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Nanodomain cubic cuprous oxide as reusable catalyst in one-pot synthesis of 3-alkyl/aryl-3-(pyrrole-2-yl/indole-3-yl)-2-phenyl-2,3-dihydro-isoindolinones in aqueous medium†

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An environmentally benign one-pot protocol has been developed for the syntheses of 3-alkyl/aryl-3-(pyrrole/indole-2/3-yl)-2-phenyl-2,3-dihydro-isoindolinones *via* a multi-component one-pot reaction involving 2-iodo-*N*-phenylbenzamides, terminal alkyne and substituted indoles/pyrroles in aqueous medium using cubic cuprous oxide nanoparticles as catalyst. It involves domino Sonogashira-5-*exo*-dig-cyclization followed by regioselective nucleophilic addition of indoles or pyrroles, in aqueous medium without using any surfactants or additional ligands.

There has been an increasing demand for the development of environment friendly chemical processes for the syntheses of a variety of organic compounds on industrial and laboratory scales.[1] Among the different methodologies, considerable attention has been given to executing organic reactions in water.[2] A number of organic transformations together with metal-mediated coupling reactions have now been accomplished at ambient temperature using water as the only solvent.[2,3] Substantial attention has also been given for the use of sonochemical processes[3b,4] for the syntheses of different pharmacophores. These processes may afford products from relatively simple starting materials and in high yield. Ultrasonic techniques disperse soluble or insoluble molecules with uniform shapes and geometry[4b] and thus, they often provide a high reaction rate compared to conventional procedures. So, the use of ultrasonication is a better option for the emerging concept of 'Green chemistry'.

Different indoles and pyrroles are essential building blocks for various pharmaceuticals and natural products.[5] Because of the structural diversity of biologically active indoles and pyrroles, there is always a challenge to develop new or improved methods for the syntheses of indole and pyrrole derivatives. Palladium, rhodium, and ruthenium salts having bidentate *N*,*P*- or *N*,*N*-ligands are widely used as catalysts in selective C–H and C–C bond functionalization.[6] However, these limit their wide applications in industry, as the catalysts are expensive. Utilization of coordinated copper(I) complexes are supposed to be one of the most enthralling alternatives.[3c,7] The presence of ancillary ligands prevent the aggregation of central metal ion by chelating the metal or by increasing its solubility and thus increases the efficiency of the metal catalyst. However, the use of copper may introduce Glaser-type homocoupling products.[8]

The significant difference of the nanostructured copper(I) oxide in comparison to bulk materials with respect to reactivity, stability in aqueous medium, environmental compatibility, non-toxicity and large surface/volume ratio,[9] makes nano-copper(I) oxide more promising compared to expensive palladium systems for the Sonogashira-type cross-coupling reactions. Various methods have been reported for the production of nanodomain copper(I) oxide having varied morphologies *viz.* spheres,[10] wires,[11] cubes,[12] polyhedral,[13] and hollow-structures.[14] But, only few applications of copper(I) oxide nanoparticles as catalyst are reported in organic synthesis.[15] In the present study we have envisaged the application of cubic cuprous oxide nanoparticles as reusable catalyst for the synthesis of 3-alkyl/aryl-3-(pyrrole/indole-2/3-yl)-2-phenyl-2,3-dihydro-isoindolinones *via* one-pot multi-component reaction involving 2-iodo-*N*-phenylbenzamides, terminal alkyne and substituted indoles/pyrroles in aqueous medium. The protocol involves domino Sonogashira-5-*exo*-dig-cyclization followed by regioselective nucleophilic addition of indoles or pyrroles. The process eliminates the use of palladium, organic solvents, ligands, or the presence of any additional activator and surfactants. Cubic cuprous oxide nanoparticles used in the reaction was synthesized by the reduction of cupric chloride

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dihydrate in aqueous medium using fructose as reducing as well as stabilizing agent at 60–65 °C. Using this methodology, a library of substituted isoindolinones was synthesized in high yield and in short reaction time. In this context, it is worthwhile to mention that cuprous oxide nanoparticles were synthesized under non-hazardous condition as mentioned earlier. The uniqueness of the protocol lies in its eco-friendly operation, effective one-pot synthesis, reusability of the catalyst and generation of unique scaffolds in excellent yield.

At the outset, we opted 2-iodo-*N*-(4-flurophenyl)benzamide (**1a**), phenylethyne (**2a**) and pyrrole (**3a**) as model reactants and investigated the feasibility of our domino one-pot strategy to produce pyrrolyl isoindolinone (**4a**) in water using commercially available bulk copper(I) salts as catalyst under sonication (Scheme 1). However, it gave poor to moderate yield (47%) in presence of K_3PO_4 and various organic or inorganic bases and even after prolonged heating at elevated temperature. K_3PO_4 acts as base as well as stabilizer of the metal ions.[16] The poor yield compelled us to add *n*-Bu_4NCl, *n*-Bu_4NBr or *n*-Bu_4NBF_4 in the reaction medium as activator.[15a] Even so the yield of the reaction remained unaffected. The use of other bases did not significantly improve the outcome of the reaction. Our previous approach towards the synthesis of similar scaffolds using copper(I) iodide as catalyst and the utilization of various ionic or non-ionic surfactants along with extra ligands produced the products in good to moderate yield.[3d] Therefore, we re-designed the reaction strategy.

Being low-priced and non-toxic in nature, cuprous oxide or cuprous oxide nanoparticles were long been used as an active catalyst in many reactions.[15] The nanodomain copper(I) oxide was synthesized from cupric chloride using fructose as reducing as well as capping agent. The formation of the nanoparticle was confirmed using various techniques. The FTIR spectrum [Fig. 1(a)] showed strong peak at 627 cm^{-1} and was assigned as the characteristic Cu(I)–O vibrational frequency for cuprous oxide.[17] The powder XRD pattern [Fig. 1(b)] of the synthesized cuprous oxide nanoparticles clearly indicated the typical reflection patterns of cuprite (JCPDS no. 77-0199).[18] The peaks with 2θ values at 29.4°, 36.4°, 42.4°, 61.4°, 73.4° and 77.5° were attributed to the crystal plane of 110, 111, 200, 220, 311 and 222 respectively. The scanning electron microscopy (SEM) [Fig. 1(c)] and transmission electron microscopy (TEM) images [Fig. 1(d)] showed the regular cubic shape of the Cu_2O particles with an average edge length of 180 ± 20 nm.

The relevance for the synthesis of 3-alkyl/aryl-3-(pyrrole/indole-2/3-yl)-2-phenyl-2,3-dihydro-isoindolinones with cuprous oxide nanoparticles was investigated next. It was found that under similar reaction condition as described earlier (Scheme 1) and in the presence of cuprous oxide nanoparticles instead of bulk salts the yield of the reaction increased significantly by 15–20% even in the absence of surfactants/activators or ligands. Sonication played a crucial role in the reaction. It dispersed all the molecules and insoluble nanocatalyst in water allowing them to come to close proximity for better reaction. It is worth mentioning that in absence of sonication the yield of the product was found to be reduced. The effect of different organic and inorganic bases, *viz.* Et_3N, DBU, $^iPr_2EtN$, K_3PO_4, Na_2CO_3, K_2CO_3 and Cs_2CO_3 was also explored subsequently (Table 1). Cs_2CO_3 appeared to be the most effective when employed in 2.0 molar equiv. and afforded the product in maximum yield (Table 1, entry 9). It may therefore be concluded that the inorganic bases worked better in comparison to organic bases.

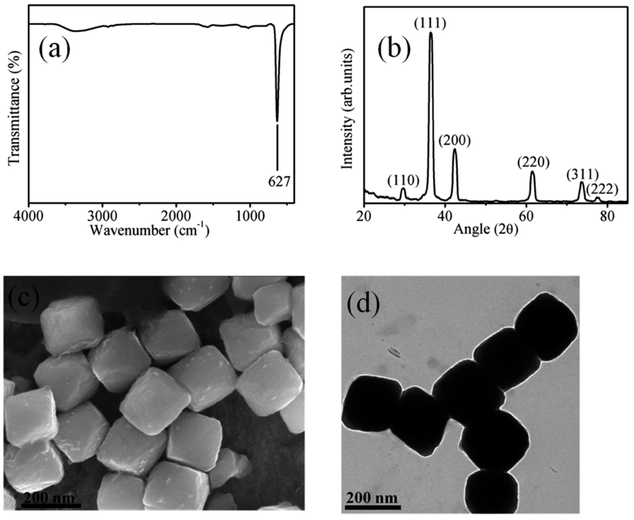
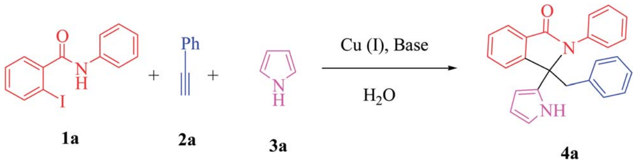


Fig. 1 (a) FTIR spectrum; (b) powder XRD patterns; (c) SEM and (d) TEM image of the synthesized cuprous oxide nanoparticles.



Scheme 1 Synthesis of **4a** in aqueous medium.

The scope and generality of this methodology was then tested with a variety of N-substituted benzamides and pyrroles/indoles (Table 2). All reactions yielded pyrrolyl- or indolyl-dihydro-isoindolinones as major product and structures of all

Table 1 Effect of the different bases on the yield of **4a**

Entry[a]	Base	Amount (mol equiv.)	Time (min)	Yield[b] (%)
1	Et_3N	2.0	30	63
2	DBU	2.0	30	59
3	$^iPr_2EtN$	2.0	30	67
4	K_3PO_4	2.0	30	60
7	Na_2CO_3	2.0	30	82
8	K_2CO_3	2.0	30	84
9	Cs_2CO_3	2.0	30	87
10	Cs_2CO_3	1.5	30	83
11	Cs_2CO_3	2.5	30	87
12	Cs_2CO_3	2.0	40	87

[a] All reactions were performed using **1a** (1 mmol), **2a** (1.5 mmol) and **3a** (1.5 mmol) in water at 50 °C under sonication in aerobic condition. Cubic Cu_2O nanomaterial (10 mol%) was used. Increase in reaction time or temperature did not provide better yield of the product. [b] Yield of isolated pure product; some loses during isolation is unavoidable in certain cases.

Table 2 Reactions of 2-iodo-*N*-phenylbenzamide (**1a–d**), ethynes (**2a–d**) and pyrroles/indoles (**3a**, **4a–e**) leading to pyrrolyl/indolyl-dihydro-isoindolinones (**5a–k**) in aqueous medium

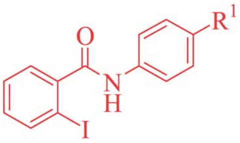
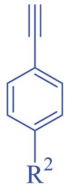
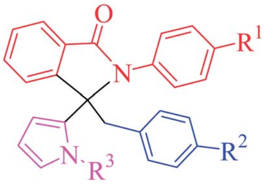
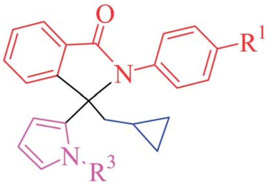
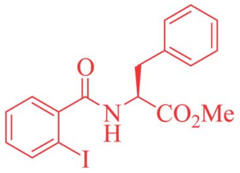
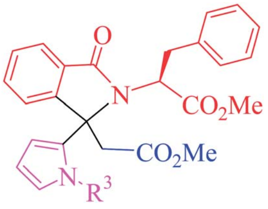
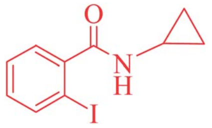
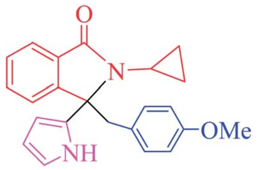
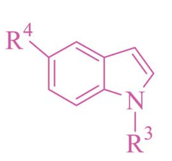
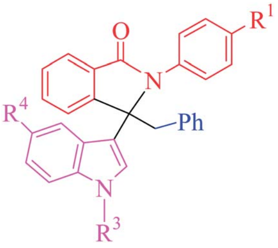
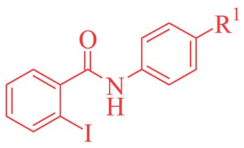
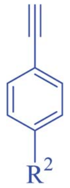
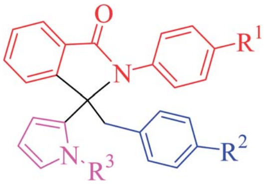
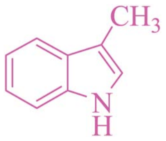
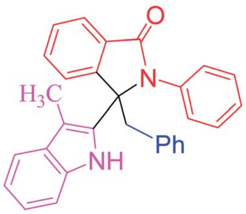
Entry[a]	Amide 	Alkynes 	Pyrroles/indole 	Product 	Yield[b] (%)
1	**1a**: $R^1 = F$	**2a**: $R^2 = H$	**3a**: $R^3 = H$	**5a**: $R^1 = F, R^2 = H, R^3 = H$	87
2	**1a**	**2b**: $R^2 = F$	**3a**	**5b**: $R^1 = F, R^2 = F, R^3 = H$	91
3	**1b**: $R^1 = OMe$	**2a**	**3a**	**5c**: $R^1 = OMe, R^2 = H, R^3 = H$	85
4	**1b**	 **2c**	**3a**	 **5d**: $R^1 = OMe, R^3 = H$	78
5	**1a**	 **2d**	**3a**	 **5e**: $R^1 = F, R^3 = H$	72
6	 **1c**	**2c**	**3a**	 **5f**	70
7	 **1d**	**2e**: $R^2 = OMe$	**3a**	 **5g**	80
8	**1a**	**2a**	 **4a**: $R^3 = H; R^4 = H$	 **5h**: $R^1 = H, R^3 = H, R^4 = H$	81
9	**1a**	**2a**	**4b**: $R^3 = H; R^4 = NO_2$	**5i**: $R^1 = H, R^3 = H, R^4 = NO_2$	80
10	**1a**	**2a**	**4c**: $R^3 = H; R^4 = OMe$	**5j**: $R^1 = H, R^3 = H, R^4 = OMe$	87

Table 2 (*Contd.*)

Entry[a]	Amide	Alkynes	Pyrroles/indole	Product	Yield[b] (%)
					
11	**1a**	**2a**	 **4e**	 **5k**	76
12	 **1d**	**2a**	**3a**	**5a**	70

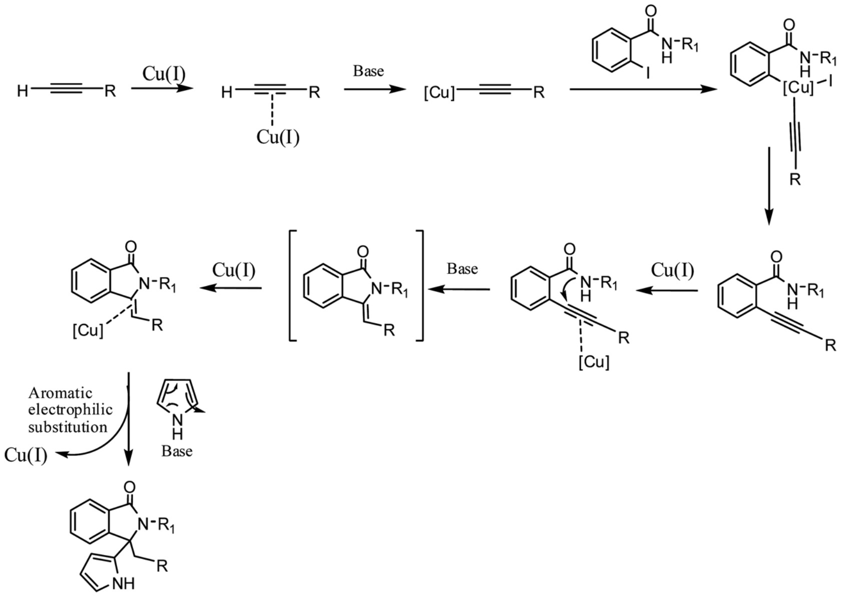
[a] All reactions were performed using **1** (1 equiv.), **2** (1.0 equiv.) and **3–4** (1.5 equiv.) in water at 50 °C for 30 min under aerobic condition in presence of nanodomain cuprous oxide (0.1 equiv.) and Cs_2CO_3 (2 equiv.). [b] Yield of isolated pure product; some loses during isolation is unavoidable in certain cases.

compounds were characterized by NMR and MS spectroscopy. With pyrroles the reaction was found to occur at C-2 where as with unsubstituted or N-substituted indoles, the reactions were found to occur selectively at C-3 as expected, and the reaction occurred at C-2 with 3-substituted indoles (Table 2, entry 11). The reaction also proceeded well with amide with an aliphatic group (Table 2, entry 6 and 7). It is interesting to mention that the aliphatic alkynes (Table 2, entry 4–6), and aryl bromides (Table 2, entry 12) gave equally good result under the same reaction condition. It may be noted that no significant amount of Glaser coupling product was obtained in any case. However, the reaction failed to proceed with substituted pyrrole such as 1-benzyl-2-(benzyloxymethyl)-1*H*-pyrrole. Other nucleophilic substrates such as furan and thiophene did not react under the same reaction condition. This is possibly because of the reduced nucleophilicity of the substrates.

A plausible mechanism for the formation of pyrrolyl/indolyl isoindolinones (**5a–k**) is shown in Scheme 2. It is expected that copper(I) initially forms pi–alkyne complex, which makes the alkyne terminal proton acidic. Subsequently, in presence of base, copper acetylide is formed. The activated acetylide reacts with iodobenzamides and Sonogashira product is generated *in situ*. The triple bond is then again activated by nanodomain cuprous oxide, which in presence of base undergoes 5-*endo*-dig cyclization. Nanodomain cuprous oxide, presumably acting as Lewis acid, activates the double bond which subsequently undergoes aromatic electrophilic substitution by indoles/pyrroles to form final compounds.

The reusability of the nanoparticles towards the synthesis of pyrrolyl dihydro-isoindolinones (**5a**) was also studied and the results are summarized in Table 3. After each reaction, using the same reaction methodology, the nanocatalyst were separated by centrifugation and thoroughly washed with EtOH–H_2O for reuse. TEM images of the Cu_2O nanocubes after three times use indicated unchanged morphology of the nanoparticles (Fig. 2). It was found that the catalyst exhibited a marginal loss in activity after three recycles. To ascertain of the reduced reactivity of the nanodomain cuprous oxide due to surface oxidation, similar reactions were carried out under anaerobic condition. The results are also summarized in Table 3.

In conclusion, we have established an efficient one pot environmentally benign and cost-effective process for the syntheses of pyrrolyl-/indolyl-dihydro-isoindolinones, in aqueous medium even under aerobic conditions. We demonstrated that inexpensive nanodomain cuprous oxide could be used as a reusable and competent catalyst for this protocol. The capping of fructose may prevent the aerial oxidation of the nanodomain cuprous oxide. However its reuse showed reduced catalytic activity. In the fourth cycle the activity of cuprous oxide is significantly dropped. To ascertain the reason we checked with a control reaction with freshly synthesized nanocuprous oxide, which under nitrogen did not show surface oxidation for extended hours in water as solvent used in the synthesis. However, under air, the catalyst after extended time of 16 h showed a positive test for the presence of cupric ion confirming surface oxidation of the



Scheme 2 Plausible mechanism for the formation of pyrrolyl/indolyl isoindolinones.

Table 3 Recoverability of cuprous oxide nanoparticles for the synthesis of pyrrolyl dihydro-isoindolinones (entry **5a**)[a]

Reusability of the catalyst	1st	2nd	3rd	4th
Yield (%) under aerobic condition	87	84	80	72
Yield (%) under anaerobic condition	89	86	84	82

[a] Yield of isolated pure product; some loses during isolation is unavoidable in certain cases.

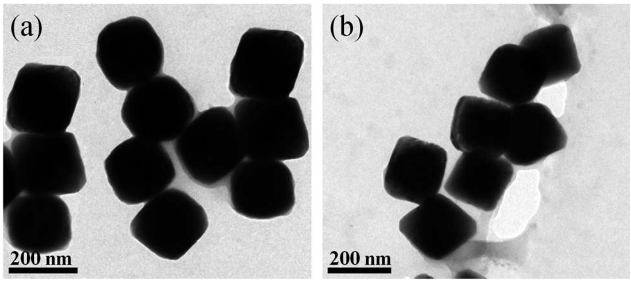


Fig. 2 (a) TEM image of cuprous oxide nanoparticles before reaction; (b) TEM image of cuprous oxide nanoparticles after 3 times use.

catalyst and this could be the reason for reduced reactivity. Therefore, for extended use of the same catalyst, the same reaction should be carried out under anaerobic conditions. Cuprous oxide acts as a heterogeneous catalyst. The use of ultrasound dispersed the catalyst evenly and increases its surface area making the reaction efficient. Even then, there is always a scope for the development of soluble catalysts. Exclusion of surfactants, additional activators or extra ligands makes the protocol significantly simple, less expensive, tolerant and versatile. Most importantly the process is environment friendly and eliminates the use of heavy metal catalysts.

Experimental

Synthesis of cubic Cu_2O nanoparticles

Typically, the nanodomain Cu_2O was synthesized by the following procedure. To a solution of $CuCl_2$ in water (0.01 M, 100 mL), NaOH (0.2 M, 10 mL) was added drop wise under constant stirring. The colour of the solution changes from green to blue due to the formation of $Cu(OH)_2$. Fructose (1 M, 10 mL) in water was then added to it and stirring was continued at 60 °C for 1 h. The precipitates gradually changed from green to yellow indicating the formation of Cu_2O nanoparticles. The solution was then allowed to settle for 1 h for complete nucleation. It was then centrifuged, and the precipitate was washed with water (×3) and ethanol (×3) and dried under vacuum.

Characterization of Cu_2O nanoparticles

The powder XRD of cubic Cu_2O nanoparticles was carried out by X-ray diffraction (ISO-DEBYEFLEX-2002-RICH, SEIFERT & CO) using CuK_α radiation with graphite monochromator. FT-IR spectra of the sample were recorded using Bruker Fourier transforms infrared spectrometer with a KBr beam splitter and DTGS/KBr detector. Morphology of Cu_2O nanoparticles was characterized by SUPRA 40VP Field Emission Scanning Electron Microscope (CARL ZEISS NTS GmbH, Oberkochen (Germany)) equipped with energy dispersive X-ray (EDX) facility. Samples for SEM were prepared by dispersing Cu_2O (3 mg) nano-particles in ethanol (10 mL) and dispersed sample (50 μL) was deposited onto brass stubs and vacuum dried. Samples for TEM were prepared by dropping dispersed solution (5 μL) of Cu_2O on a carbon coated copper TEM grid (400 mess) and then allowing to dry under vacuum. Imaging was performed by using Tecnai

20 G2 300 kV, STWIN model, Transmission Electron Microscope (TEM) with an acceleration voltage of 200 kV.

General procedure for the preparation of 3-alkyl/aryl-3-(pyrrole/indole-2/3-yl)-2-phenyl-2,3-dihydro-isoindolinones derivatives

In an open round-bottomed flask containing water (20 mL), iodobenzamides (**1**, 1.0 equiv.), alkynes (**2**, 1.5 equiv.), indoles or pyrroles (**3** or **4**, 1.5 equiv.), cuprous oxide nanomaterials (0.1 equiv.) and Cs_2CO_3 (2.0 equiv.) were added and stirred vigorously under sonication for 30 min at 50 °C when TLC indicated completion of the reaction. The mixture was then centrifuged to separate nanoparticles; supernatant was extracted with ethyl acetate (3 × 30 mL) and washed thoroughly with water. Column chromatography (petroleum–EtOAc) produced pure product (**5a–k**). The nanoparticles were washed with ethanol–water twice for reuse.

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