomposition of reaction solvent 1,3-propanediol (boiling point

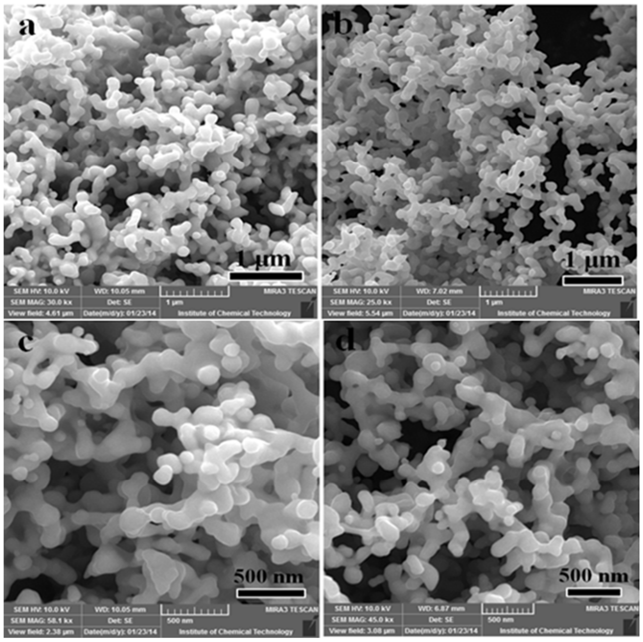


Fig. 2 FEG-ESM images of Cu/Cu_2O NPs

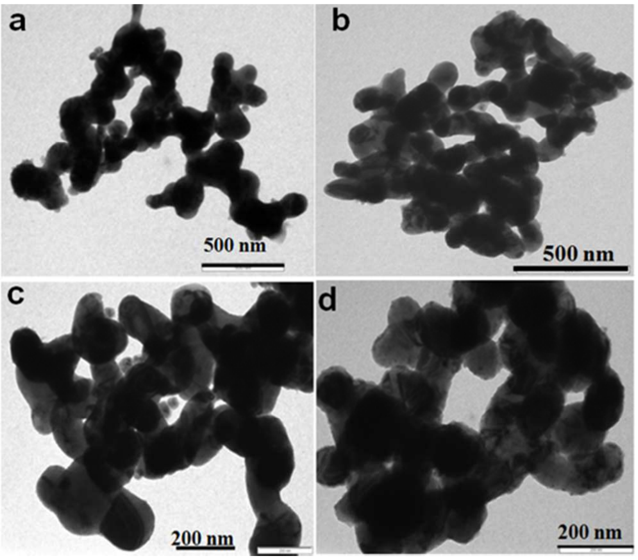
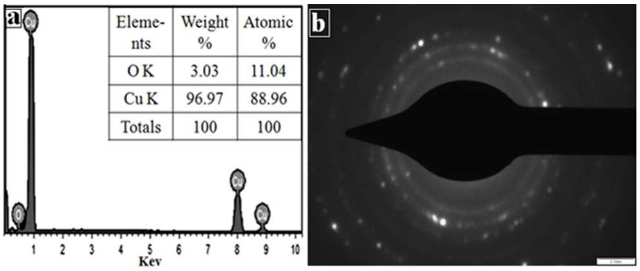


Fig. 3 TEM images of Cu/Cu_2O NPs



Eleme-nts	Weight %	Atomic %
O K	3.03	11.04
Cu K	96.97	88.96
Totals	100	100

Fig. 4 a) EDS spectrum b) SAED pattern of Cu/Cu_2O NPs

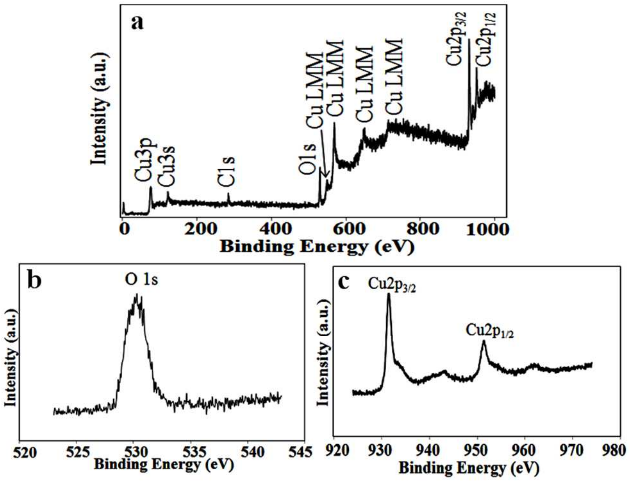


Fig. 5 XPS spectra of Cu/Cu_2O NPs (a) survey spectrum (b) O 1s region (c) Cu 2p region

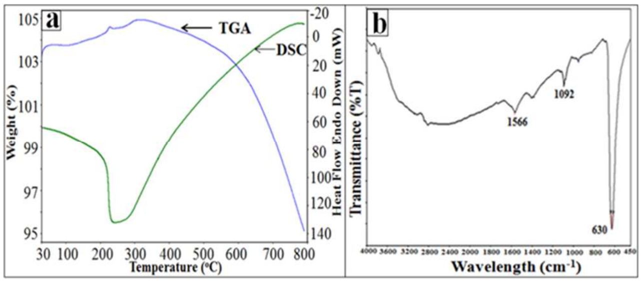


Fig. 6 a) DSC/TGA curve b) FT-IR spectrum of Cu/Cu_2O NPs

217 ºC) which was used as reaction solvent for the synthesis of Cu/Cu_2O NPs. The exothermic curve shows mass gain in DSC at 285 ºC due to oxidation of catalyst takes place.[15] According to Duval[16] the oxidation of Cu_2O starts at about 285 °C and oxygen comes from decomposition gases. In Fig. 5b the sharp peak arises at 630 cm^{-1} in FT-IR spectrum for Cu/Cu_2O NPs indicates the Cu-O stretching band. In H_2-temperature programmed reduction (H_2-TPR) analysis of as synthesized Cu/Cu_2O NPs showed in Fig. 6. In H_2-TPR curve, the sample was heated under a temperature ramp in a hydrogen environment and it was observed that the reduction of Cu_2O in to Cu(0) takes place at 280 °C.

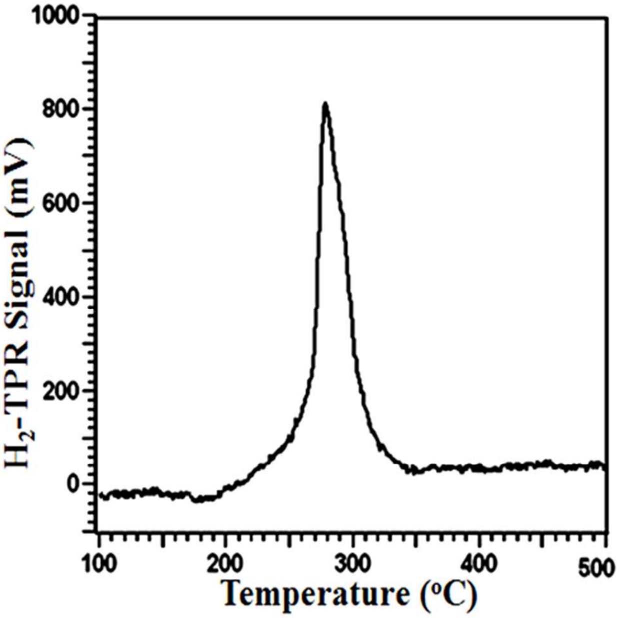
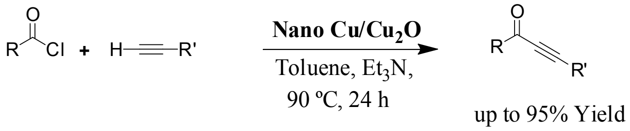


Fig. 7 H_2-TPR curve of Cu/Cu_2O NPs

Evaluation of catalytic activity of Cu/Cu_2O NPs

The catalytic activity of synthesized Cu/Cu_2O NPs was checked for the synthesis of ynone using terminal alkynes and acyl chlorides (Scheme 2). The ynone product has great applications for the development of valuable organic compounds.[17] Recently, Sun *et al.* reported the synthesis of ynone using silica gel and γ-Al_2O_3 supported Cu NPs.[18] In the survey of literature, the synthesis of ynone was carried out using various catalyst such as palladacycle complex,[19] $FeBr_2$,[20] Pd/C,[21] $Pd(PPh_3)Cl_2/CuI$,[22] PdNPs-PPS,[23] $PdCl_2(PPh_3)_2$,[24] $Pd(OAc)_2$,[25] $ZnBr_2$,[26] palladium(II) acyclic diaminocarbene complex,[27] CuI/cryptand-22 complex,[28] $Pd(PPh_3)_4/ZnCl_2$,[29] polystyrene-supported palladium(0) complex.[30] However, some of the above protocols are having several disadvantageous like use of various air and moisture sensitive ligands (phosphine ligands), necessity of additive and surfactant, high reaction temperature, requirement of co-catalyst and high catalyst loading. To overcome these drawbacks, we have checked the catalytic activity of Cu/Cu_2O NPs for synthesis of ynone and it was found that Cu/Cu_2O NPs are an efficient catalyst for the Sonogashira coupling reaction of acyl chlorides and alkynes (Scheme 2). Notably the reaction does not require any ligand source as well as lower catalyst loading; low reaction temperature with good to excellent yield of desired products makes the protocol attractive. The literature reveals that, both Cu(I) and Cu(0) are acts as a catalyst for the reaction.[31] This is one of the efficient, ecological and ligand-free protocols for the synthesis of ynone.



Scheme 2 Cu/Cu_2O NPs catalyzed synthesis of ynone

Initially, the reaction of phenylacetylene with benzoyl chloride was chosen as a model reaction, and the effects of assorted parameters such as the catalyst loading, solvents, bases, temperature and time were studied. At the beginning, the reaction was carried out in absence of catalyst but reaction did not proceed (Table 1, entry 1). Then, we have screened the catalyst loading using model reaction (Table 1, entries 2–4) and it was found that the 10 mol% of catalyst gave the excellent yield (92%) of the desired product (Table 1, entry 3). Next, we have screened various solvents such as toluene, DMSO, DMF, acetonitrile, dichloromethane and 1,4-dioxane to increase the reaction outcome (Table 1, entries 3, 5–9). Among these solvents the catalyst shows good activity in toluene (Table 1, entry 3).

Furthermore, we have studied the reaction without using base and it was observed that reaction did not work without base (Table 1, entry 10). After onwards, the effect of various bases such as NEt_3, K_2CO_3, Na_2CO_3, N-Methyl morpholine, DBU and KOH were studied (Table 1, entries 3, 11–15) and it was

Table 1 Optimization of reaction conditions[a]

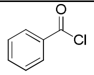
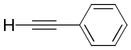
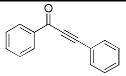
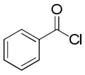
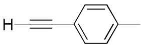
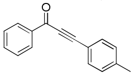
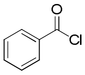
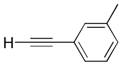
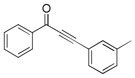
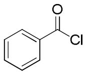
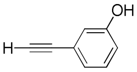
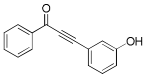
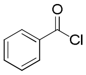
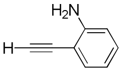
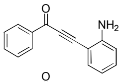
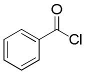
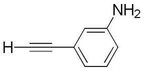
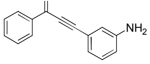
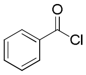
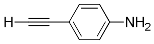
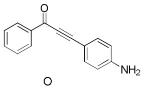
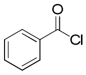
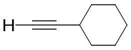
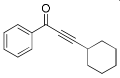
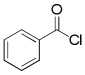
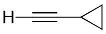
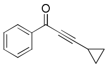
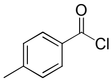
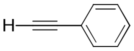
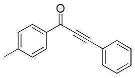
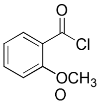
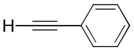
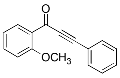
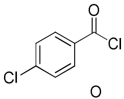
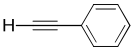
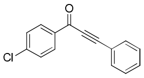
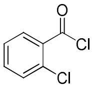
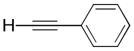
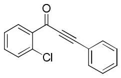
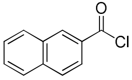
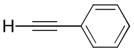
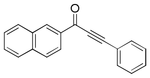
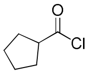
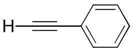
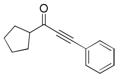
Entry	Catalyst (mol%)	Solvent	Base	Temp. (°C)	Time (h)	Yield [%][b]
Effect of catalyst loading						
1	--	Toluene	NEt_3	80	24	n.r.
2	5	Toluene	NEt_3	80	24	60
3	10	Toluene	NEt_3	80	24	92
4	15	Toluene	NEt_3	80	24	94
Effect of solvent						
5	10	DMSO	NEt_3	80	24	24
6	10	DMF	NEt_3	80	24	Trace
7	10	Acetonitrile	NEt_3	80	24	40
8	10	Dichloroethane	NEt_3	80	24	Trace
9	10	1,4-Dioxane	NEt_3	80	24	32
Effect of base						
10	10	Toluene	-	80	24	n.r.
11	10	Toluene	N-Methyl morpholine	80	24	45
12	10	Toluene	K_2CO_3	80	24	22
13	10	Toluene	Na_2CO_3	80	24	Trace
14	10	Toluene	DBU	80	24	n.r.
15	10	Toluene	KOH	80	24	20
Effect of Temperature						
16	10	Toluene	NEt_3	70	24	66
17	10	Toluene	NEt_3	90	24	95
18	10	Toluene	NEt_3	100	24	84
19	10	Toluene	NEt_3	90	24	62[c]
Effect of Time						
20	10	Toluene	NEt_3	90	10	60
21	10	Toluene	NEt_3	90	15	67
22	10	Toluene	NEt_3	90	20	72
23	10	Toluene	NEt_3	90	24	95
24	10	Toluene	NEt_3	90	30	68

[a] Reaction condition: Phenylacetylene (1 mmol), Benzoyl chloride (1.2 mmol), nano Cu/Cu_2O (mol%), Et_3N (2 mmol), Toluene (2 ml), N_2 atmosphere. [b] GC yield. [c] Without N_2 atmosphere, n.r.: No reaction

observed that NEt_3 gives excellent yield of the desired product (Table 1, entry 3). Subsequently, we have investigated the effect of reaction time and temperature (Table 1, entries 3, 16–24), it was found that the highest yield of the desired product was obtained at 90 °C within 24 hours (Table 1, entry 17). It was observed that the inert atmosphere gives good yield of desired product. However, the yield decreases in the absence of N_2 atmosphere (Table 1, entry 19).

Thus, the optimized reaction conditions were phenylacetylene (1 mmol), benzoyl chloride (1.2 mmol), nano Cu/Cu_2O (10 mol%), Et_3N (2 mmol), toluene (2 mL) at 90 ^oC for 24 h under N_2 atmosphere.[32] By considering these optimized reaction conditions, the scope of the developed protocol was extended for the synthesis of various derivatives of alkynes and acyl chlorides (Table 2). The various substrates of phenylacetylene at ortho-, meta- and para-positions were proceeded well (Table 2, entries 1–7). The cyclic derivatives of alkynes also gave good yield of respective products (Table 2, entries 8 and 9). Furthermore, the substituted benzoyl chloride with –Me, –OMe, –Cl and 2-naphthoyl chloride also furnished the good yield of the respective product (Table 2, entries 10–14). However, the strong electron withdrawing group such as ortho nitro benzyl chloride gives trace yield at the optimized reaction conditions. The cyclic derivatives of acyl chloride also smoothly undergo the coupling reaction and provided good yield of the desired product (Table 2, entries 15).

Table 2 Substrate study for the coupling reaction of alkynes and acyl chlorides[a]

Entry	acyl chlorides	alkynes	Product	Yield [%][b]
1				95
2				86
3				90
4				99
5				95
6				98
7				93
8				84
9				70
10				82
11				78
12				94
13				87
14				80
15				63

[a] Reaction condition: Alkynes (1 mmol), acyl chlorides (1.2 mmol), nano Cu/Cu_2O (10 mol%), Et_3N (2 mmol), Toluene (2 ml), 90 ºC, 24 h, N_2 atmosphere. [b] GC yield.

Conclusions

In summary, the simple and facile protocol for synthesis of Cu/Cu_2O NPs was developed using 1,3-propanediol using microwave irradiation. 1,3-propanediol itself acts as a versatile roles such as solvent, reactant, promoter and capping agent in a reaction. The reaction time is considerably less as compared to other existing methods and no requirement of other extraneous chemicals for the synthesis of Cu/Cu_2O NPs. This is one of the faster, additives and template free, economical and greener protocol since it avoids multiple reaction steps for the synthesis of Cu/Cu_2O NPs. Furthermore, we have showed the excellent catalytic applicability of synthesized Cu/Cu_2O NPs for Sonogashira coupling reaction of alkynes and acyl chlorides. Under the optimized reaction conditions various derivatives of alkynes and acyl chlorides provided good to excellent yield of the respective products.

Acknowledgement

Author M. A. Bhosale is grateful to Council of Scientific and Industrial Research (CSIR), India for the financial support. We are thanking to Department of Science and Technology (DST), India for financial support for this work under Nano Mission Project No. SR/NM/NS-1097/2011. XPS measurements were conducted at the Research Hub for Advanced Nano Characterization, the University of Tokyo, supported by the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan. This work is supported by JSPS and DST under the Japan-India Science Cooperative Program.

Notes and references

[a] *Department of Chemistry, Institute of Chemical Technology, Matunga, Mumbai 400019, India.*
[b] *Department of Complexity Science and Engineering, Graduate School of Frontier Sciences, The University of Tokyo, 5-1-5, Kashiwanoha, Kashiwa, Chiba 277-8561, Japan. E-mail: takehiko@k.u-tokyo.ac.jp*
*Corresponding author *Tel: +91 22 3361 2601; Fax: +91 22 3361 1020; E-mail: bm.bhanage@ictmumbai.edu.in, bm.bhanage@gmail.com*

† Electronic Supplementary Information (ESI) available: General information, experimental procedure for the reaction, Characterization of nanocatalyst, analysis of product by GC-MS. See DOI: 10.1039/b000000x/

1 P. Lignier, R. Bellabarba and R. P. Tooze, *Chem. Soc. Rev.*, 2012, **41**, 1708.
2 M. Baghbanzadeh, L. Carbone, P. D. Cozzoli and C. O. Kappe, *Angew. Chem. Int. Ed.*, 2011, **50**, 11312.
3 (a) S. Sun, C. Kong, H. You, X. Song, B. Ding and Z. Yang, *CrystEngComm.*, 2012, **14**, 40; (b) D. Jana and G. De, *RSC Adv.*, 2012, **2**, 9606.

4 (a) A. J. Wang, J. J. Feng, Z. H. Li, Q. C. Liao, Z. Z. Wang and J. R. Chen, *CrystEngComm.*, 2012, **14**, 1289; (b) Y. Zhao, Y. Li, Z. He and Z. Yan, *RSC Adv.*, 2013, **3**, 2178.

5 (a) J. Kou, A. Saha, C. Bennett-Stamper and R. S. Varma, *Chem. Commun.*, 2012, **48**, 5862; (b) S. U. Son, I. K. Park, J. Park and T. Hyeon, *Chem. Commun.*, 2004, 778

6 S. B. Kalidindi, U. Sanyal and B. R. Jagirdar, *Phys. Chem. Chem. Phys.*, 2008, **10**, 5870.

7 M. Diab, B. Moshofsky, I. J. L. Plante and T. Mokari, *J. Mater. Chem.*, 2011, **21**, 11626.

8 (a) K. S. Park, S. D. Seo, Y. H. Jin, S. H. Lee, H. W. Shim, D. H. Lee and D. W. Kim, *Dalton Trans.*, 2011, **40**, 9498; (b) J. Y. Xiang, J. P. Tu, Y. F. Yuan, X. H. Huang, Y. Zhou and L. Zhang, *Electrochem. Commun.*, 2009, **11**, 262.

9 B. Zhou, H. Wang, Z. Liu, Y. Yang, X. Huang, Z. Lu, Y. Sui and W. Su, *Mater. Chem. Phys.*, 2011, **126**, 847.

10 M. Salavati-Niasari and F. Davar, *Mater. Lett.*, 2009, **63**, 441.

11 Z. Ai, L. Zhang, S. Lee and W. Ho, *J. Phys. Chem. C*, 2009, **113**, 20896.

12 A. Radi, D. Pradhan, Y. Sohn and K. T. Leung, *ACS Nano*, 2010, **4**, 1553.

13 (a) J. A. Dahl, B. L. S. Maddux and J. E. Hutchison, *Chem. Rev.*, 2007, **107**, 2228; (b) J. Kou and R. S. Varma, *ChemSusChem.*, 2012, **5**, 2435.

14 (a) K. D. Bhatte, D. N. Sawant, K. M. Deshmukh and B. M. Bhanage, *Particuology*, 2012, **10**, 384; (b) M. A. Bhosale, K. D. Bhatte and B.M. Bhanage, *Powder Technol.*, 2013, **235**, 516; (c) K. D. Bhatte, P. Tambade, S. Fujita, M. Arai and B. M. Bhanage, *Powder Technol.*, 2010, **203**, 415; (d) M. A. Bhosale and B. M. Bhanage, *RSC Adv.*, 2014, **4**, 15122.

15 L. A. Silva, J. R. Matos and J. B. de Andrade, *Thermochim. Acta*, 2000, **360**, 17.

16 C. Duval, *Inorganic Thermogravimetric Analysis*, 2nd Edition, Elsevier, Amsterdam, 1963.

17 (a) C. Francois-Endelmond, T. Carlin, P. Thuery, O. Loreau and F. Taran, *Org. Lett.*, 2010, **12**, 40; (b) S. Roy, M. P. Davydova, R. Pal, K. Gilmore, G. A. Tolstikov, S. F. Vasilevsky and I. V. Alabugin, *J. Org. Chem.*, 2011, **76**, 7482; (c) L. Feng, A. Zhang and S. M. Kerwin, *Org. Lett.*, 2006, **8**, 1986; (d) M. Zora, A. Kivrak and C. Yazici, *J. Org. Chem.*, 2011, **76**, 6726.

18 W. Sun, Y. Wang, X. Wu and X. Yao, Green Chem., 2013, **15**, 2356.

19 D. A. Alonso, C. Najera and M. C. Pacheco, *J. Org. Chem.*, 2004, **69**, 1615.

20 B. Wang, S. Wang, P. Li and L. Wang, *Chem. Commun.*, 2010, **46**, 5891.

21 P. R. Likhar, M. S. Subhas, M. Roy, S. Roy and M. L. Kantam, *Helv. Chim. Acta*, 2008, **91**, 259.

22 (a) L. Chen and C. J. Li, *Org. Lett.*, 2004, **6**, 3151; (b) R. J. Cox, D. J. Ritson, T. A. Dane, J. Berge, J. P. H. Charmant and A. Kantacha, *Chem. Commun.*, 2005, 1037.

23 S. Santra, K. Dhara, P. Ranjan, P. Bera, J. Dash and S. K. Mandal, *Green Chem.*, 2011, **13**, 3238.

24 S. Atobe, H. Masuno, M. Sonoda, Y. Suzuki, H. Shinohara, S. Shibata and A. Ogawa, *Tetrahedron Lett.*, 2012, **53**, 1764.

25 (a) I. R. Baxendale, S. C. Schou, J. Sedelmeier and S. V. Ley, *Chem. Eur. J.*, 2010, **16**, 89; (b) S. S. Palimkar, P. H. Kumar, N. R. Jogdand, T. Daniel, R. J. Lahoti and K. V. Srinivasan, *Tetrahedron Lett.*, 2006, **47**, 5527.

26 K. Y. Lee, M. J. Lee and J. N. Kim, *Tetrahedron*, 2005, **61**, 8705.

27 D. S. Ryabukhin, V. N. Sorokoumov, E. A. Savicheva, V. P. Boyarskiy, I. A. Balova and A. V. Vasilyev, *Tetrahedron Lett.*, 2013, **54**, 2369.

28 E. Mohammadi, B. Movassagh and M. Navidi, *Helv. Chim. Acta*, 2014, **97**, 70.

29 H. Yuan, Y. Shen, S. Yu, L. Shan, Q. Sun and W. Zhang, *Synth. Commun.*, 2013, **43**, 2817.

30 M. Bakherad, A. Keivanloo, B. Bahramian and M. Rajaie, *Tetrahedron Lett.*, 2010, **51**, 33.

31 (a) J. Lindley, *Tetrahedron*, 1984, **40**, 1433; (b) F. A. Cotton, G. Wilkinson, C. A. Murillo and M. Bochmann, *Advanced Inorganic Chemistry*, John Wiley & Sons, 1999, 854-876.

32 Typical experimental procedure for reaction: In a 25 mL seal tube containing a magnetic stir bar was charged with phenylacetylene (1 mmol) and benzoyl chloride (1.2 mmol), nano Cu/Cu_2O (0.1 mmol, 10 mol%) as catalyst, Et_3N (2 mmol) as base and toluene (2 mL) as solvent under N_2 atmosphere. The reaction mixture was stirred for 24 h at 90 ºC. The reaction progress was monitored on GC analysis (Perkin–Elmer, Clarus 400). After completion of the reaction, the reaction mixture was filtered and the filtrate was washed with sat. $NaHCO_3$ solution (1 × 15 mL) and the product was extracted with ethyl acetate (3 × 10 mL) and dried over Na_2SO_4 and evaporated under vacuum. The all obtained products are well known in the literature and were confirmed by GC-MS (Shimadzu GCMS-QP 2010) analysis by the comparison with those of literature data.