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Copper nanoparticles in an ionic liquid: an efficient catalyst for the synthesis of bis-(4-hydroxy-2-oxothiazolyl)methanes

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Abstract

Copper nanoparticles were synthesized and characterized by TEM, XRD and UV–vis techniques. The copper nanoparticles in an ionic liquid were employed as a recyclable catalyst for the synthesis of bis-(4-hydroxy-2-oxothiazolyl)methanes in excellent yields and in short reaction times.

Keywords: Copper nanoparticles; Ionic liquid; Thiazolidine-2,4-dione; Aromatic aldehydes

Recently, research has been directed towards the synthesis and application of metal nanoparticles in view of their unique properties compared to the bulk metals.[1,2] Among various metal nanoparticles, copper nanoparticles have received considerable attention because of their unusual properties and potential applications in diverse fields.[3] The various synthetic procedures for their synthesis include microemulsion techniques,[4] the use of reverse micelles,[5] reduction of aqueous copper salts,[6] UV-light irradiation,[7] physical vapour deposition[8] and impregnation methods.[9,10] The core–shell particles are of great interest due to their potential applications in diverse fields including catalysis, drug delivery, photonics, sensors, etc.[11] Copper nanoparticles, in particular, being cheap, require only mild reaction conditions to produce high yields of products in short reaction times compared to traditional catalysts and can also be recycled. Rothenberg[12] and co-workers recently reported the use of copper nanoparticles, which are less harmful to the environment than any other metals in Suzuki cross-coupling reactions. The condensation of aromatic halides (except fluorine) catalyzed by copper, the Ullmann reaction, has gained tremendous laboratory and industrial interest due to its wide applicability in the synthesis of symmetrical and unsymmetrical biaryls and polyaryls with different functional groups which are otherwise difficult to obtain. The adsorption of aromatic halides on metal particles is strong because of the interaction of delocalized π-electrons with the metal. The mechanism of the Ullmann condensation reaction is believed to be a nucleophilic attack of copper on an aromatic carbon carrying a halogen substituent. Cu nanoparticles are also used as efficient and selective catalysts in aza-Michael reactions of *N*-alkyl- and *N*-arylpiperazines with acrylonitrile.[13]

There is considerable interest in the use of room temperature ionic liquids as substitutes for volatile organic solvents.[14] Ionic liquids have been employed as reaction media for several organic reactions, including alkylation,[15] hydrogenation[16] and oxidation.[17] As a result of their tunable polarity and hydrophobicity, they can solvate various organic, inorganic and polymeric compounds, and have been used as green solvents for liquid–liquid separations, extractions and recycling in homogeneous catalysis.

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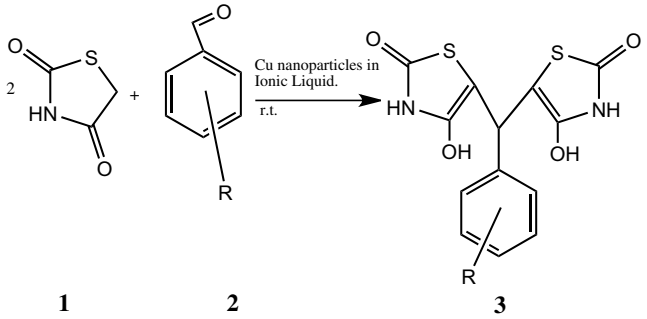
As a part of our ongoing research on the synthesis and catalytic applications of metal nanoparticles, we herein report a novel and simple method for the synthesis of Cu nanoparticles. The nanoparticles were synthesized and characterized by XRD, TEM and UV–vis techniques and were employed as a recyclable catalyst for the condensation between thiazolidine-2,4-dione **1** and aromatic aldehydes **2** (Scheme 1)[20–23] to produce the bis-(4-hydroxy-2-oxothiazolyl)methanes **3** in very high yields and in short reaction times.

The Cu nanoparticles were prepared as follows: In a round-bottom flask, 1 ml of ionic liquid **4** and 5 mg of copper nitrate was treated with excess $NaBH_4$ in methanol. A black coloured solution was obtained rapidly indicating the presence of Cu(0) particles. Stirring was continued for 6 h. The solution was taken in ethanol (20 ml) and then centrifuged at 3000 rpm for 10 min and the supernatant was decanted to afford the Cu nanoparticles as a solid.

The Cu nanoparticles were characterized by TEM, XRD and UV–vis techniques. The X-ray powder diffraction pattern of the catalyst showed a signature for Cu(0) as shown in Figure 1. The peaks at 44.580° and 60.956° confirmed the presence of Cu(0) in the sample. Recycling of the catalyst five times did not result in any changes in the structure and the morphology of the catalyst during the course of the reaction and is a sign of its stability.

Transmission electron microscope (TEM) studies of the Cu nanoparticles were carried out to investigate the shape and the size of the particles. Figure 2 shows the transmission electron micrographs for fresh and used Cu nanoparticles of 50–60 nm in diameter with spherical shape.

The UV–vis absorption spectrum of Cu nanoparticles dispersed in ethanol showed a band around 583 nm due to surface plasma resonance, which is within the range 500–600 nm reported as the band characteristic of copper nanoparticles, see Figure 3.[12] The observed band for the Cu nanoparticles suggests that the effective particle size of the Cu nanoparticles is within the range 50–60 nm as observed from TEM studies. The shifts in the plasmon band depend on the size and the shape of the nanoparticles.[24–26] Copper nanoparticles of 30–50 nm diameter show a plasmon band at 579 nm, whereas nanorods show a plasmon band at 586 nm.[27] The observed plasmon band at 583 nm for the Cu nanoparticles suggests that the effective particle size of the Cu nanoparticles is within the range 50–60 nm.



1 **2** **3**

Scheme 1.

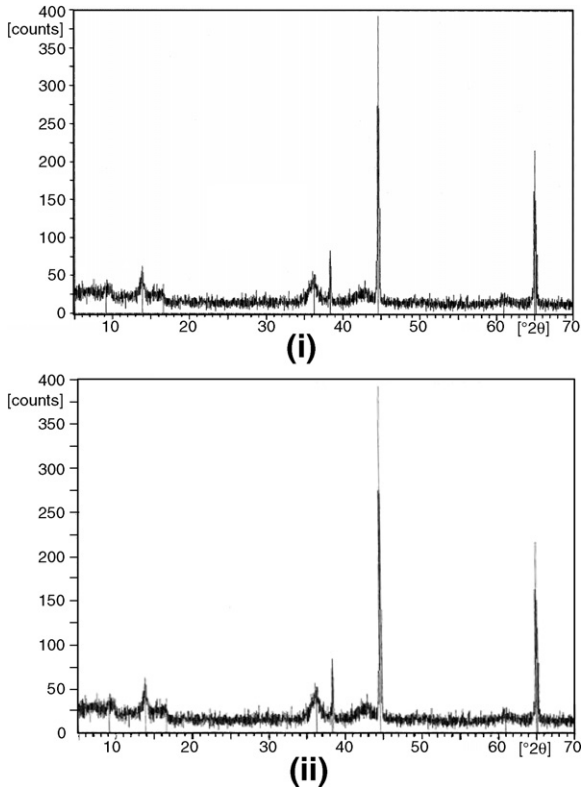
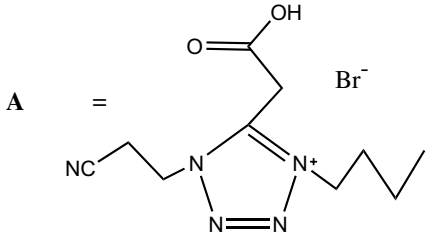


Fig. 1. Powder-XRD curves of Cu nanoparticles: (i) fresh Cu nanoparticles and (ii) used Cu nanoparticles.



Ionic Liquid 4

We have found that copper nanoparticles in ionic liquid **4**[18] act as an efficient catalyst for the condensation reaction between thiazolidine-2,4-dione **1** and benzaldehyde, see Table 1.[19]

The activity of the synthesized Cu nanoparticles for the conjugate addition of a variety of aromatic aldehydes with thiazolidine-2,4-dione in the presence of 5 mg of Cu nanoparticles in ionic liquid **4** at room temperature was studied and the results are summarized in Table 2. All the reactions gave the corresponding products within 5–30 min and the yields of the desired products were good to excellent.

In summary, we have shown that Cu nanoparticles in ionic liquid **4** catalyzed the reaction between thiazolidine-

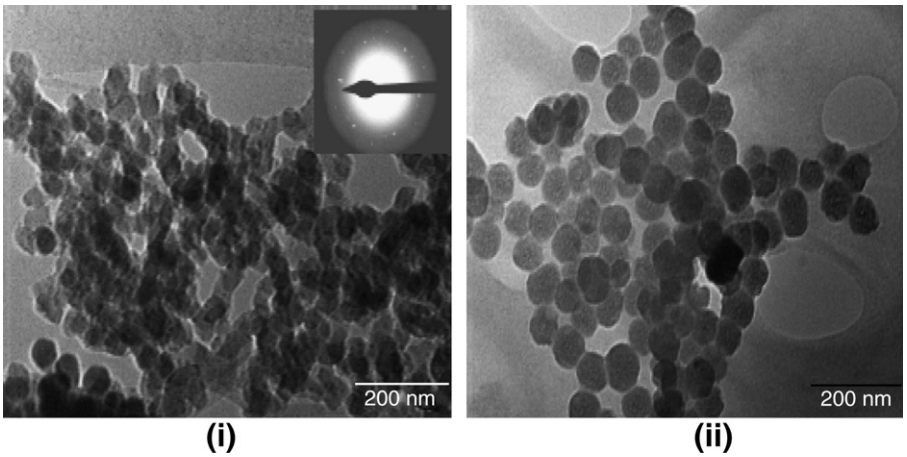


Fig. 2. TEM of the synthesized copper nanoparticle synthesized: (i) fresh Cu nanoparticles and (ii) used Cu nanoparticles.

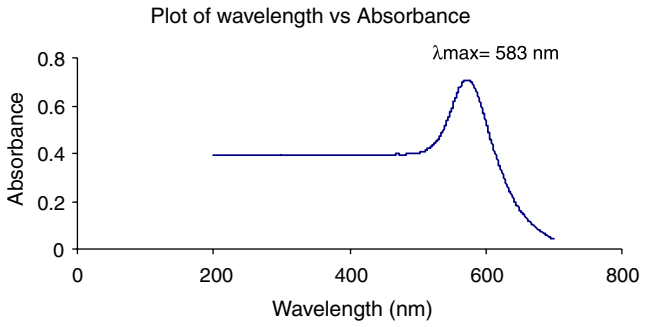


Fig. 3. UV–vis absorption spectrum of copper nanoparticles in ethanol.

Table 1
Optimization of the catalyst for the synthesis of bis-(4-hydroxy-2-oxothiazolyl)methanes **3**[a]

Entry	Catalyst	Time (min)	Yield (%)
1	—	45	65
2	Cu nanoparticles	8	75
3	Ionic liquid **4**	15	70
4	Cu nanoparticles in ionic liquid **4**	5	92
5	Boric acid	15	75

[a] The reaction was carried using catalyst (0.005 g), thiazolidine-2,4-dione (20 mmol), benzaldehyde (10 mmol), rt.

2,4-dione and aromatic aldehydes in high yields and in short reaction times. Our protocol avoids the use of expensive reagents, high temperatures and the reaction being performed in an ionic liquid and serves as an efficient method and also allows easy recyclability of the catalyst. Further catalytic applications of Cu nanoparticles for condensation reactions with complex structures of biological significance are currently under investigation.

Acknowledgement

This work is dedicated to the late Dr. N.N. Ghosh, my mentor and my supervisor (P.S.).

Table 2
Synthesis of bis-(4-hydroxythiazol-2-one)methanes by reaction between thiazolidine-2,4-dione and aromatic aldehydes in the presence of copper nanoparticles in an ionic liquid

Entry	R	Product	Yield[a] (%)
1	C_6H_5	**3a**	92
2	4-$OCH_3C_6H_4$	**3b**	88
3	4-OHC_6H_4	**3c**	85
4	2-OHC_6H_4	**3d**	89
5	2,4-$Cl_2C_6H_3$	**3e**	82
6	2-ClC_6H_4	**3f**	88
7	4-FC_6H_4	**3g**	85
8	4-$N(CH_3)_2C_6H_4$	**3h**	92
9	3,4-$(OCH_3)_2C_6H_3$	**3i**	90
10	3-OHC_6H_4	**3j**	95
11	2-$OHC_{10}H_7$	**3k**	91
12	C_4H_3CHO[b]	**3l**	89

[a] Yield from GC.
[b] 2-Formylthiophene.

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17. *Experimental procedures*. Synthesis of the ionic liquid: In a 50 ml round-bottom flask, 10 mmol of 1-*H*-tetrazole-5-acetic acid and 15 mmol of acrylonitrile in 20 ml of acetonitrile were stirred for 2 h. The extent of the reaction was monitored by TLC. On completion, the solvent and excess acrylonitrile were removed under reduced pressure. To 10 mmol of the above compound in 25 ml of acetonitrile, 15 mmol of bromobutane was added. The mixture was refluxed for 6 h and then the solvent and excess bromobutane were evaporated under reduced pressure to afford the ionic liquid **4** (yield 92%).
18. *Experimental procedure*: In a typical experiment, a mixture of copper nanoparticles (0.005 g), thiazolidine-2,4-dione (20 mmol) and benzaldehyde (10 mmol) in ionic liquid **4** (3 mL) was stirred at room temperature for the appropriate time. After completion of the reaction, as indicated by TLC, the product was extracted with ethyl acetate (3×10 mL). The combined organic extracts were concentrated in vacuum and the resulting product was purified by column chromatography on silica gel with ethyl acetate and *n*-hexane (3:7) as eluent to afford the pure product. The remaining material containing the catalyst was preserved for the next run. Structural assignments of the products were based on ^{1}H NMR, ^{13}C NMR, IR and mass analysis. Analysis of spectral and compositional data revealed the formation of bis-(4-hydroxy-2-oxothiazolyl)methane **3a** in 92% yield.
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