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A facile one-step approach for the synthesis of uniform spherical Cu/Cu_2O nano and microparticles and its catalytic application in Buchwald-Hartwig amination reaction

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An efficient, rapid, and additive free protocol for synthesis of uniform spherical Cu/Cu_2O nano/microparticles and application in Buchwald-Hartwig amination reaction.

Cite this: DOI: 10.1039/c0xx00000x

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ARTICLE TYPE

A facile one-step approach for the synthesis of uniform spherical Cu/Cu_2O nano and microparticles with high catalytic activity in Buchwald-Hartwig amination reaction

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

In present work, we have developed a rapid, one step, calcination free protocol for the synthesis of uniform spherical Cu/Cu_2O nano/microparticles (NMPs). The synthesis of Cu/Cu_2O NMPs was achieved by microwave irradiation of copper acetate as a precursor and 1,4-butanediol as a solvent in few minutes. The prepared Cu/Cu_2O NMPs gave 100% yield of uniform spherical morphology. 1,4-butanediol plays a crucial role in reaction such as a solvent, reactant, stabilizer and capping agent which control the crystal morphology. The resultant product was characterized with the help of different techniques such as XRD, FEG-SEM, EDS, TEM, FT-IR, TPR, DSC-TGA, XPS and BET surface area analyser. The results confirm that the Cu/Cu_2O NMPs were well crystalline and essentially pure. This is a simple, faster, inexpensive and additive free protocol for synthesis of nanocrystalline Cu/Cu_2O than conventional method. These Cu/Cu_2O NMPs showed excellent catalytic activity in Buchwald-Hartwig amination coupling reaction. Notably the reaction does not require the any ligand source, low catalyst loading, low temperature with catalyst recyclability.

1. Introduction

Recently, the synthesis of shape selective nano and microstructures has received considerable interest due to their unique structures and its different properties such as, optical, catalytic, electrical, magnetic and thermal which have widespread applications.[1,2] As a result of the diverse structures and properties, the copper and copper oxide (i.e., Cu_2O and CuO) are considered as interesting materials in current research. Copper is used as an inexpensive, versatile metal in several applications. The Cu, Cu_2O and Cu/Cu_2O NMPs have various applications such as photocatalysis,[3] solar-energy conversion, magnetic storage, and gas sensors,[4,5] as electrodes in electrochemistry,[6] catalysis,[7] lithium ion batteries,[8] electronics, optics and electrocatalysis[9] and the degradation of dyes.[10]

Davar *et al*. has demonstrated the synthesis of Cu and Cu_2O nanoparticles by thermal decomposition.[11] Ai *et al.* has reported Cu@Cu_2O core-shell microspheres via hydrothermal synthesis.[12] Recently, Wang *et al.* has reported the synthesis of Cu/Cu_2O hollow microspheres by solvothermal method.[13] However, most of these protocols have disadvantages like high reaction temperature (greater than 200 °C), long reaction time (12□48 hours) and need of external additives, stabilizers, reducing agents and capping agents. Other methodologies for synthesis of Cu/Cu_2O nanoparticles by using different techniques have also one or more same drawbacks.[14] In order to overcome these drawbacks, there is a necessity to develop a simple, rapid, one step, economic and additive free protocol for the nanomaterial synthesis.

Currently, the microwave assisted methods are gaining a lot of interest for synthesis of nanomaterials because of its several advantages like rapidity, efficient and volumetric heating, selectivity, homogeneity, fast kinetics, less energy requirements, ease of operation, compactness of equipments and environmentally benign protocols as there are no by-products formed.[15] 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 resolves the ability of the a material to heat in the microwave field. The 1,4-butanediol has a higher value of dielectric loss constant (ε'') and a high boiling point of 235 °C. We have showed the importance of microwave assisted method for synthesis of ZnO, MgO nanoparticles.[16]

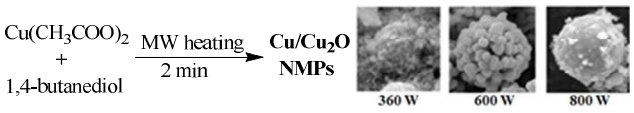
It is beneficial to develop an alternative method to produce nanoparticles with uniform shape and size without using templates or capping agents.[17] Here, we propose a facile, rapid, template free, capping agent free, calcination free and additive free method for the synthesis of uniform spherical Cu/Cu_2O NMPs via microwave-assisted route using only two reagents such as, $Cu(CH_3COO)_2$ as starting material and 1,4-butanediol as a solvent. 1,4-butanediol plays crucial role in a reaction to control the size and shape of the nanoparticles. In this study, we focused on synthesis of uniform shape and size of nano/microstructures. Furthermore, the growth of Cu/Cu_2O NMPs at different electrical powers in watts (W) has been studied. We also demonstrate the

catalytic activity of Cu/Cu_2O NMPs for C-N bond formation in Buchwald-Hartwig coupling reaction. Under the optimized reaction conditions, we have studied the various electron donating and electron withdrawing derivatives of aryl halides with aromatic amines which shows good to excellent yield of the respective N-arylation products.

2. Experimental section

Materials: Copper acetate [$Cu(CH_3COO)_2.H_2O$] and 1,4-butanediol were procured from S.D. Fine Chemicals Pvt. Ltd. India and they were used as received without further purification.

Synthesis of Cu/Cu_2O NMPs: Synthesis of uniform spherical Cu/Cu_2O NMPs by microwave irradiation was carried out in domestic microwave oven (LG intellowave) operating at 100% power of 800 watt (W) and frequency of 2.45 GHz. In experimental procedure, a mixture of 0.4 g of Copper acetate in 8 mL 1,4-butanediol was taken in a 50 mL glass beaker and placed in microwave oven for 2 min at different electrical powers in watts i.e. 360 W, 600 W and 800 W with on/off mode having time interval of 20s (Scheme 1). The reaction progress was monitored by observing the change in colour of the reaction mixture from blue to brick-red precipitate at the bottom of reaction flask indicating formation of Cu/Cu_2O materials (inset image in Fig. 1). The product was taken out after decanting the reaction solvent. The isolated product was then washed with distilled water and absolute ethanol 4□5 times and dried under vacuum at 80 °C for 30 min to obtain dried Cu/Cu_2O NMPs and no need of further calcination in furnace



Scheme 1 Synthesis of Cu/Cu_2O NMPs by using microwave method and its FEG-SEM images at different watts.

Characterization of Cu/Cu_2O NMPs: The as prepared Cu/Cu_2O nanomaterial was characterised by X-ray diffractometer (Shimadzu XRD-6100 using CuK_α = 1.54 Å) with scanning rate 2° per min and 2 theta (θ) angle ranging from 20° to 80° with current 30 mA and voltage 40 kW, Field emission gun-scanning electron microscopy (FEG-SEM) analysis was done by Tescan MIRA 3 model with secondary electron (SE) detector between 10.0 kV to 20.0 kV. The energy dispersive X-ray spectrum (EDS) was recorded by using Oxford instrument (model 51-ADD0007). Fourier transform infrared spectroscopy (FT-IR) was 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. The surface area measured on ASAP 2010 (Micromeritics, USA) instrument.

3. Results and Discussion

To study the effect of microwave irradiation time and electrical powers on material, the synthesis of Cu/Cu_2O NMPs was carried out at different electrical powers i.e. at 360 W, 600 W, 800 W for

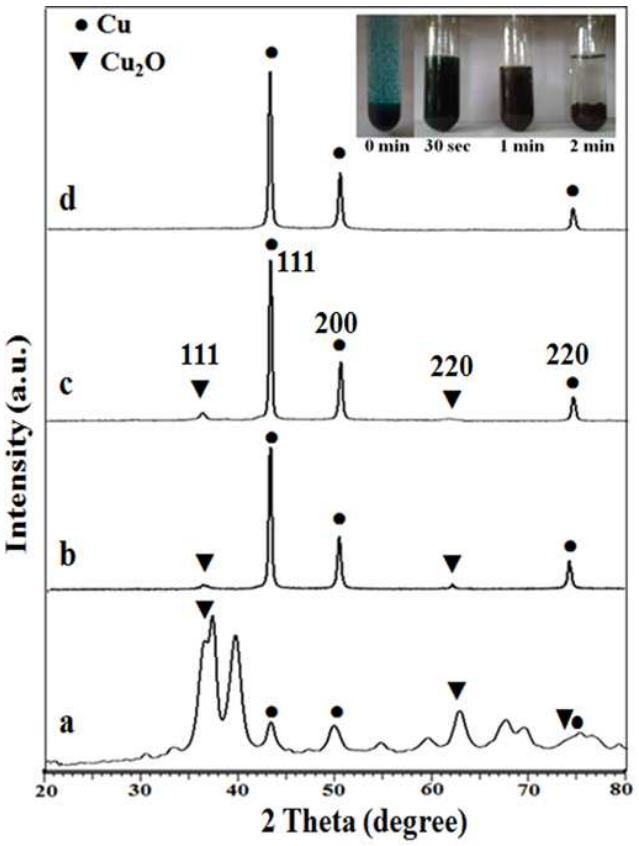


Fig. 1 XRD pattern of Cu/Cu_2O NMPs a) at 360 W for 2 min b) 600 W for 2 min c) 600 W for 5 min d) 800 W for 2 min with reaction progress observed by colour change (inset)

2 min, and at 600 W for 5 min. In the X-ray crystallography (Fig. 1), the diffraction peaks at 2θ values of 43.2º, 50.3º, 74.0º corresponds to (111), (200), (220) phases for Cu (JCPDS No. 04-0836) and diffraction peaks at 2θ values of 36.3º, 61.4º corresponds to (111) and (220) phases for Cu_2O (JCPDS No. 05-0667) respectively.[6,7d] XRD analysis indicates that the formation of Cu/Cu_2O takes place at 360 W, 600 W for 2 minutes and 600 W for 5 min (Fig. 1a-c), the complete reduction of Cu^{II} into Cu^0 takes place at 800 W for 2 min (Fig. 1d). In Fig. 1a (360 W for 2 min) some additional diffraction peaks are observed which are due to incomplete reduction of copper acetate. The reaction progress was observed by gradual change in colour of reaction mixture under the microwave irradiation (inset Fig. 1).

The FEG-SEM images of Cu/Cu_2O NMPs (Fig. 2a-e) show slow growth for the formation of particles along with some aggregation at 360 W for 2 min. The EDS spectrum in this case (Fig. 2f) shows only copper and oxygen. The particle growth of Cu/Cu_2O NMPs was enhanced at 600 W for 2 min shown in FEG-SEM images (Fig. 3a-e). It displays the formation of uniform spherical shape and size of nano/microspheres having a rough outer surface which contains number of nanoparticles attached to the microsphere. TEM analysis (inset Fig. 3a-e) matches to the morphological results of FEG-SEM. The EDS spectrum (Fig. 3f) of Cu/Cu_2O NMPs synthesized at 600 W for 2 min shows the copper and oxygen elements only and no other peak of impurities are observed. It confirms the purity of Cu/Cu_2O catalyst. The selected area electron diffraction (SAED) pattern (inset Fig. 3f) points out the crystalline nature of

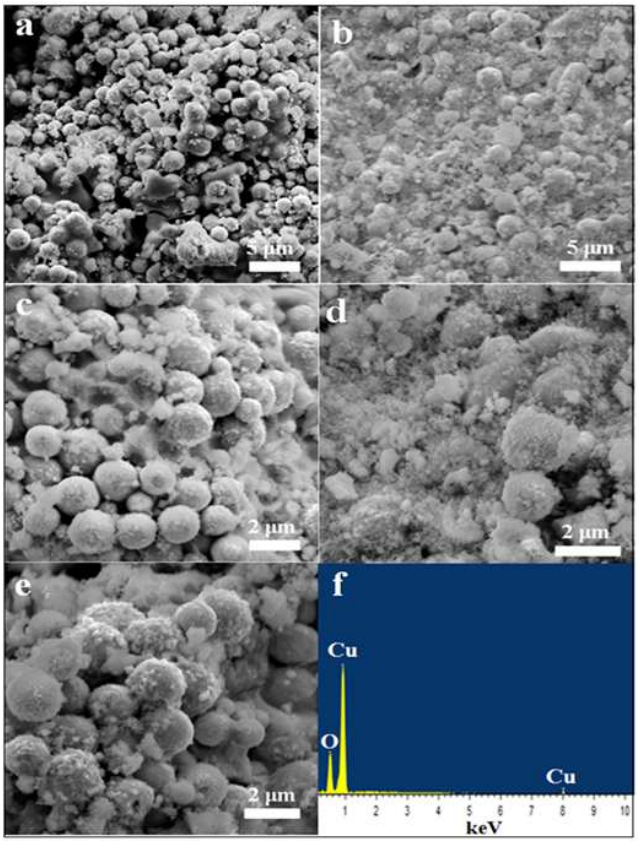


Fig. 2 a-e) FEG-SEM images f) EDS spectrum of Cu/Cu_2O NMPs at 360 W for 2 min.

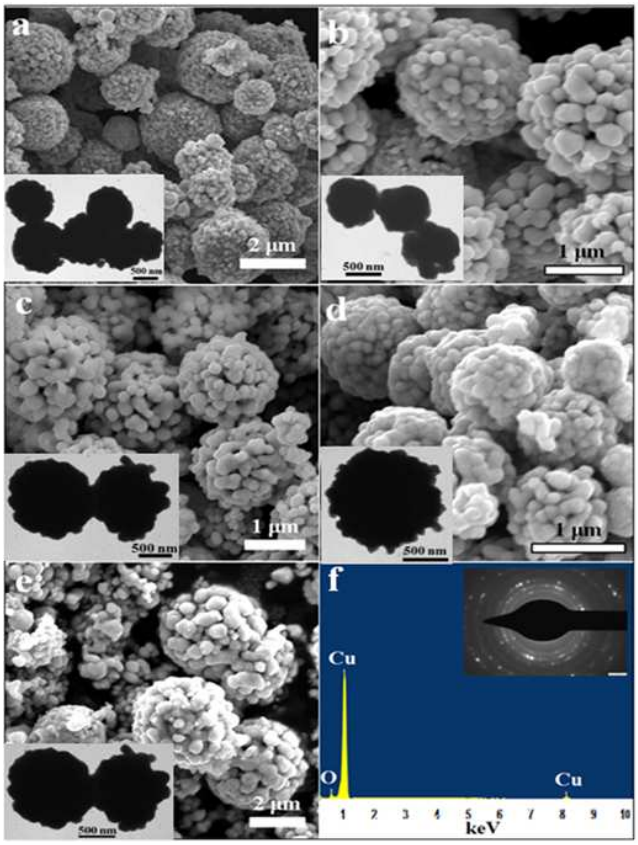


Fig. 3 a-e) FEG-SEM images (insets are TEM images) f) EDS spectrum (inset SAED pattern) of Cu/Cu_2O NMPs at 600 W for 2 min.

synthesized Cu/Cu_2O NMPs.

The high magnified FEG-SEM images (Fig. 4) of Cu/Cu_2O nanoparticles synthesized at 600 W for 2 min reveal the formation of nanosized dendrimeric like clusters which are roughly spherical in shape. The material also exhibits significant porosity (Fig. 4b). The size of the nanoparticle attached to dendrimeric like cluster is about 100 nm to 150 nm and the individual branched dendrons are about 7 nm to 12 nm in size (Fig. 4c-f). The number of nanoparticles tends to aggregate and formation of dendrimeric like cluster (microsphere) was observed.

When the time of microwave irradiation was increased from 2 min to 5 min at applied electrical power of 600 W the typical morphology of Cu/Cu_2O NMPs displayed as seen in Fig. 5a-e. It shows uniform spherical in shape and almost equivalent in size. At this time no dendrimeric like clusters formation was observed. The EDS spectrum for these nanoparticles shows copper and oxygen (Fig. 5f). At an electrical power of 800 W for 2 min Cu NMPs, by the evidence of its XRD Fig. 1d and EDS Fig. 6f, were found to be well dispersed and possessing uniform spherical shape with an average diameter of about 1 µm (Fig. 6a-e). The material spread on microspheres is due to the excess growth of particles at high electrical power (800 W). EDS spectrum (Fig. 6f) indicates only copper element which shows the purity of material.

The gradual changes in the growth and morphology of Cu/Cu_2O NMPs synthesized at different applied electric powers

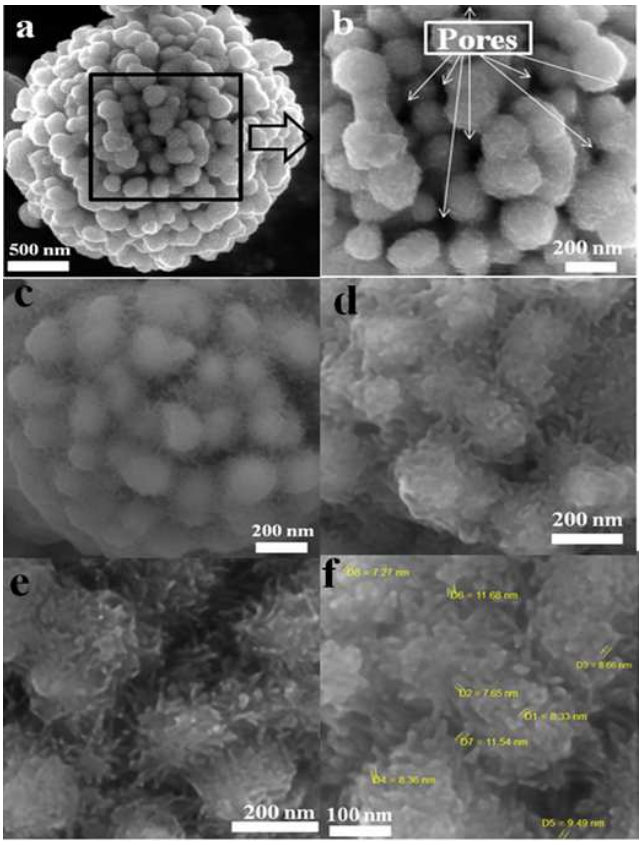


Fig. 4 Magnified SEM images of Cu/Cu_2O NMPs at 600 W for 2 min.

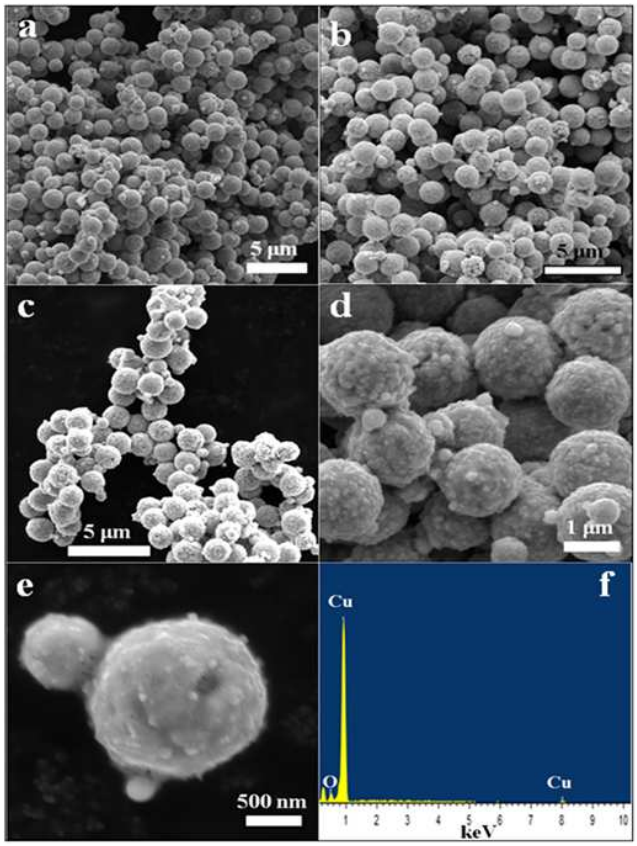


Fig. 5 a-e) FEG-SEM images f) EDS spectrum of Cu/Cu_2O NMPs at 600 W for 5 min.

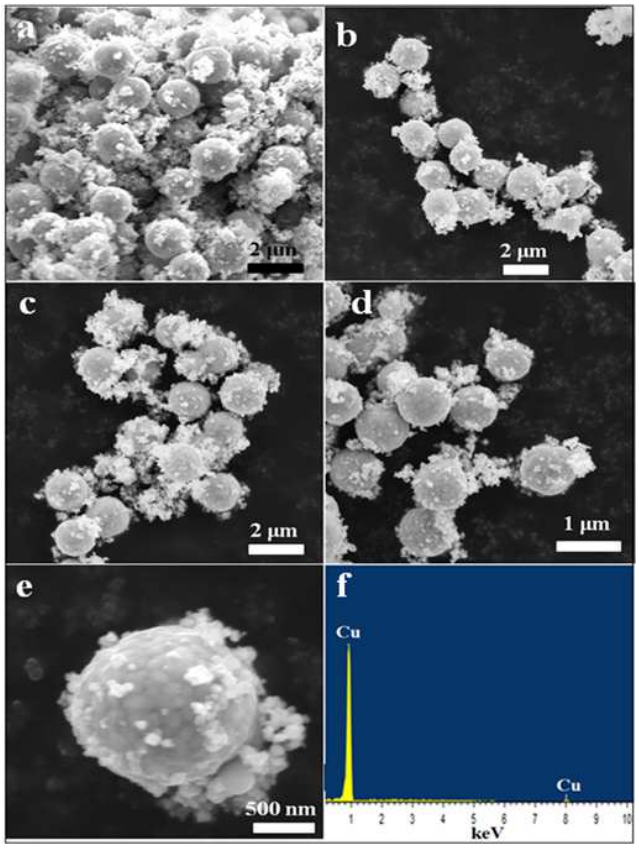


Fig. 6 a-e) FEG-SEM images f) EDS spectrum of Cu/Cu_2O NMPs at 800 W for 2 min.

in watts are displayed in Fig. 7. On microwave irradiation for 2 min at 360 W, the particles are more aggregated and spherical growth was started (Fig 7a). Whereas, in Fig. 7b the growth of particles was enhanced at 600 W for 2 min, in which nanosize dendrimeric like clusters are aggregated and formation of uniform spherical microspheres was observed. To investigate the time effect on size and morphology of particles, the reaction time of catalyst synthesis was increased from 2 min to 5 min. At this extended time, the formation of dispersed microspheres was observed (Fig. 7c). Similarly synthesis of Cu/Cu_2O NMPs carried out at 800 W shows spherical Cu microspheres with attached outgrowth on the outer surface indicative of excess growth (Fig. 7d).

We prefer further characterization of Cu/Cu_2O NMPs synthesized at 600 W for 2 min because it showed good catalytic activity in preliminary screening for Buchwald-Hartwig amination reaction (Table 1). The energy dispersive X-ray elemental mapping for Cu/Cu_2O NMPs synthesized at 600 W for 2 min, shows that Cu (Fig. 8b) and oxygen (Fig. 8c) species coexist in the material. The detailed analysis of the Cu (green) and oxygen (red) maps reveal that the concentration of Cu is more than that of oxygen. H_2-TPR curves of Cu/Cu_2O NMPs synthesized at an electric power of 600 W for 2 min is showed in Fig. 9a. The H_2 consumption peak is located between 240-340 ºC. The complete reduction of Cu_2O to Cu^0 was observed at 279 ºC. The phase purity was confirmed by thermal analysis using DSC/TGA measurement of Cu/Cu_2O NMPs synthesized at an electric power of 600 W for 2 min in the inert N_2 atmosphere (20

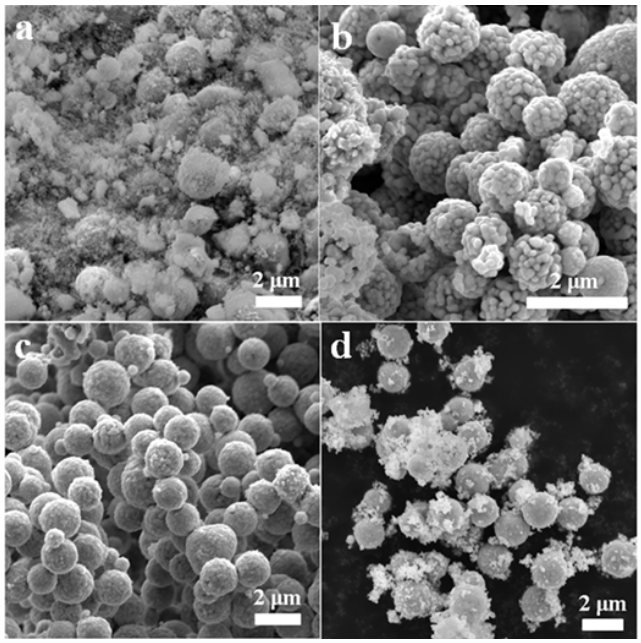


Fig. 7 Growth of Cu/Cu_2O NMPs a) at 360 W for 2 min b) 600 W for 2 min c) 600 W for 5 min d) 800 W for 2 min

mL/min) for the range from room temperature to 400 ºC with a ramp rate of 10 ºC/min (Fig. 9b). The TGA curve (Fig. 9b, blue) shows a mass loss between 60 ºC and 140 ºC which can be ascribed to the moisture present in the Cu/Cu_2O NMPs. The second mass loss observed in the range of 230 ºC to 300 ºC is due

to the evaporation of 1,4-butanediol (boiling point 235 ºC) which was used as the reaction solvent. The DSC curve (Fig. 9b, red) shows thermal stability of Cu/Cu_2O catalyst. The DSC curve of Cu/Cu_2O exhibits a broad endothermic peak around 90 ºC which corresponds to evaporation of water content. The second endothermic peak between 230 ºC and 300 ºC is due to the thermal evaporation of reaction solvent 1,4-butanediol.

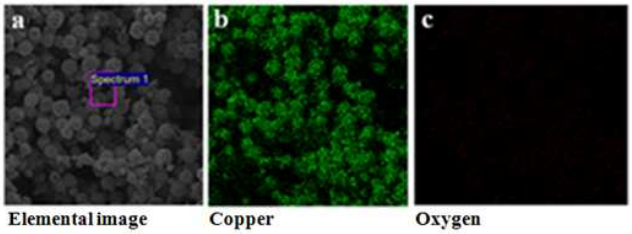


Fig. 8 EDS composition mapping a) FEG-SEM image b) Copper (green) c) oxygen (red) for Cu/Cu_2O NMPs at 600 W for 2 min.

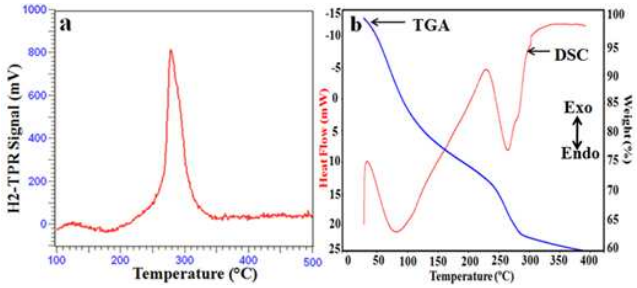


Fig. 9 a) H_2-TPR spectrum b) DSC/TGA graph of Cu/Cu_2O NMPs at 600 W for 2 min.

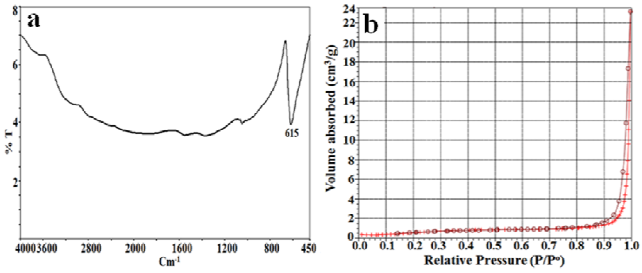


Fig. 10 a) FT-IR spectra b) N_2 adsorption-desorption isotherm of Cu/Cu_2O NMPs at 600 W for 2 min.

Fig. 10a shows the FT-IR of Cu/Cu_2O NMPs in which a sharp peak at 615 cm^{-1} indicates the Cu-O stretching band. The N_2 adsorption and desorption isotherms of the Cu/Cu_2O NMPs is shown in Fig. 10b. The specific surface area was calculated as 24.82 m^2/g. The typical XPS spectra (Fig. 11) (VG Scientific ESCA-3000 spectrometer) of Cu/Cu_2O NMPs synthesized at 600 W for 2 min. The Fig. 11a is the typical survey spectrum in which the major XPS peaks are marked for Cu and O present on the surface of catalyst. The corresponding O 1s spectrum (Fig. 11b) for nanocatalyst shows at 531.5 eV, attributed to Cu oxide (Cu_2O). The peaks at 932.6 eV corresponding to Cu $2p_{3/2}$ which can be attributed to Cu_2O. The peaks at 952.9 eV corresponding to Cu $2p_{1/2}$ which can be attributed to Cu (Fig. 11c). The Cu $2p_{3/2}$ peaks at 932.6 eV can be assigned to Cu_2O in accordance with data in the literature.[17]

Evaluation of catalytic activity of Cu/Cu_2O NMPs.

Copper catalyzed cross coupling reaction has become one of

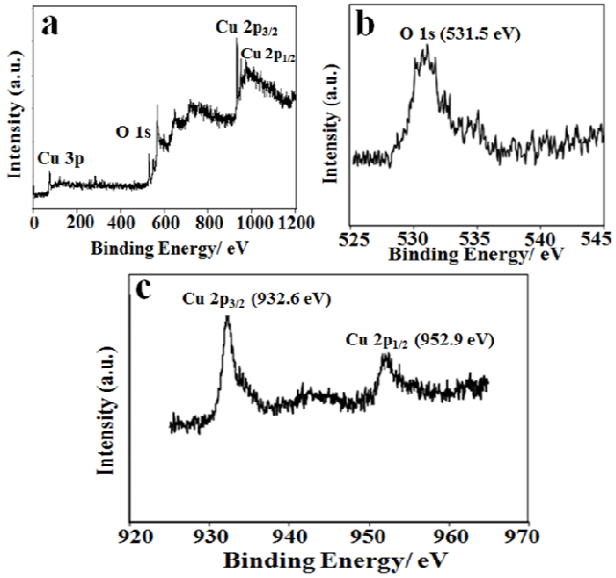
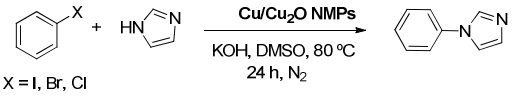


Fig. 11 a) XPS survey spectrum b) O 1s region c) Cu $2p_{3/2}$ region for Cu/Cu_2O NMPs

the most reliable and facile tools for the C-N bond formation reactions. In this aspect, some groups have reported Buchwald-Hartwig amination reactions using various homogenous copper catalysts.[18] Along with these, several protocols having disadvantages like use of high reaction temperature,[19] use of air sensitive and hygroscopic bases such as Cs_2CO_3[20] and *t*-BuOK,[21] essential of phase transfer catalysts,[22] use of additives[19a,23] and necessity of various air and moisture sensitive ligands.[24] Along with homogeneous copper precursors the various copper nanoparticles such as Cu_2O coated Cu nanoparticles,[7d] CuO/acetylene black nanoparticles[19c] and Cu_2O nanoparticles[19d] etc. are reported for the Buchwald-Hartwig amination reaction. Theses nanoparticle catalysed protocols are also suffering from the drawbacks as mentioned above.

To overcome these drawbacks, we have developed Cu/Cu_2O NMPs catalysed an efficient, economical, ligand-free and heterogeneous protocol for Buchwald-Hartwig amination reaction using aryl halides and aromatic amines (Scheme 2). Notably the reaction does not require the any ligand source, low catalyst loading, low temperature with excellent catalyst recyclability.



Scheme 2 Cu/Cu_2O NMPs catalysed Buchwald-Hartwig amination reaction.

Initially, the reaction of iodobenzene with imidazole was chosen as a model reaction and the effects of various parameters like effect of catalyst loading, solvents, bases, temperature and time were studied. At first, we have used nanocrystalline Cu/Cu_2O synthesized at different electric powers in watts (i.e. at 360 W, 600 W, and 800 W) as catalyst for Buchwald-Hartwig amination reaction using iodobenzene and imidazole (Table 1).

All the synthesized catalysts show massive catalytic activity due to large surface area and porosity of catalyst. Among the all Cu/Cu_2O nanoparticles prepared at different watts, the Cu/Cu_2O catalyst synthesized at 600 W for 2 min shows excellent catalytic

Table 1 Screening of Cu/Cu_2O NMPs prepared at different electric powers in watts[a]

Entry	Catalyst	Electric power in watt (Time)	Yield [%][b]
1	Cu/Cu_2O	360 W (2 min)	80
2	Cu/Cu_2O	600 W (2 min)	96
3	Cu/Cu_2O	600 W (5 min)	90
4	Cu	800 W (2 min)	84

[a] Reaction conditions: aryl iodide (1 mmol), imidazole (1.2 mmol), nano-catalyst (10 mol%), KOH (2 mmol), DMSO (2 ml), 80 ºC, 24 h, N_2 atmosphere. [b] GC yield.

activity and gave 96% yield of the respective N-arylation product (Table 1, entry 2). It can be due to uniform spherical shape, size (100 nm to 150 nm) and porosity of the particles (Fig. 4). Further investigation was carried out by using Cu/Cu_2O nanoparticles prepared at 600 W within 2 min.

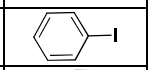
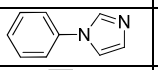
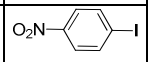
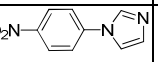
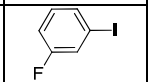
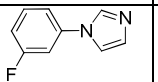
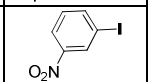
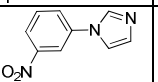
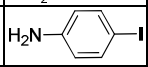
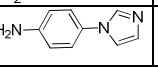
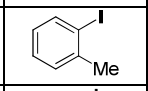
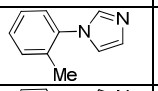
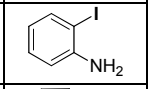
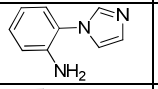
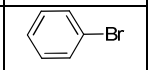
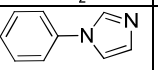
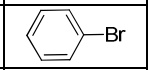
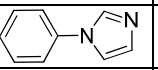
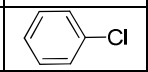
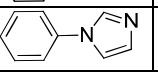
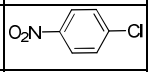
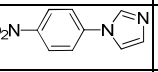
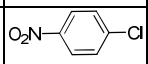
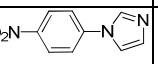
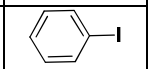
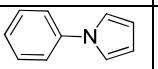
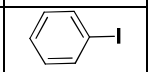
Next, to verify the catalytic activity for prepared Cu/Cu_2O NMPs, the reaction was carried out in absence of catalyst but reaction did not proceed (Table 2, entry 1). We have also examined the catalyst loading using model reaction (Table 2, entries 2–4) and it was found that the 10 mol% of catalyst is enough to furnished excellent yield of the desired product (Table 2, entry 3). Furthermore, the influence of various solvents like toluene, DMF, xylene, DMSO and n-butanol were studied (Table 2, entries 3, 5–8). Among the various screened solvents the activity of catalyst was found to be significantly higher in DMSO (Table 2, entry 3). Subsequently, we have investigated the effect of various bases such as KOH, Na_2CO_3, NaOH, K_3PO_4, Cs_2CO_3, DBU, and NEt_3 (Table 2, entries 3, 9□14) and it was observed that KOH gives excellent yield of the desired product in the

Table 2 Optimization of reaction parameters for Buchwald-Hartwig amination reaction[a]

Entry	Catalyst Conc. (mol%)	Solvent	Base	Temp. (ºC)	Time (h)	Yield [%][b]
		Effect of catalyst loading				
1	—	DMSO	KOH	80	24	NR
2	5	DMSO	KOH	80	24	75
3	10	DMSO	KOH	80	24	96
4	15	DMSO	KOH	80	24	98
		Effect of solvent				
5	10	Toluene	KOH	80	24	57
6	10	DMF	KOH	80	24	90
7	10	Xylene	KOH	80	24	trace
8	10	n-butanol	KOH	80	24	NR
		Effect of base				
9	10	DMSO	Na_2CO_3	80	24	49
10	10	DMSO	NaOH	80	24	94
11	10	DMSO	K_3PO_4	80	24	80
12	10	DMSO	Cs_2CO_3	80	24	94
13	10	DMSO	DBU	80	24	NR
14	10	DMSO	NEt_3	80	24	20
		Effect of Temperature				
15	10	DMSO	KOH	70	24	80
16	10	DMSO	KOH	90	24	86
17	10	DMSO	KOH	80	24	70[c]
		Effect of Time				
18	10	DMSO	KOH	80	18	42
19	10	DMSO	KOH	80	20	68
20	10	DMSO	KOH	80	30	48

[a] Reaction conditions: aryl halide (1 mmol), amine (1.2 mmol), nano-catalyst (10 mol%), KOH (2 mmol), DMSO (2 ml), 80 ºC, 24 h, N_2 atmosphere. [b] GC yield. [c] Absence of N_2 atmosphere. NR- No reaction.

Table 3 Substrate study for Buchwald-Hartwig amination reaction[a]

Entry	Aryl halide	Amine	Product	Yield [%][b]
1				96
2				99
3				96
4				90
5				49
6				60
7				78
8				60
9				82[c]
10				0
11				34
12				80[c]
13				96
14				97
15				54
16				71
17				28
18				58
19				66
20				46
21				52

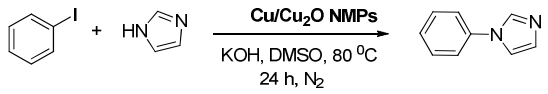
[a] Reaction conditions: aryl halide (1 mmol), amine (1.2 mmol), nano-catalyst (10 mol%), KOH (2 mmol), DMSO (2 ml), 80 ºC, 24 h, N_2 atmosphere. [b] GC yield. [c] Reaction temp. at 150 ºC.

presence of Cu/Cu_2O catalyst (Table 2, entry 3). Simultaneously, the effect of temperature and time on a reaction outcome was also

studied (Table 2, entries 3, 15□20), and it was found that 80 ºC was the optimum temperature to achieve excellent yield of the desired product within 24 hours (Table 2, entry 3). It was observed that the yield of desired product was decreases upto 70% in the absence of N_2 atmosphere (Table 2, entry 17), that means inert atmosphere is essential to get the better yield.

Thus, the optimized reaction conditions are aryl halide (1 mmol), amine (1.2 mmol), nano Cu/Cu_2O (10 mol%), KOH (2 mmol), DMSO (2 ml) at 80 ^oC for 24 h under N_2 atmosphere.[25] In order to study the general applicability of developed methodology, we have studied the various derivatives of aryl halides and aromatic amines for Buchwald-Hartwig amination reaction (Table 3). A variety of aryl iodides with electron-withdrawing (NO_2, F) and electron-donating (Me, NH_2) groups at *ortho*-, *meta*- and *para*-positions were successfully transformed into the desired N-arylation product with good to excellent yield under the optimized reaction conditions (Table 3, entries 1□7). We have also applied the present catalytic protocol for the N-arylation of aryl bromide and chloride (Table 3, entries 8□12). In presence of aryl chloride such as chlorobenzene, we disastrous to isolate desired coupled product (Table 3, entry 10). However, the electron withdrawing aryl chloride derivatives furnished the excellent yield of the respective N-arylation product under the optimised reaction conditions (Table 3, entries 11, 12). Afterwards, we have also studied different nitrogen containing aromatic amines, aryl amines as well as alkyl amines for Buchwald-Hartwig amination reaction. It was observed that the nitrogen containing aromatic amines provided good to excellent yield of the respective product under the optimized reaction conditions (Table 3, entries 13□16). Furthermore, the developed protocol was applied for aryl amines as well as alkyl amines and it was seen that these amines gives slightly less yield of respective product than the nitrogen containing aromatic amines (Table 3, entries 17□21).

Table 4 Investigation into the reuse of Cu/Cu_2O nanocatalyst



Entry	Run	Yield (%)[a]
1	1	96
2	2	92
3	3	86
4	4	75

[a] Yields were determined by GC analysis.

The reusability of catalyst reduces the cost in process chemistry, eliminates involvement in the synthesis and resale process. We examined the reuse of Cu/Cu_2O nanocatalyst for Buchwald-Hartwig amination reaction using aryl iodide such as iodobenzene and imidazole as substrates (Table 4). The Cu/Cu_2O nanocatalyst can be reused successfully upto fourth run without significant loss in catalyst activity. The catalyst was reused after each run by just simple filtration technique. The residue was washed with distilled water (3 × 2 mL) and absolute alcohol (3 × 2 mL) to remove the organic impurities. The obtained Cu/Cu_2O nanocatalyst was dried under vacuum and used as catalyst for recyclability study.

4. Conclusions

The simple, efficient, rapid and calcination free protocol has been developed for synthesis of uniform spherical Cu/Cu_2O NMPs via microwave method without using templates. The Cu/Cu_2O NMPs were synthesized using only two reagent like copper (II) acetate as starting material and 1,4-butanediol as solvent. Here 1,4-butanediol performs different roles in reaction such as solvent, reactant, stabiliser and capping agent which eliminates the need of any other extraneous additives. In addition, the synthesized Cu/Cu_2O NMPs showed excellent catalytic applicability for C-N bond formation in Buchwald-Hartwig amination reaction. Under the optimized reaction conditions various aryl halides and aromatic as well as aliphatic amines furnished good to excellent yield of the respective N-arylation and N-alkylation products.

Acknowledgement

Author M. A. Bhosale is thankful to Council of Scientific and Industrial Research (CSIR), India for providing a Junior Research Fellowship (JRF) and the financial assistance for this work by Department of Science and Technology (DST), India under Nano Mission Project No. SR/NM/NS-1097/2011 is gratefully acknowledged. We are thankful to Dr. C.V. Rode and C. S. Gopinath from National Chemical Laboratory, Pune for providing XPS analysis.

Notes and references

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

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25 Typical experimental procedure for Buchwald-Hartwig amination reaction:- In a 25 mL seal tube containing a magnetic stir bar was charged with iodobenzene (1 mmol) and immidazole (1.2 mmol), Cu/Cu_2O NMPs (0.1 mmol, 10 mol%) as nanocatalyst, KOH (2 mmol) as base and DMSO (2 mL) solvent under N_2 atmosphere. The reaction mixture was stirred for 24 h at 80 °C. After completion of the reaction, the reaction mixture was poured into 15 ml water and the product was extracted with ethyl acetate (3 × 10 mL). The reaction solvent was dried over Na_2SO_4 and evaporated under vacuum. All products are well known in the literature and were confirmed by GC-MS analysis by the comparison with those of literature data.