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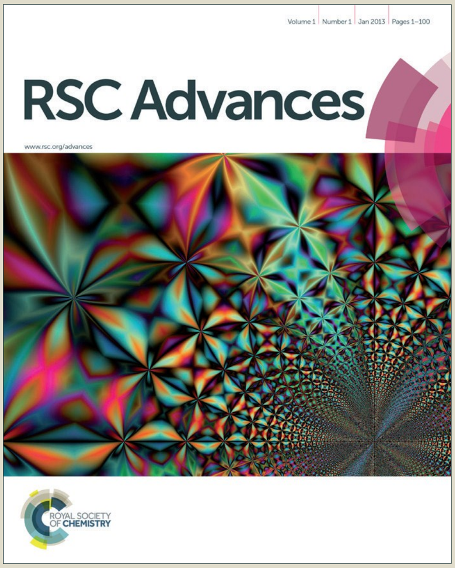

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# Effect of solvent ratio and counter ions on the morphology of copper nanoparticles: Its catalytic application in β-enaminones synthesis

Aravind L. Gajengi,[a] T. Sasaki[b] and Bhalchandra M. Bhanage[a]

This work reports the synthesis of shape selective copper nanoparticles (NPs) under microwave irradiation method using diverse ratios of ethylene glycol (EG)/water system. The solvent ratio of EG/water plays a pivotal role for the selective formation of CuO NPs. The alteration of counter ion of copper precursor lead to selective synthesis of copper (CuO, $Cu_2O$, $Cu(OH)_2$ NPs has been observed. The synthesized copper NPs are well characterized by FEG-SEM, TEM, XRD, XPS, $NH_3$-TPD and BET surface area. The prepared CuO NPs shows high activity towards the synthesis of β-enaminones and β-enamino esters from 1,3 diketones and amines.

## Introduction

Nanomaterials and microstructures has gained the valuable importance due to their distinctive structures and diverse properties such as optical, electrical, magnetic, thermal, catalytic and extensive applications.[1] Consequently, due wide variety structures and properties, copper nanoparticles are considered to as interesting applications in current research. Nowadays, copper NPs have found various applications in the different fields such as catalysis,[2] sensors,[3] photocatalyst,[4] fuel cells,[5] lithium batteries,[6] water-splitting systems.[7] There are different methods of synthesis of copper NPs such as wet chemical method,[8] biological method,[2a] microwave methods,[9] physical vapour deposition in ionic liquids,[10] solvothermal route,[11] polyol method.[12]

Microwave-assisted synthesis has attracted much attention because it has advantages of being fast, simple, easy operation and more energy efficient.[9a,13] The microwave synthesis enhances the kinetics of reactions by one or two orders of magnitude over conventional methods due to rapid initial heating and generation of the localized high pressure zone at reaction sites. The microwave process is more efficient than the conventional processes for the preparation of various metal oxide NPs due to shape selective synthesis of NPs.[14,15] It is well known that the morphology of NPs varies by variation of reaction parameters such as heating power of microwave, volume ratios of mixed solvent and counter ions.[16,17] The mixed solvent system of EG and water was used for the morphology controlled synthesis of CuO superstructures.[18]. There are some methods where they used the synthesis of CuO by using mixed solvents of EG and water.[3,18] Recently, Zhou *et al*. synthesized $Cu_2O$/CuO microparticles by using EG/water as a mixed solvent in the autoclave by using copper acetate as a precursor.[3] In this protocol they used only one volume ratio of EG/water *i.e.* 9:1 and observed the formation of $Cu_2O$/CuO microparticles.

The β-enaminones and β-enamino esters are important starting materials for the synthesis organic compounds.[19] These compounds used for synthesis of heterocycles,[20] nitrogen containing compounds[21], pharmaceutical drugs as an anticonvulsant,[22] natural alkaloids,[23] antibacterial.[24] There are various methods have been developed for the synthesis of enaminones such as condensation of carbonyl compounds with amines by using various catalysts such as $CoCl_2$,[25] $Yb(OTf)_3$,[26] Cu NPs,[27] Ag NPs,[28] perchlorates,[29] $InBr_3$,[30] tungstophosphoric acid[31] and by ultrasonic method.[32] These reported methods having one or more disadvantages such as uses of moisture sensitive metal triflates and difficulties in the work up,[26] use of harmful reagents,[29] use of homogenous catalyst.[25] There is need to develop an efficient catalytic method for the synthesis of β-enaminones which operates at mild reaction conditions.

In this report, we synthesized and characterized the CuO NPs under microwave irradiation by using different volume ratios of EG/water as solvent. The effect of various copper precursor leads to shape selective formation of Copper NPs such as $\mathrm{CuO}$, $\mathrm{Cu_2O}$, $\mathrm{Cu(OH)_2}$. This synthesized CuO NPs having acidic in nature and shows excellent catalytic activity towards the synthesis of β-enaminones and β-enamino esters from 1,3 di-ketones and amines at mild conditions.

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[a] Department of Chemistry, Institute of Chemical Technology, Matunga, Mumbai-400 019, 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.
*corresponding author, Tel.: + 91- 22 33612603; Fax: +91 33611020.
E-mail address: bm.bhanage@gmail.com, bm.bhanage@ictmumbai.edu.in

† Footnotes relating to the title and/or authors should appear here.

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## Experimental

### Chemicals and reagents

Copper acetate [$Cu(CH_3COO)_2·H_2O$], Copper chloride [$CuCl_2·2H_2O$], copper nitrate [$Cu(NO_3)_2$] and ethylene glycol were procured from S.D. Fine Chemicals Pvt. Ltd. India and they were used as received without further purification.

### Preparation of CuO NPs

For the synthesis of CuO NPs, the mixture of 200 mg of copper acetate is dissolved in different volume ratios of EG/water in mL (*i.e*. 1:9, 3:7, 5:5, 7:3, 9:1) and transferred to 100 mL glass beaker and kept inside the microwave oven for 4 min at 600 W with on–off mode of microwave oven having time interval of 30 s. After microwave heating, the colour of the reaction mixture changes to blue to black precipitate indicating formation of CuO NPs. The product was separated by centrifugation at 7000 rpm for 10 min and washed with distilled water and ethanol for several times. The obtained product was dried in the oven and used for further characterization. The CuO NPs prepared at different volume ratios of EG/water *i.e* 1:9, 3:7, 5:5, 7:3, 9:1in mL are labelled as CuO (a), CuO (b), CuO (c), CuO (d) and CuO (e) respectively.

### Preparation of $Cu_2O$ NPs

In the synthesis of $Cu_2O$ NPs, the mixture of 188 mg of $Cu(NO_3)_2$ was dissolved in 3:7 and 7:3 volume ratios of EG/water in mL and transferred to 100 mL glass beaker and kept inside the microwave oven for 4 min at 600 W with on–off mode of microwave oven having time interval of 30 s. After microwave heating, the colour of the reaction mixture changes blue to red precipitate indicating formation of $Cu_2O$ NPs. The product was separated by centrifugation at 7000 rpm for 10 min and washed with distilled water and ethanol as several times. The obtained product was dried in the oven and used for further characterization.

### Preparation of $Cu(OH)_2$ NPs

In the synthesis of $Cu(OH)_2$ NPs, the mixture of 170 mg of copper chloride was dissolved in 3:7 and 7:3 volume ratios of EG/water in mL and transferred to 100 mL glass beaker and kept inside the microwave oven for 4 min at 600 W with on–off mode of microwave oven having time interval of 30 s. After microwave heating, the colour of the reaction mixture changes to blue to green precipitate indicating formation of $Cu(OH)_2$ NPs. The product was separated by centrifugation at 7000 rpm for 10 min and washed with distilled water and ethanol several times. The obtained product was dried in the oven and used for further characterization.

### Characterization methods of CuO, $Cu_2O$, $Cu(OH)_2$ NPs

The prepared CuO, $Cu_2O$ and $Cu(OH)_2$ NPs were characterized using various analytical techniques. X-ray diffract meter (Shimadzu XRD-6100 using Cu Kα = 1.54 Å) with a scanning rate 2° per min and 2 theta (θ) angle ranging from 20° to 80° with current 30 mA and voltage 40 kV, 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. For Transmission electron microscopy (TEM), Philips, CM 200, was used as operating voltage of 200 KV model CM 200). X-ray photoelectron spectroscopy (XPS) was carried out using PHI 5000 Versa Probe Scanning ESCA Microprobe, The Brunauer–Emmett–Teller (BET) surface area by was analyzed on ASAP 2010 (Micromeritics, USA) instrument. $NH_3$-Temperature programmed desorption ($NH_3$-TPD) was recorded on Thermo scientific TPDRO 1100.

### General procedure for synthesis of β-enaminones and β-enamino esters

The experiment was carried out in 25 mL reaction vial, in a typical reaction procedure; the CuO NPs as a catalyst was introduced into a reaction vial containing acetylacetone (1 mmol) and an amine (1 mmol). The reaction mixture was stirred at 60 °C temperature for 9 h. The progress of the reaction was monitored by TLC. After completion of the reaction, the catalyst was recovered by filtration. The mixture was concentrated under vacuum. The residue was purified by chromatography to afford the desired compound. All products are well known in the literature and were characterized using GC-MS (Shimadzu QP 2010) and were also compared with authentic samples.

## Results and discussion

### Effect of morphology of CuO NPs with different ratio of EG/water

Initially, by using the copper acetate as the metal precursor we started investigation for the synthesis CuO NPs with different of volume solvent ratio of the EG/water under the microwave irradiation at 600W for 4 minutes. The variation of volume ratio of EG/water leads to change in morphology (Fig. 1). By using the 1:9 of the EG/water ratio the aggregation of sphere like CuO NPs was observed in SEM (Fig. 1a). When the composition ratio of EG/water changes to 3:7, the spindle shaped CuO NPs are observed (Fig. 1b). The disturbed spindle shaped morphology was observed when 5:5 of EG/water was used (Fig. 1c). Interestingly, flower like morphology observed in SEM as well as TEM when 7:3 EG/water was used (Fig. 1d and Fig. 1f). In case of 9:1 ratio of EG/water spherical CuO micro particles is observed (Fig. 1e). From this it was concluded that the volume ratio of EG/water controls the shape and size of the CuO NPs.

After the successful synthesis of NPs we further characterized these NPs by using the various techniques such as XRD, XPS and $NH_3$-TPD. The XRD pattern of CuO NPs which synthesized at volume of 3:7 and 7:3 in mL of EG/water (Fig.2) shows lattice planes of (-111) and (200) planes which corresponding Braggs angles at 35.6° and 38.8°. Which matches the characteristic peaks of pure monoclinic CuO crystallites (JCPDS card 05-0661).[33] The XRD of patterns of CuO NPs which were synthesized at different volume of EG/water ratios also matches to the standard (ESI-S1, Fig. 1).

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For the determination of surface analysis of synthesised NPs we further characterized by using the XPS analysis. The presence of Cu and O elements were confirmed by XPS analysis (Fig. 3a). The peak observed at a binding energy of 529.5 eV which corresponds to O1s and confirms $O^{2-}$ from of CuO (Fig. 3b). The peaks observed at a binding energy of 933.6 eV, 952.9 eV corresponds to $Cu2p_{3/2}$ and $Cu2p_{1/2}$ (Fig. 3c) which can be attributed to CuO and are well reported in the literature.[34] Along with the $Cu2p_{3/2}$ and $Cu2p_{1/2}$ peaks satellite peaks also observed at ~940 eV and ~959.8 eV which are characteristic of partially filled d-orbitals ($3d^9$ in this case of $Cu2^+$).[35]

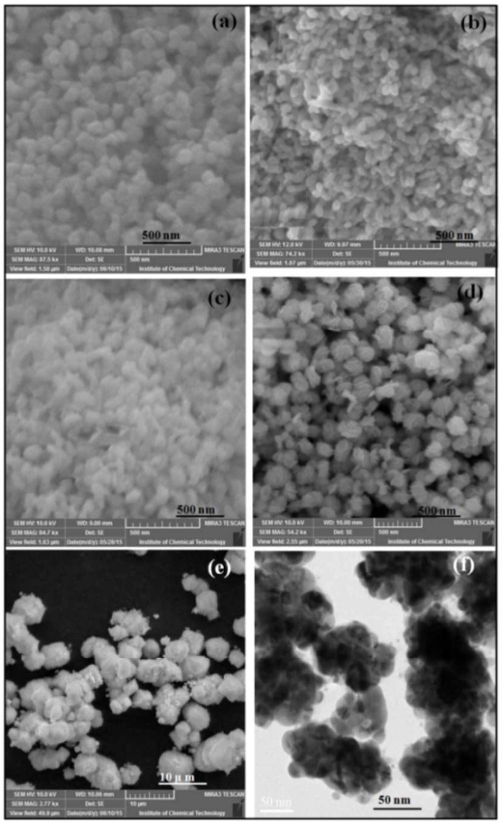

**Fig. 1** FEG-SEM images of CuO NPs synthesized at different volume ratio of EG/water in mL (a) 1:9 (b) 3:7 (c) 5:5 (d) 7:3 (e) 9:1 (f) TEM image of 7:3 of EG/water synthesized at 600 W for 4 min.

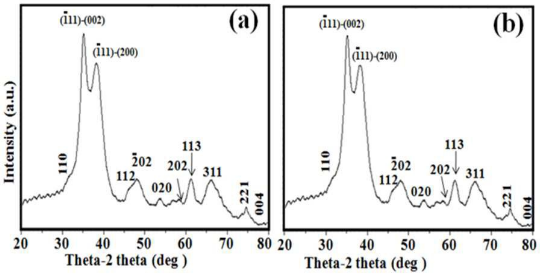

**Fig. 2** XRD pattern of CuO NPs (a) 3:7 and (b) 7:3 of EG/ water as solvent system

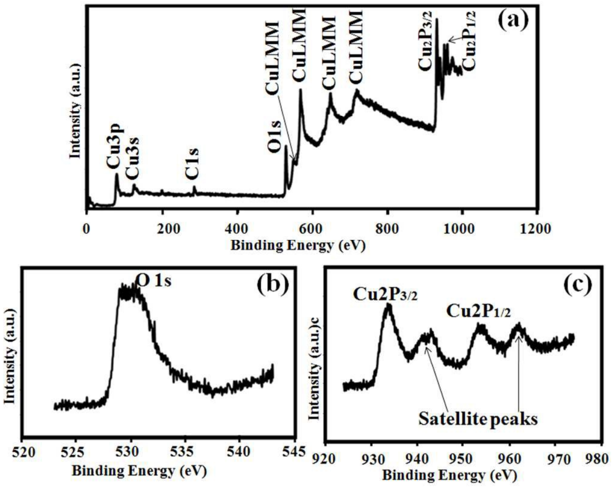

**Fig. 3** XPS spectra of CuO NPs (d): (a) survey spectrum, (b) O1s region and (c) Cu2p region.

### Effect of counter ion for synthesis of CuO, $Cu_2O$ and $Cu(OH)_2$

Further study of the effect of morphology was investigated by changing the counter ions of Cu metals at the 3:7 and 7:3 ratios of EG/water under microwave irradiation. Surprisingly, it was observed that the use of copper nitrate as a precursor provide the formation of $Cu_2O$ NPs (Fig. 4a and 4b). While the use of copper chloride as a precursor affords the formation of disturbed spherical particles $Cu(OH)_2$ particles when 3:7 EG/water was used (Fig. 4c) and fibre, flake like morphology obtained when 7:3 EG/water was used (Fig. 4d).

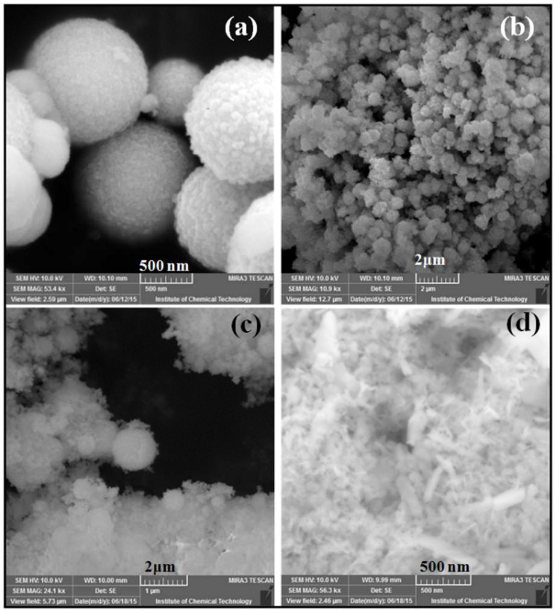

**Fig. 4** SEM images of Cu NPs by changing the metal precursor (a) and (b) $Cu_2O$ NPs from $Cu(NO_3)_2$ (c) and(d) $Cu(OH)_2$ microparticles synthesised from $CuCl_2$.

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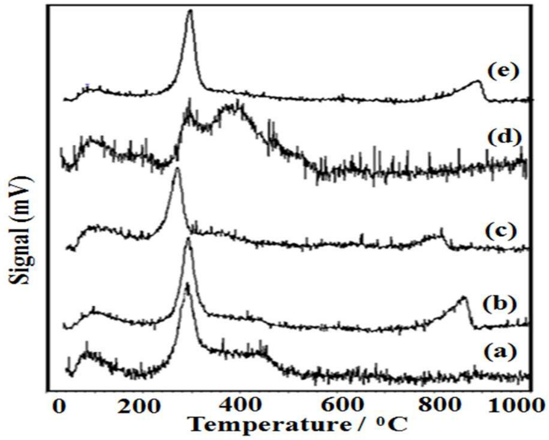


**Fig. 5** Comparative $NH_3$-TPD of synthesized CuO NPs.

The XRD patterns of $Cu_2O$ NPs and $Cu(OH)_2$ also matches with reported JCPDS data (ESI S1, Fig. 2 ).[36,37] Hence, the ratio of EG/water controls the morphology of the particles and precursor for the selective formation of copper NPs. The $NH_3$-TPD of synthesized CuO NPs was recorded and it was observed that the acidity of NPs varies with morphology (Fig. 5). The amount of $NH_3$ desorbed for CuO (a), CuO (b), CuO (c), CuO (d) and CuO (e) are 1817, 2502, 2751, 9813 and 2106 µmol/g respectively. The CuO NPs (d) having flower like morphology showed the highest $NH_3$ desorption (9813 µmol/g) hence, expected to have highest acidity.

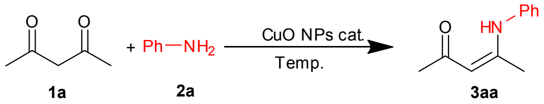
BET-Specific surface area of the catalyst is an important parameter for the high catalytic activity and the observed BET specific surface area for CuO (a), CuO (b), CuO (c), CuO (d) and CuO (e) are 98, 115, 118, 123 and 25 m²/g respectively.

### Catalytic application of β-enaminones and β-enamino esters using CuO NPs

To investigate the catalytic application of the synthesized NPs, the reaction of 1,3-dicarbonyl compound **1a** and amines **2b** carried out to synthesize β-enaminones **3aa**. Initially, the reaction was carried out without the catalyst and it was observed that only trace amount of product **3aa** was obtained (Table 1, entry 1). Then, we screened various CuO NPs (Table 1, entries 2-6), among them CuO NPs (d) shows highest catalytic activity and providing yield up to 58 % (Table 1, entry 5). The higher catalytic activity of the flower shaped CuO (d) may be due higher acidity and BET specific surface area (123 $m^2/g$) than other catalyst. The sphere like CuO (a) and micro sized CuO (e) shows lesser acidity and BET specific surface area due this giving a lesser yield of the product **3aa** (Table 1, entries 2 and 6). Also, spindle shaped CuO (b) gave less yield of product **3aa** due less acidity and BET surface area as compared to CuO (d) (Table 1, entry 3). The disturbed spindle shaped CuO (c) shows a higher acidity and BET specific surface area than CuO (b) and showing higher yield of product **3aa** than that of catalyst CuO (b) (Table 1, entry 4). So acidity and specific surface area are important for the catalytic activity of CuO NPs

In order to further optimise the reaction conditions, the CuO NPs (d) was chosen for the synthesis of β-enaminones and β-enamino esters due to its high activity. In a study of catalyst loading, an increase in the catalyst from 1.5 to 2.5 mol% increases the yield of **3aa** (Table 1, entries 7-8). However, an increase from 3.0 to 7.5 mol%, slightly decreases the yield of product **3aa** (Table 1, entries 8-10). Importantly, to check the optimum time for reaction, for this reaction carried at 3h, 6h, 9h and 12 h and it was observed that the increase in time from 3h to 9h there was an increase in the yield of product **3aa** and further increase in the time to 12 h there was no effect on the yield of the product **3aa** (Table 1, entries 11-13). Next, in the solvent study the use of solvent such as methanol, ethanol, acetonitrile and toluene gave the lesser yield than the reaction carried under neat condition (Table 1, entries 14-17). Finally, temperature study was done at RT, 40°C, 50°C, 60°C and 70 °C The increase in the temperature form RT to 60 °C there was an increase in the yield of product **3aa** and further increase in the temperature there was slightly changed in the yield of product **3aa** (Table 1, entries 18-22). So, the final optimum reaction conditions were catalyst: 2.5 mol % and time: 9 h at 60 °C under solvent free condition.

**Table 1** Optimisation of reaction conditions[a]



| Entry | Catalyst | Mol % | Solvent | Temp. (°C) | Time (h) | Yield [%][b] |
|---|---|---|---|---|---|---|
| Effect of catalyst screening | | | | | | |
| 1 | - | | Methanol | 60 | 9 | Trace |
| 2 | (a) | 5 | Methanol | 60 | 9 | 38 |
| 3 | (b) | 5 | Methanol | 60 | 9 | 45 |
| 4 | (c) | 5 | Methanol | 60 | 9 | 50 |
| 5 | (d) | 5 | Methanol | 60 | 9 | 58 |
| 6 | (e) | 5 | Methanol | 60 | 9 | 39 |
| Effect of catalyst loading | | | | | | |
| 7 | (d) | 1.5 | Methanol | 60 | 9 | 50 |
| 8 | (d) | 2.5 | Methanol | 60 | 9 | 64 |
| 9 | (d) | 3.0 | Methanol | 60 | 9 | 60 |
| 10 | (d) | 7.5 | Methanol | 60 | 9 | 57 |
| Effect of time | | | | | | |
| 11 | (d) | 2.5 | Methanol | 60 | 3 | 51 |
| 12 | (d) | 2.5 | Methanol | 60 | 6 | 57 |
| 13 | (d) | 2.5 | Methanol | 60 | 12 | 60 |
| Effect of solvent | | | | | | |
| 14 | (d) | 2.5 | Ethanol | 60 | 9 | 68 |
| 15 | (d) | 2.5 | Acetonitrile | 60 | 9 | 33 |
| 16 | (d) | 2.5 | Toluene | 60 | 9 | 39 |
| 17 | (d) | 2.5 | - | 60 | 9 | 83 |
| Effect of temperature | | | | | | |
| 18 | (d) | 2.5 | - | RT | 9 | 44 |
| 19 | (d) | 2.5 | - | 40 | 9 | 63 |
| 20 | (d) | 2.5 | - | 50 | 9 | 70 |

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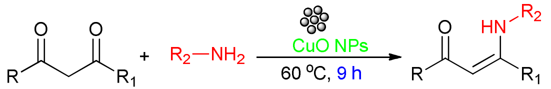
| | | | | | | |
|---|---|---|---|---|---|---|
| 21 | (d) | 2.5 | - | 60 | 9 | 83 |
| 22 | (d) | 2.5 | - | 70 | 9 | 84 |

[a] Reaction conditions: acetylacetone (1.0 mmol), aniline (1.0 mmol), CuO NPs (mol% with respect to starting material), under $N_2$ atmosphere, [b] GC Yield. The GC yield was quantified with external standard using methyl 4-(phenylamino)pent-3-en-2-one.

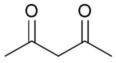
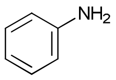
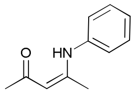
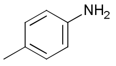
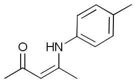
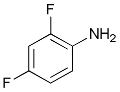
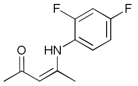
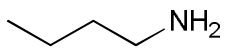
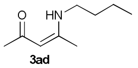
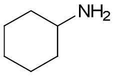
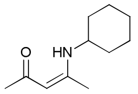
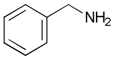
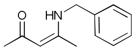
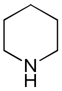
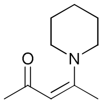
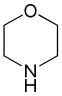
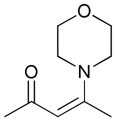
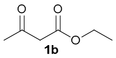
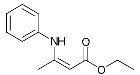
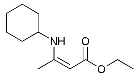
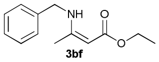
On the basis of the above optimized reaction conditions, the scope of substrates for β-enaminones and β-enamino esters synthesis was evaluated (Table 2). The condensation of aniline **1a** with acetylacetone **2a** provided an excellent yield of **3aa** (Table 2, entry 1). The effect of electron donating and withdrawing groups on aniline was studied. It was found that electron donating group –Me and withdrawing group –F produced corresponding products **3ab-3ac** in good yields (Table 2, entries 2 and 3). Then studied the aliphatic primary amine such as **2d**, **2e** and **2f** gives the desired products **3ad-3af** (Table 2, entries 4-6). The heterocyclic secondary amines such as **2g** and **2h** give the excellent yield of product **3ag-3ah** (Table 2, entries 7-8). Next, reaction carried out by change of 1,3-carbonyl compound such as ethylacetoacetate **1b** and methyacetoacetate **1c** with various amines. The reactions of **1b** with **2a**, **2e**, **2f**, **2g and 2h** give good to excellent yield of product **3ba-3bh** (Table 2, entries 9-13). Finally, the reaction of **1c** with **2a**, **2f** and **2h** gives the corresponding yield of product **3ca-3ch** (Table 2, entries 14-16).

After detail substrate study, moved towards study recyclability of heterogeneous catalytic system. The recyclability of CuO NPs catalyst was studied for synthesis of β-enaminone **3aa** under optimised reaction condition. After the completion of the reaction, the catalyst was separated through simple filtration technique. The catalyst washed with distilled water and ethanol, dried under vacuum and then reused for successive runs. Importantly, the catalyst was found to be effective up to three consecutive runs without any significant much loss in its catalytic activity (Fig.6). After recycle study catalyst analysed by TEM (Fig. 7a) it was observed that there is a slightly change in the morphology of the catalyst. In the XRD pattern, it was observed that there is no much change in its pattern (Fig. 7b). The comparison of the present catalytic system takes less duration than some of the reported protocol as shown in Table 3. Proposed mechanism for formation of β-enaminones and β-enamino esters has been shown in scheme 1. In this carbonyl groups of 1,3-dicarbonyl compound interact with CuO NPs to form the intermediate **A** which further interacts with amine to give the intermediate **B** and which on elimination of water gives the product β-enaminone.

**Table 2** Synthesis of β-enaminones and β-enamino esters catalysed by CuO NPs[a]



1a-1c 2a-2h 3aa-3ce

| Entry | Dicarbonyl compound | Amine | Product | Yield [%][b] |
|---|---|---|---|---|
| 1 | <br>**1a** | <br>**2a** | <br>**3aa** | 83 |
| 2 | **1a** | <br>**2b** | <br>**3ab** | 80 |
| 3 | **1a** | <br>**2c** | <br>**3ac** | 78 |
| 4 | **1a** | <br>**2d** | <br>**3ad** | 93 |
| 5 | **1a** | <br>**2e** | <br>**3ae** | 97 |
| 6 | **1a** | <br>**2f** | <br>**3af** | 98 |
| 7 | **1a** | <br>**2g** | <br>**3ag** | 90 |
| 8 | **1a** | <br>**2h** | <br>**3ah** | 95 |
| 9 | <br>**1b** | **2a** | <br>**3ba** | 78 |
| 10 | **1b** | **2e** | <br>**3be** | 75 |
| 11 | **1b** | **2f** | <br>**3bf** | 90 |

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| | | | |
|---|---|---|---|
| 12 | **1b** | **2g** | 68 |
| 13 | **1b** | **2h** | 80 |
| 14 | | **2a** | 70 |
| 15 | **1c** | **2f** | 98 |
| 16 | **1c** | **2h** | 70 |

[a] Reaction conditions: 1,3-dicarbonyl compound (1.0 mmol), amine (1.0 mmol), CuO NPs (2.5 mol%), solvent free, 60 °C, 9 h under $N_2$ atmosphere, [b] Isolated Yield.

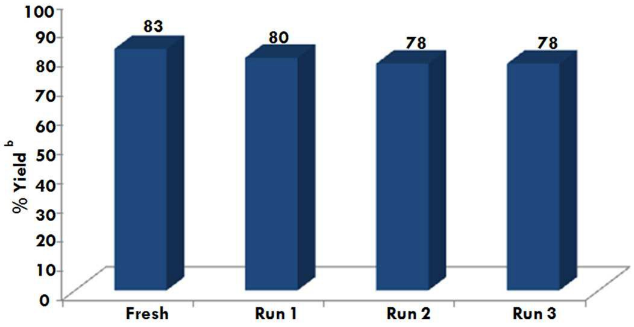


**Fig. 6** Recyclability in the synthesis of β-enaminones from 1,-3 dicarbonyl compounds and amine catalysed by CuO NPs. Reaction conditions: 1, 3-dicarbonyl compound (1mmol), amine (1mmol), 60 °C, 9 h, [b]GC Yield. The GC yield was quantified with external standard using methyl 4-(phenylamino)pent-3-en-2-one.

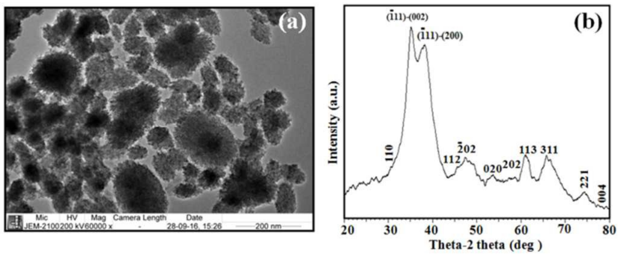
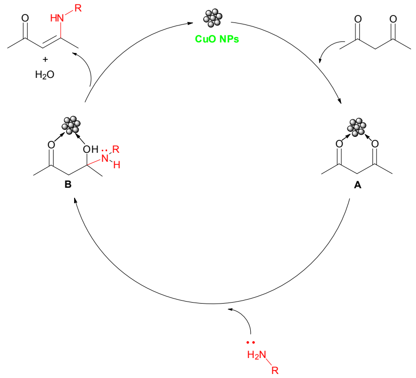


**Fig. 7** (a) TEM and (b) XRD analysis of CuO NPs after recycle.

**Table 3** Comparison of duration of reaction of present protocol with other reported catalyst for synthesis of β- enaminones and β- enamino esters.

| No | Catalyst | Time (h) | Reference |
|---|---|---|---|
| 1 | $Yb(OTf)_3$ | 12 h | 26 |
| 2 | $Pd(PPh_3)_4$ | 10 h | 38a |
| 3 | Ag/CNT | 10 h | 38b |
| 4 | Montmorillonite K-10 | 24 h | 38c |
| 5 | $Co_2(CO)_8$ | 18 h | 38d |
| **6** | **CuO NPs** | **9 h** | **This work** |



**Scheme 1** Reaction mechanism for the synthesis of β-enaminones catalysed by CuO NPs.

## Conclusions

In summary, we have prepared shape selective and catalytic active CuO NPs by different volume ratios of EG/water under microwave irradiation method. The change of morphology of CuO NPs with changes in the volume ratio of EG/water of Cu NPs was observed. Interestingly, by changing the counter ion of copper the change in Cu NPs were observed such as $Cu(OAc)_2$ provides CuO, $Cu(NO_3)_2$ provides $Cu_2O$ and $CuCl_2$ provides the $Cu(OH)_2$. Additionally, the synthesized CuO shows high catalytic activation for the synthesis of β-enaminones and β-enamino esters. The developed methodology proceeds under solvent free, utilizes mild reaction conditions and recyclable up three cycles.

## Characterisation data of products

### 4-(phenylamino)pent-3-en-2-one (Table 2, entry 1)[39]

$^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 12.45 (s, 1H), 7.31 (m, 2H), 7.17 (m, 1H), 7.10 (d, J = 7.6 Hz, 2H), 5.17 (s, 1H), 2.09 (s, 3H), 1.98 (s, 3H). GC-MS (EI, 70 eV): *m/z* (%) = 176 (6) [$M^+$], 175 (45), 160 (100), 132 (56), 118 (38), 77 (35), 51 (19), 44 (39).

### 4-(cyclohexylamino)pent-3-en-2-one (Table 2, entry 5)[39]

$^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 10.95 (s, 1H), 4.88 (s, 1H), 3.35 (s, 1H), 1.96 (s, 3H), 1.91 (s, 3H), 1.83 (s, 2H), 1.74 (s, 2H), 1.55 (d, J = 9.6 Hz, 1H), 1.36 – 1.21 (m, 5H). GC-MS (EI, 70 eV): *m/z* (%) = 182 (16) [$M^+$], 181 (76), 166 (30), 138 (61), 100 (78), 84 (83), 58 (100), 43 (49).

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### 4-(benzylamino)pent-3-en-2-one (Table 2, entry 6)[40]

$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 11.14 (s, 1H), 7.32 (d, J = 7.1 Hz, 2H), 7.25 (t, J = 7.5 Hz, 3H), 5.03 (s, 1H), 4.44 (d, J = 6.3 Hz, 2H), 2.02 (s, 3H), 1.90 (s, 3H). GC-MS (EI, 70 eV): *m/z* (%) = 190 (9) [$M^+$], 189 (48), 174 (33), 146 (26), 105 (12), 91 (100), 65 (19), 42 (17).

### Ethyl 3-(cyclohexylamino)but-2-enoate (Table 2, entry 10)[32]

$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.61 (s, 1H), 4.37 (s, 1H), 4.06 (q, J = 7.1 Hz, 2H), 3.29 (d, J = 5.3 Hz, 1H), 1.91 (s, 3H), 1.75 – 1.53 (m, 3H), 1.31 – 1.19 (m, 10H). GC-MS (EI, 70 eV): *m/z* (%) = 212 (11) [$M^+$], 211 (31), 182 (7), 166 (25), 130 (100), 122 (35), 84 (96), 55 (31), 41 (39).

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# Effect of solvent ratio and counter ions on the morphology of copper nanoparticles: Its catalytic application in β-enaminones synthesis

Aravind L. Gajengi,[a] Takehiko Sasaki,[b] Bhalchandra M. Bhanage[a,]*

[a] Department of Chemistry, Institute of Chemical Technology, Matunga,
Mumbai- 400 019, 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.

## Graphical Abstract