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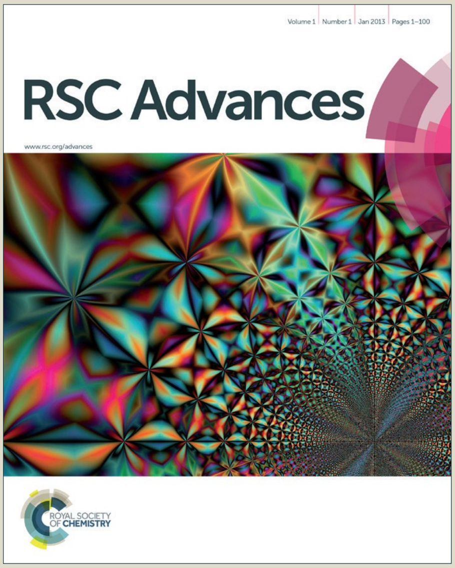

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ARTICLE

On-water synthesis of phenols using biogenic Cu_2O nanoparticles without using H_2O_2

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Rupom Borah, Eramoni Saikia, Sankar Jyoti Bora and Bolin Chetia*

In the recent years biogenic synthesis of metal oxide nanoparticles using natural resources have received significant attraction due to their easy availability, low cost and environmental benign protocol. In this study, Cu_2O nanoparticles have been synthesised using *Syzygium jambos (L.) Alston* plant extracts without using toxic chemicals. The average size of the nanoparticles is 7.6 nm which found to have excellent catalytic activity in the *ipso*-hydroxylation of arylboronic acids without using H_2O_2. Mild reaction condition, excellent yield, easy separation and reusability of the catalyst are the advantages of this method.

Introduction

Development of metal oxide nanoparticles in the current years has inspired the interest of scientists and researchers due to their unique properties and potential applications. Cu_2O nanoparticles are found to be an important p-type semiconductor with a band gap approximately 2.1 eV[1] and a promising inorganic catalyst in various fields[2-8]. The conventional procedure for the synthesis of Cu_2O nanoparticles includes the hydrothermal[9], electro-deposition[10] and chemical reduction methods[11] having more or less shortcomings e.g. high temperature, hazard chemicals, supporting media etc[12] (Table 1). To overcome these shortcomings, biogenic synthesis of nanoparticles is considered as one of the most convenient procedure as it is environmental benign, cost effective and easy process. Although a lot of reports are found in literature for the synthesis of Cu_2O NPs using chemical reduction method, however only a few reports for biosynthesis[13] are obtained. Herein attempts were made to synthesis Cu_2O NPs using *Syzygium jambos (L.) Alston* plant leaves extract.

Syzygium jambos (L.) Alston leaves extracts shows good antimicrobial[14], anti-nociceptive[15], and antioxidant[16] activity, and the plant rich in vitamin C and many polyphenols[17]. Therefore this plant was chosen to be the biogenic reducing agent for the synthesis of Cu_2O NPs. The synthesised Cu_2O NPs were also found to have good catalytic activity in the *ipso*-hydroxylation of arylboronic acids. Most of the *ipso*-hydroxylation of arylboronic acids involve the use of H_2O_2[18] in presence of various catalysts (biosilica, acidic alumina etc.) and there are only a few reports without using H_2O_2 ($CuSO_4$/phenanthroline, $CuCl_2$ Brij S-100, $[Ru(byp)_3Cl_2$, NH_2OH, $NaClO_2$ etc.).[19] Even all the existing processes are effective for the conversion, but most of the methods have some limitations such as use of strong oxidising agent, base, ligands and also not recyclability of the catalyst (Table 2). We have designed an alternative protocol to synthesis phenolic derivatives from arylboronic acids without using H_2O_2, base, ligands, external oxygen source etc. The simple catalytic system, recyclability of the catalyst and mild reaction condition give advantages to the conversion.

Experimental section

General Information

Chemicals and reagents were purchased from commercial suppliers and used without further purification. Reactions were monitored by thin layer chromatography (TLC) on silica gel plates (60 F254), visualizing with ultraviolet light. ^1H-NMR and ^{13}C-NMR spectras were determined in $CDCl_3$ solution by using 400 MHz spectrometer taking tetramethylsilane (TMS, δ=0.00) as internal standard and expressed in ppm. Spin multiplicities are given as s (singlet), d (doublet), t (triplet) and m (multiplet) as well as b (broad). Infrared spectra were recorded on a FT-IR spectrometer.

Biosynthesis of Cu_2O NPs

Leaves of *Syzygium jambos (L.) Alston* were washed with distilled water, air dried and 10 g of the leaves were placed into 100 ml of distilled water in a round bottomed flask, heated at 50°C for 15 min and filtered. 10 ml of 1 mM copper acetate solution was added to 2 ml of 1 mmol sodium hydroxide solution and to the resulting solution 5 ml of aqueous extract was added and was stirred

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Department of Chemistry, Dibrugarh University, Dibrugarh-786004, Assam, India.
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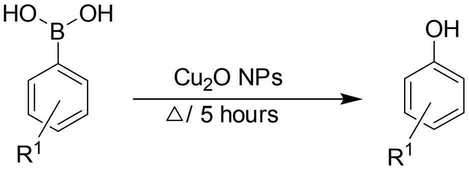
vigorously at 60°C for 2 hr. Sodium hydroxide solution was added to the mixture to form copper(II) hydroxide from copper acetate. The Cu_2O NPs were then separated by centrifugation at 1200 rpm for 10 min and then washed with ethanol several times and dried in an oven at 50°C. Some existing technologies to produce Cu_2O nanoparticles were compared with our biosynthesis method (table 1) and it is clear that biosynthesis method is more efficient and gives smaller size nanoparticles within a short period.

Table 1: Comparison of methodologies to synthesis Cu_2O nanoparticles

Type	Reducing agent	Temp	Time	Size	Ref.
Hydrothermal	o-anisidine	200 °C	8 h	445 nm	9 (a)
Hydrothermal	-	200 °C	1-32 h	150-300 nm	9 (b)
Chemical	Fehling solution, glucose	90 °C	1-2 h	590-1600 nm	11 (a)
Biosynthesis	Plant extracts	60 °C	2 hr	4-10 nm	Our present work

Ipso-hydroxylation of arylboronic acids by Cu_2O NPs



Scheme 1: Synthesis of phenols using Cu_2O NPs

In a typical reaction 5 mg (0.041 mM) of phenyl boronic acid and 2 mg (0.014 mmol) of Cu_2O NPs were added to 5 ml of water under stirring at 60°C. The reaction was monitored by TLC. After completion of the reaction the reaction mixture was diluted with 20 mL of water and extracted with 20 mL of diethylether and the combined organic layer was washed with brine and dried over by Na_2SO_4 and evaporated in a rotary evaporator under reduced pressure. The products were confirmed by ^{1}H-NMR, ^{13}C-NMR and FT-IR spectroscopy without any further purification by column chromatography. The reaction was also performed using molecular oxygen but the yield was same.

Result and Discussion

The biogenic Cu_2O NPs were well characterized by powder XRD-diffraction method as shown in the figure 1. The diffraction peaks appeared at 2θ = 29.58°, 36.5°, 42.36°, 61.64°, 73.62° and 77.62° corresponding to the planes (110), (111), (200), (220), (311) and (222) respectively and shows clearly the presence of pure crystalline Cu_2O octahedra. The strong and sharp peaks of the prepared Cu_2O octahedra indicate the high crystallinity of the NPs.

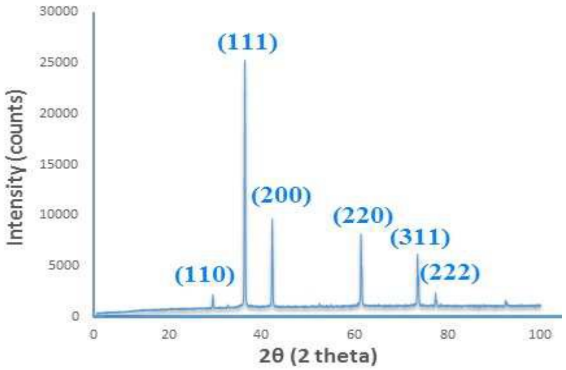


Fig. 1 Powder XRD pattern of the synthesized octahedral Cu_2O Nanoparticles.

The monodispersity and pure octahedral structures of the nanocrystals (figure 2a and 2b) and extensive aggregation of the small particles (figure 2c) were observed from the SEM images. The Energy Dispersive X-ray (EDX) spectrum (figure 2d) shows the presence of copper, oxygen and carbon element in which copper and oxygen present in the ratio almost 2:1. Furthermore the morphology and size of the Cu_2O nanocrystals were also determined through TEM and HR-TEM images (figure 3). The inset figure (3b) shows the selected area electron diffraction (SAED) pattern of the Cu_2O NPs and contains the concentric diffraction rings due to the (111), (200) and (220) reflection of the octahedral Cu_2O NPs. From the HR-TEM image (figure 3c) the separation of the fringes was found to be 2.4 Å, which is good agreement with the (111) plane and another magnified lattice fringe was found with a spacing of 3.01 Å which corresponds to the lattice plane (110) of Cu_2O NPs. The average diameter of the NPs was found around 7.62 nm (figure 4).

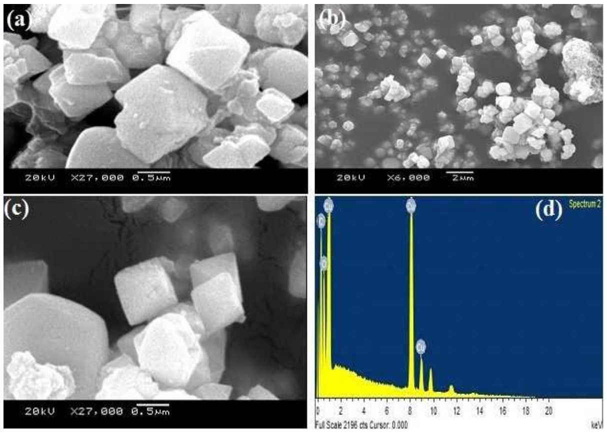


Fig. 2 SEM images of the pure Cu_2O octahedral (a, b, c) and (d) EDX images of the nanooctahedra.

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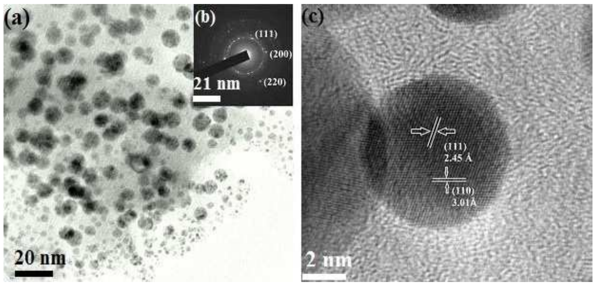

Fig. 3 (a) TEM images and (b) corresponding SAED pattern of the nanoparticles and (c) HR-TEM image of selected region of one nanoparticle.

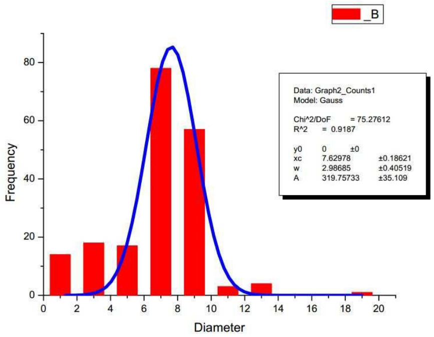

Fig. 4 Size distribution of the NPs

***Ipso*-Hydroxylation of aryl boronic acids:**

Using the above mentioned reaction conditions 12 different types of arylboronic acids were converted to the corresponding phenols with high yields.

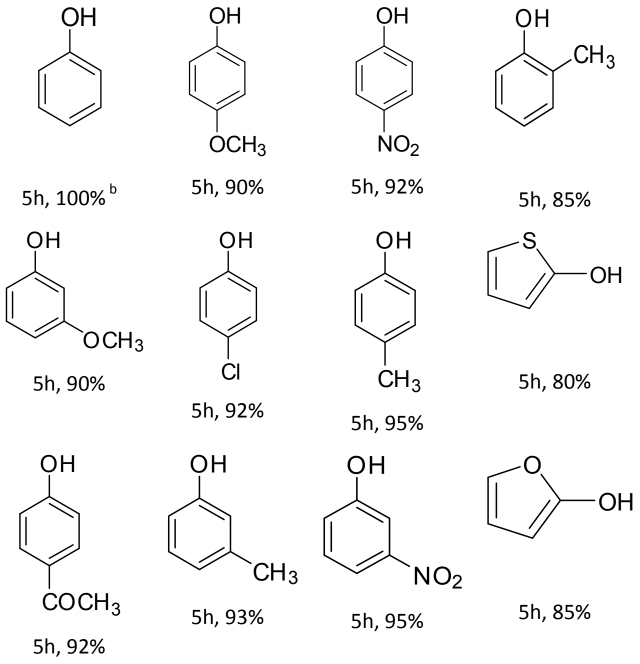

Fig. 5 Substrate scope: variation of the arylboronic acids[a]

[a] Reaction conditions: arylboronic acid (0.041 mmol), Cu_2O NPs (0.014 mmol) in 5 ml water at 60 °C.

[b] Isolated yields.

Some of the recently reported catalyst systems and their comparison with the Cu_2O nanoparticles catalyst are illustrated in table 2. It is clear that Cu_2O nanoparticles catalyst is more efficient and greener catalyst than most of the reported catalysts.

Table 2: Comparison of efficiency of Cu_2O nanoparticles with some reported catalysts for the *ipso*-hydroxylation of aryl boronic acids

Catalyst	Time	Yield (%)	Recyclability	Reference
$CuSO_4$-phenanthroline	2 h	95	No	19 (a)
$CuCl_2$ Brij S-100	24 h	95	No	19 (b)
$[Ru(byp)_3Cl_2].6H_2O$	48 h	93	No	19 (c)
NH_2OH	18 h	94	No	19 (d)
Cu_2O nanoparticles	5 h	100	Yes	Present work

Recyclability Test

Recyclability of the catalyst is another attractive feature of this protocol. As the catalyst is heterogeneous in nature, the catalyst is recycled up to 5th cycle without significant loss of catalytic activity (figure S1). Taking phenylboronic acid as model substrate we carried out the catalyst recyclability test. After completion of the reaction, products were extracted with diethylether and catalysts separated from product was washed with more diethylether and reused. The loss of the product yields after 5th cycle is due to the loss of nanoparticles during the recycling process. There is no change in the morphology and crystallinity of nanoparticles as observed in the analysis of TEM images and XRD patterns of the recycled nanoparticles after 5th cycle (figure 6).

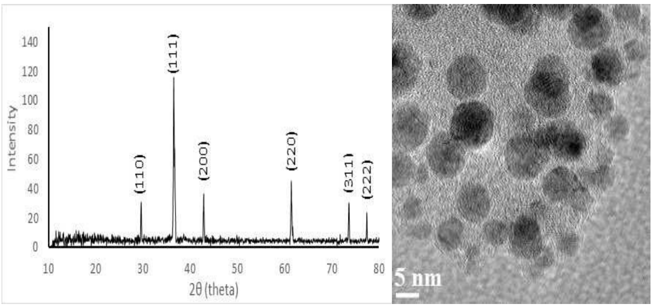

Fig. 6 Powder XRD and TEM image of Cu_2O nanoparticles after 5th catalytic cycle of reaction

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Mechanism

The exact mechanism for the *ipso*-hydroxylation of aryl boronic acids is unknown. But a proposed reaction mechanism is given below (figure 7). The reaction occurs via oxidative addition followed by reductive elimination of the boronic acid.[20] As the reaction is heterogeneous and the powder XRD and TEM image taken after recycling of the catalyst exhibits the identical peaks and size of the Cu_2O nanoparticles. These experimental results clearly reveal that the reaction takes place on the surface of the Cu_2O nanoparticles.

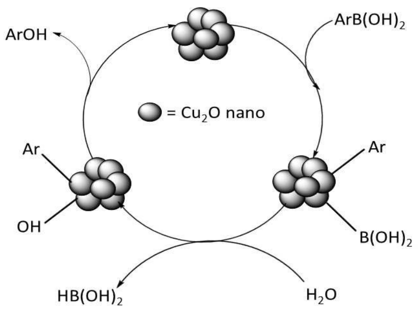

Fig. 7 Proposed mechanism for *ipso*-hydroxylation of aryl boronic acids with Cu_2O nanoparticles

Conclusion

Herein we have reported for the first time a facile, environment friendly biogenic route to synthesis pure octahedral Cu_2O NPs using *Syzygium jambos (L.) Alston* leaves extracts. The synthesized NPs were found in the average size range between 4 to 10 nm (TEM). The biogenic Cu_2O nanoparticles are directly utilised on water for the *ipso*-hydroxylation of arylboronic acids with various substituents with excellent yields. The catalyst works without using H_2O_2, base, ligand, molecular oxygen and can be recycled several times without significant loss of activity. The present catalytic system shows better results and has some advantages in comparison to other techniques to synthesis phenols from arylboronic acids. We believe that this is the most greener and efficient protocol for *ipso*-hydroxylation of arylboronic acids to phenols from the environmental and economical point of view.

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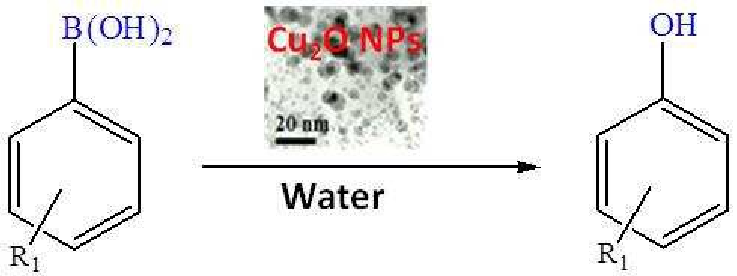

Facile synthesis of phenols using biogenic Cu_2O NPs
Without using H_2O_2, ligand, base