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Ultrasonic irradiation assisted preparation of Cu₂O-nanocubes and their high catalytic activity in synthesis of quinazolines

Amol B. Raut, Abhishek R. Tiwari and Bhalchandra M. Bhanage*[a]

Abstract: In this work, we report a facile, green ultrasonic irradiation assisted synthesis of Cu₂O-nanocubes at room temperature. The Cu₂O-nanocubes were examined using different characterization techniques such as XRD, FEG-SEM, TEM, EDS, UV-vis, DSC-TGA and FTIR. The Cu₂O nanocubes were employed as a heterogeneous nanocatalyst and was found to be highly active in preparation of quinazolines *via* tandem cyclization of 2-bromobenzaldehydes with amidines under ligand free condition. Various quinazolines could be prepared in excellent yields within very short reaction duration. Further, the Cu₂O nanocatalyst was recycled and could be reused consecutively up to four times without any significant loss of catalytic activity.

Introduction

In recent years, synthesis of specific structure of nanomaterials in material science has been of great interest to researchers. Cuprous oxide (Cu₂O) is a *p*-type semiconductor (a direct band gap of about 2.17 eV)^[1] that has received considerable attention recently because of its potential applications in dye degradation,^[2] gas sensing, magnetic devices, solar energy conversion,[3,4] catalysis,^[5] lithium ion batteries,^[6] CO oxidation,^[7] and photo activated water splitting into H2 and O2.[8] Cuprous oxide nanoparticles synthesized through bottom-up approaches are known to have different morphologies such as nanospheres, hollow spheres, wires, cubes, pyramids, octahedral and squares.^[9] Generally, bottom-up approaches have been achieved successfully by various methods which include hydrothermal, solgel process, surfactant assisted route, chemical vapour deposition.^[10] The physical, chemical and optical properties such as high surface area, low density, and tunable shell structure/composition are found to be dependent on the shape and size of nanomaterials. Therefore, it becomes very important to explore and to control the growth mechanism that lead to a particular shape and size of nanomaterials.^[9] It has been well documented that the morphology and microstructure of cuprous oxide nanoparticles can be controlled by modifying the reaction conditions and starting materials such as capping agents, reducing agents, precursors, reaction temperature, pH value, ultrasonication, and microwave. ^[1,6,11]

As a new strategy, the sonochemical technique has been given much attention to prepare various inorganic nanomaterials such as monometallic, bimetallic, carbide and oxide.^[12] A different

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technique from other conventional chemical methods, the sonochemical technique is based on acoustic cavitation phenomena. The ultrasound wave frequencies usually ranges from 20 kHz to 10 MHz.^[13] The ultrasound wave through a liquid medium causes the formation and subsequent collapse of acoustic cavitation micro bubbles. The constant collapse is an adiabatic process; ultrasound wave generates localized hot spots with high temperatures of 5000-25000 K, pressures of 1800 atm, and cooling rates in 1010 K/s. These extreme surroundings help in the collapse of bubbles and have been exploited to prepare nanomaterials.^[14,15] The sonochemical technique is favorable, powerful, cost-effective and environment friendly and is easy to develop reaction parameters that will help to increase selectivity and yield of products.^[13] The sonochemical technique has also been employed to synthesize various shapes and size of CuO and Cu₂O nanoparticles. Ge et al. have synthesized uniform hierarchical Cu₂O hollow sub-microsphere using sonochemical process at room temperature.^[16] Wang et al. have synthesized CuO and Cu₂O nanoparticles having different shapes such as truncated cubic, cubic, cubic octahedral and octahedral via green sonochemical process without the use of any surfactant and template.^[12] Vijaykumar et al. have composite nanomaterial containing Cu₂O nanocrystalline and Cu nanoparticle embedded in polyaniline matrices have been prepared by green sonochemical process using aniline or 1% v/v aniline -water was used as solvent.^[17] Li et al. have synthesized Cu₂O porous microcube via green ultrasound rout using with and without polyvinylpyrrolidone.^[1] Huang et al. have synthesized different crystal morphology of Cu₂O nanoparticle using ethylene glycol and various concentrations of polyvinylpyrrolidone.[18] Recently, K. Kaviyarasan et. al. have documented the sonochemical synthesis of Cu₂O nanocubes by ultrasound irradiation of copper sulfate in the presence of polyvinylpyrrolidone and ascorbic acid. The polyvinylpyrrolidone acts as a stabilizing agent, whereas ascorbic acid acts both as an antioxidant and reducing agent. The pH at 11 was maintained by aqueous NaOH solution.^[19] Herein, we wish to report a simple and green synthesis route for Cu₂O nanocubes using sonochemical energy. Further, an attempt was made to check the catalytic activity of Cu₂O nanoparticles for synthesis of quinazolines via tandem cyclization of 2-halobenzaldehyde with amidines.

Results and Discussion

The X-ray diffraction patterns of the inorganic compound of Cu₂O cubic nanoparticles prepared using copper salt are shown in Figure 1. The XRD data of the prepared nanoparticles were found to be in good agreement with those of Cu₂O (JCPDS NO. 05–0667). The six typical peaks located at 29.6°, 36.5° , 42.4° , 61.5° , 73.6° and 77.3° which were attributed to the (110), (111),

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Figure 1. XRD pattern of Cu_2O cubic prepared by ultrasonic irradiation at room temperature for 15 min.

(200), (220), (311) and (222) planes of Cu₂O respectively. From the XRD data, it is very clear that there was no formation of Cu, Cu (OH)2 or CuO as the corresponding characteristic peaks were absent thereby reveals that pure Cu₂O nanoparticle could be successfully obtained using copper salt. FEG-SEM was employed to investigate the size and shape of Cu₂O nanoparticles and the results are shown in Figure 2 (a-e). The Cu₂O nanoparticles synthesized using copper chloride has a cubic shape; it can be clearly observed that the surface morphology of Cu₂O cubes are very smooth with clear distinction of the edges and corner. The average width of the Cu₂O cubes is 100-200 nm. TEM images show the well dispersion of cubic shaped Cu₂O nanoparticle (Figure 2f-h).The shape and particle size of Cu₂O nanocubes in TEM monographs show good similarity to the results obtained by FEG-SEM. The purity of the synthesized Cu₂O nanocubes was further confirmed by energy dispersive X-ray spectrum (EDS) figure 3a.The EDS shows the peaks only for copper and oxygen. To resolve the interband transitions, the optical property of Cu₂O nanocubes sample was determined using UV-vis spectroscopy. The absorption spectrum of prepared red-colored Cu₂O nanocubes was obtained by dispersing in ethanol. The electronic spectral information clearly indicates that there is a strong absorbance band at 550 nm for Cu₂O nanocubes, which is in good agreement with the previous report (figure 3b). The phase purity of Cu₂O nanocubes was confirmed by thermal analysis using DSC/TGA measurement in N2 atmosphere (20 mL min⁻¹) for the range from room temperature to 600°C with a ramp rate of 10°C min⁻¹ (Fig. 4a). A mass loss between 30°C and 150°C in the TGA curve (Fig. 4a, red line) is due to the moisture content present in the sample. The second mass loss observed in the range of 200°C to 300°C is due to the evaporation of starch which was used during the preparation of Cu₂O nanocubes. The DSC curve (Fig. 4a, blue line) shows thermal stability of Cu₂O nanocubes. The endothermic peak between 230°C and 300°C is due to the thermal decomposition of starch. The synthesized Cu₂O nanocubes were further subjected to FTIR study (figure 4b). A very strong band at 628 cm⁻¹ is due to the stretching vibration of copper (I)-O (Cu₂O), which is in good agreement to the previous



Figure 2. (a-e) FEG-SEM images and (f-h) TEM images of Cu_2O cubic prepared by ultrasonic irradiation at room temperature for 15 min.



Figure 3: (a) EDS spectrum of as-prepared Cu₂O cubic (b) Absorption spectrum of as-prepared Cu₂O cubic dispersed in ethanol.

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Figure 4: (a) DSC/TGA graph (b) FT-IR spectra of Cu₂O cubic prepared by ultrasonic irradiation at room temperature for 15 min.

reports.^[10] The spectra also confirm the absence of CuO, whose band usually appears at around 530 cm⁻¹. As the FTIR spectrum contains only one peak, the synthesized product is pure Cu₂O.

Evalution of the catalytic activity of Cu₂O nanocubes

In order to check the catalytic activity of the prepared Cu₂O nanocubes. This nanocatalyst was employed for the tandem cyclization of 2-halobenzaldehydes with amidines to synthesize quinazolines, which are one of the most important central building block of many organic medicinal compounds.^[20] Attempts were made to synthesize various derivatives of quinazoline under ligand free condition, in green reaction media and for very short reaction time. Previously known protocols for the tandem cyclization of 2-halobenzaldehyde with amidines have involved the use of non-recyclable copper catalyst with suitable ligand. Further, they are limited by (i) the use of toxic solvents such as DMF, DMSO, (ii) the need of high reaction time and (iii) good yields.^[21-22]

The reaction was initiated by choosing 2-bromobenzaldehyde (1a) and benzamidine hydrochloride (2a) as model substrates in the presence of Cu₂O nanocatalyst, base, solvent under domestic microwave for 4 minutes. The tandem cyclization of 2bromobenzaldehyde (1a) with benzamidine hydrochloride (2a) in the presence of 5 mol% Cu₂O nanocatalyst, 2.0 equivalent of Cs₂CO₃ in ethylene glycol at 160W (domestic microwave) for 4 minutes furnished 2-phenylquinazoline (3aa) in 51% yield (Table 1, entry 1). This result clearly indicates that quinazolines could be synthesized by reacting 2-halobenzaldehydes with amidine hydrochlorides. However, in order to enhance the practicality and applicability of this interesting synthetic method, there was a need to optimize the reaction conditions. With this objective in mind, next, attempts were made to increase the yield of the 3aa by increasing the power of the domestic microwave from 160 W to 460 W (Table 1, entries 1-4). As per our expectation, increase in the power from 160 W to 360 W resulted into a considerable amount of increase in the yield of the desired product 3aa, providing maximum 92% yield (Table 1, entries 2 and 3). Further increase in power to 460 W did not affect the yield of the desired product 3aa (Table 3, entry 4). Experiments with different time interval were performed at 360 W (Table 1, entries 5 and 6) and

Table 1. Optimization of reaction parameters for the synthesis of 2-phenylquinazoline $\ensuremath{^{[a]}}$

Q	0 H + N `Br		Cataly Solvent	yst, Base , MW, Time		
1a		2a			3	
Entry	Catalyst	Watt [W]	Solvent [ml]	Base	Time [min]	Yield [%] ^[b]
1	Cu ₂ O	160	EG	Cs ₂ CO ₃	4	51
2	Cu ₂ O	260	EG	Cs ₂ CO ₃	4	78
3	Cu ₂ O	360	EG	Cs ₂ CO ₃	4	92
4	Cu ₂ O	460	EG	Cs_2CO_3	4	92
5	Cu ₂ O	360	EG	Cs_2CO_3	6	93
6	Cu ₂ O	360	EG	Cs_2CO_3	2	92
7	Cu ₂ O	360	Glycerol	Cs_2CO_3	2	54
8	Cu ₂ O	360	H ₂ O	Cs ₂ CO ₃	2	Trace
9	CuCl ₂	360	EG	Cs ₂ CO ₃	2	38
10	CuBr	360	EG	Cs_2CO_3	2	47
11	Cu ₂ O	360	EG	K ₂ CO ₃	2	55
12	Cu ₂ O	360	EG	Na ₂ CO ₃	2	49
13	Cu ₂ O	360	EG	Cs ₂ CO ₃	2	69 ^[c]
14	-	360	EG	Cs ₂ CO ₃	2	-
15	Cu ₂ O	360	EG	Cs ₂ CO ₃	2	55 ^[d] , 93 ^[e]

[a] Reaction condition: 2-bromobenzaldehyde (1a) (1mmol), benzamidine hydrochloride (2a) (1.1 mmol), catalyst (5 mol %), base (2 mmol), solvent (3 mL), [b] GC yield based on area %, [c] base (1 mmol), [d] catalyst (3 mol%), [e] catalyst (8 mol%).

it was found that the reaction time could reduce to 2 minutes (Table1, entry 6). However, no considerable increase in the yield of 3aa could be noted when reaction carried out for 6 minutes (Table 1, entry 5). Only 54% yield of 3aa was observed when reaction was performed in glycerol (Table 1, entry 7) and trace amount of desired product 3aa could be noted when reaction performed in water (Table 1, entry 8). In order to compare the catalytic activity of our prepared cubic shaped Cu₂O nanocatalyst, experiments were performed with different copper catalyst such as CuCl₂ and CuBr. However, the desired product 3aa could be obtained in poor yields (Table 1, entries 9 and 10). The desired product 3aa was noted in low yields when the reactions were carried out with inorganic bases such as K2CO3 and Na2CO3 (Table 1, entries 11 and 12) and these two results indicate that neutralization of amidine hydrochlorides is crucial for this organic transformation. Reduction in the amount of Cs₂CO₃ to 1.0 mmol resulted in substantial decreased in the yield of 3aa (Table 1, entry 13). In the absence of Cu₂O nanocatalyst, not even traces

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anocatalyst ^[a]								
O Br	H + NH ₂	HCI Cu ₂ O, Cs ₂ EG, 360 W,	CO_3 $2 \min$	\bigcirc				
Entry	2a	2	Product (3)	Yield				
1		NH HCI NH ₂ 2a	N Jaa	<u>[%]</u> 92				
2	1a		A A A A A A A A A A A A A A A A A A A	95 ^[c]				
3	1a	NH HCI NH ₂ 2c F	A State of the sta	87 ^[c]				
4	1a	NH HCI NH ₂	3ad CI	89				
5	1a	NH-HCI NH ₂ 2e Br		89				
6	1a	NH+HCI NH ₂ 2f NO ₂	N 3af NO ₂	81				
7		2a	Storn 3ba	95 ^[c]				
8	1b	2b	SUN Jabb	96				
9	1b	2c	Store P	91 ^[c]				
10		2a		90				
11	O Id Br	2a		88				

Table 2. Substrate study for the synthesis of quinazoline using Cu₂O



[a] Reaction condition: (1a) (1mmol), (2a) (1.1 mmol), Cu₂O nanocatalyst (5 mol%), Cs2CO3 (2 mmol), EG (3 mL), [b] GC yield based on area %,, [c] Isolated Yields.

of 3aa were formed (Table 1, entry 14). This result shows the decisive role of the Cu₂O nanocatalyst for this reaction. In the next set of experiments, different concentration of Cu₂O nanocatalyst was checked (Table 1, entry 15). The yield of 3aa dropped considerably when reaction was carried out with 3 mol% of Cu₂O nanocatalyst neither the yield could be improved further using 8 mol% of nanocatalyst. To summarize, the highest yield (92%) of 2-phenyl quinazoline (3aa) was obtained when the reaction between 1a (1.0 mmol) and 2a (1.1 mmol) was performed with 5 mol% Cu₂O nanocatalyst, and 2.0 mmol of Cs₂CO₃ in EG (3 mL) at 360 W for 2 minutes. It should be noted that the synthesis of quinazolines presented here is the first examples of a Cu₂O nanocubes catalyzed synthesis of heterocycles in EG and domestic microwave.

With these optimized reaction conditions in hand, the scope of the developed new method was extended to other substrates of 2-bromobenzaldehydes and amidines, results are summarized in table 2. The reaction of 2-bromobenzaldehyde (1a) with benzamidine hydrochloride (2a) produced 92% yield of 3aa (Table 2, entry 1). Next, the reaction of 2a with amidines having different electron donating and electron withdrawing groups were employed and they provided the corresponding products 3ab-3af in excellent to very good yields (Table 2, entries 2-6). In the next set of experiments, 6-bromobenzo[d] [1,3]dioxole-5-carbaldehyde (1b) and 2-bromo-5-chlorobenzaldehyde (1c) were made to react with different amidines (2a, 2b and 2c), resulted into respective products (3ba-3ca) in excellent yields (Table 2, entries 7-10). Further, 1-(2-bromophenyl)ethanone (1d) could also be converted into desired products 3da and 3db successfully (Table 2, entries 11-12). Interestingly, when the aliphatic amidines (2g and 2h) were employed for this transformation they also resulted into the formation of the desired products 3ag and 3ah (Table 2, entries 13-14)



Scheme 1. A plausible reaction mechanism.

A plausible reaction mechanism has been proposed as shown in the scheme 1. The reaction starts with the neutralization of benzamidine hydrochloric salt (2a) to give 2a' which then reacts

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with **1a** to give an imine intermediate (**A**). Next, Ullmann type ^[23] N-arylation of **A** takes place to give the desired product **3a**.

Recycle study

The reusability of catalytic system makes the developed protocol more economical and eco-friendly process. Hence, we tested the recycle catalytic activity and stability of Cu₂O nanocatalyst for the synthesis of 2-phenylquinazoline (3aa) usina 2bromobenzaldehyde (1a) and benzamidine hydrochloride (2b). After the completion of reaction, the reaction mixture was allowed to cool at room temperature. Then, the catalyst was recycle by simple filtration. The catalyst was washed with distilled water (5 mL) and ethanol (5 mL) consecutively 3 to 4 times to remove the other organic and inorganic impurities, followed by catalyst drying under vacuum rotary evaporator. Then it was further used as catalyst for next run. The Cu₂O nanocatalytic system could be reused for four time successive recycles without significant loss in its catalytic activity (Figure 5).



Figure 5. Recyclability study of synthesis of Cu₂O nanocatalyst. Reaction conditions: Reaction condition: (1a) (1mmol), (2a) (1.1 mmol), Cu₂O nanocatalyst (5 mol%), Cs₂CO₃ (2 mmol), EG (3 mL).

Conclusions

In summary, a facile, green ultrasonic irradiation assisted synthesis of Cu₂O-nanocubes at room temperature has been achieved successfully. The Cu₂O nanocubes were used a heterogeneous nanocatalyst for the synthesis of quinazolines *via* tandem cyclization of 2-bromobenzaldehydes with amidines. Various quinazolines could be prepared in excellent yields under ligand free condition and for very short reaction time. Further, the Cu₂O nanocatalyst was reused consecutively up to four times without any significant loss of catalytic activity.

Experimental section

The chemicals and reagents were purchased from firms of repute in the highest purity available and were used without further purification. The reactions were monitored by using thin layer chromatography with Merck silica gel 60 F254 plates. The yields for the quinazolines as well were confirmed by using Perkin Elmer Clarus 400 gas chromatography equipped with a flame ionization detector and a capillary column (elite-1, 30 m×0.32 μ m×0.25 μ m). The prepared Cu₂O nanomaterial was characterized by X-ray

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diffract meter (Shimadzu XRD-6100 using CuKa-1.54 Å) with scanning rate 2θ per min and 2 theta (θ) angle ranging from 20 θ to 80 0 with current 30 mA and voltage 40 kW, Field emission gunscanning 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. Differential scanning calorimetry-Thermo gravimetric analysis (DSC-TGA) was done on Perkin Elmer STA 6000. The isolated products were confirmed by GC-MS, ¹H NMR and ¹³C NMR spectroscopic techniques. The properties of the GC-MS (Shimadzu QP 2010) instrument (Rxt-17, 30 m×25 mm, film thickness 0.25 $\mu m.$ df) were: column flow=2 mL min, at 180 °C increasing to 240 °C at 10 °Cmin⁻¹. IR spectra were recorded with a Shimadzu IR Affinity-1, Fourier-transform infrared spectroscopy (FTIR) was recorded on a JASCO-FTIR-400 spectrometer. ¹H and ¹³C NMR spectra were obtained with a Bruker Avance 400 MHz NMR spectrometer with CDCl₃ as the solvent system.

Procedure for the preparation of Cu₂O-nanocubes

In a typical experiment procedure to synthesize Cu₂O nanoparticle, 1.0 g starch was dissolved in 80 mL hot deionized water (80 °C), then 0.1 M copper precursors dissolved in deionized water was added to starch solution under stirring for 10 min. Then, 10 mL of 0.1 M sodium borohydride solution dissolved in deionized water was added drop wise to the above mixture under stirring to form a black solution. The solution was transferred to ultrasonic irradiation under 20 kHz ultrasonic waves at the output power 5 seconds on and 5 seconds off mode for 15 min at room temperature. The reaction progress was observed by change in color for black to brick red, indicating the formation of Cu₂O nanoparticles. Finally, the brick red product were collected by centrifugation, washed with distilled water and dried under vacuum at 80 °C for 8 h.

General procedure for the synthesis of quinazolines (3)

To an ovan dried reaction vial 2-bromobenzaldehydes (1, 1.0 mmol), amidine (2, 1.1 mmol), Cu₂O nanocatalyst and (5 mol%), Cs₂CO₃ (2.0 mmol) were added followed by addition of ethylene glycol (3.0 mL). This reaction mixture was stirred at room temperature for 1 minute. Thereafter, it was subjected to domestic microwave irradiation using power of 360 W for 2 minutes. After the completion of reaction, the reaction mixture was diluted with water (10 mL) and diluted reaction mixture was extracted with ethyl acetate (3 × 10 mL), dried over Na₂SO₄ and concentrated on the rotary evaporator. The obtained crude product was purified using column chromatography over silica gel using pet ether/ethyl acetate as eluent.

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Keywords: Cuprous oxide • nanoparticles • quinazolines • recycle

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