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Short communication

Green synthesis of CuO nanoflakes from copper pincer complex for effective *N*-arylation of benzimidazole

P. Jerome [a], G. Kausalya [b], T. Daniel Thangadurai [b,*], R. Karvembu [a,*]

[a] Department of Chemistry, National Institute of Technology, Tiruchirappalli 620 015, India
[b] Department of Nanoscience and Technology, Sri Ramakrishna Engineering College, Coimbatore 641 022, India

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ABSTRACT

Nanostructured CuO is synthesized in water using copper pincer complex as precursor without any stabilizing agent and characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and energy dispersive X-ray analysis (EDAX). The selected area electron diffraction (SAED) and magnetization measurements indicate lattice fringes spacing of 0.25 nm for (111) plane and ferromagnetic nature of the CuO nanoflakes, respectively. Benzimidazole undergoes *N*-arylation reaction with aryl halides in the presence of CuO nanoflakes and K_2CO_3 in *N*,*N*-dimethylacetamide (DMAc) at 120 °C. The reusability of the CuO nanoflakes is also tested and the results are found to be good.

1. Introduction

Metal oxide nanomaterials have attracted great interest because of many unique properties linked to the nanometer size of the particles [1–3]. The oxides of transition metal elements are an imperative class of semiconductors, which have applications in solar energy transformation, magnetic storage media, electronics, catalysis, etc. [4–6]. Among the metal oxides, CuO nanomaterials are of special interest because of their versatility in catalysis [7–9].

N-arylation of heterocycles is an important reaction in organic synthesis due to the application of *N*-arylated products in various fields such as pharmaceuticals, natural product synthesis, materials chemistry, etc. [10–15]. To be specific, *N*-arylated benzimidazoles such as MRL-1237 and Telmisartan have been used as drug molecules, and 2,2′,2″-(1,3,5-benzinetriyl)-tris(1-phenyl-1-H-benzimidazole) was found to be a useful OLED material [16]. Many homogeneous Cu catalysts have been reported for *N*-arylation of heterocycles [17]. Even though the homogeneous systems are active, they could not be commercialized due to the difficulty in the separation of catalyst and reusability. Hence many researchers have focused on the development of heterogeneous catalysts for the *N*-arylation reaction [7]. Among the various heterogeneous catalysts, nano-CuO was found to be efficient and highly reusable [18]. CuO nanostructured materials have been prepared from various sources like $CuCl_2 \cdot 5H_2O$, CuI, $Cu(NO_3)_2$, etc. [19–22].

To the best of our knowledge, no one has utilized Cu pincer complex as precursor for producing CuO nanomaterials. Cu pincer complexes have found importance mainly in homogeneous catalysis [23–24]. We have used Cu pincer complex as a precursor for the preparation of nano-CuO and studied its catalytic application towards *N*-arylation of benzimidazole under heterogeneous conditions. Nano-CuO prepared from Cu pincer complex was found to possess a flake structure and exhibited very good catalytic efficiency and reusability in aforesaid reaction. CuO with different morphologies have been used as catalysts in various organic transformations but the use of nanoflake CuO in catalysis is rare [25].

2. Experimental

2.1. Synthesis of CuO

Cu pincer complex (50 mg) was synthesized by following a literature procedure [26–27] and then it was dissolved in 20 mL of distilled water under reflux condition. To the above solution K_2CO_3 (40 mg) was added and the resulting mixture (pH = 6–7) was refluxed for 45 min. Then, the solution was cooled to room temperature and the solid product was separated by centrifugation, washed with distilled water and dried in hot air oven at 110 °C (Scheme 1).

2.2. Procedure for N-arylation of benzimidazole

CuO (15 mg, 5 mol%) was added to a mixture of aryl halide (1 mmol), benzimidazole (142 mg, 1.2 mmol) and K_2CO_3 (276 mg, 2 mmol) in *N*,*N*-

* Corresponding authors.
E-mail addresses: danielt@srec.ac.in (T. Daniel Thangadurai), kar@nitt.edu (R. Karvembu).

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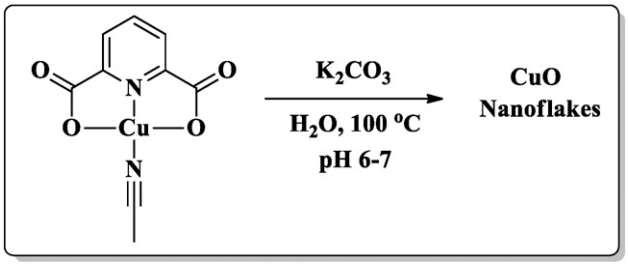

Scheme 1. Synthesis of CuO nanoflakes.

dimethylacetamide (DMAc) (3 mL) and stirred at 120 °C. After the required time, the reaction mixture was cooled to room temperature and the catalyst was separated by centrifugation. The product was extracted with ethyl acetate, dried over anhydrous sodium sulfate and analyzed by GC. The recovered catalyst was washed thoroughly with water, ethanol and toluene, and dried under vacuum before reuse.

3. Results and discussion

3.1. Catalyst characterization

The X-ray diffraction pattern of the prepared material (Fig. 1) is in good agreement with that of reported CuO [16], which confirms the formation of CuO. The sharp and intense peaks indicated that the CuO is pure, crystalline and well arranged in specific orientation. The XRD reflections for CuO are observed at 2θ value of 32.17°, 35.37°, 38.80°, 48.87°, 58.36°, 61.57° and 66.04° representing (110), ($\bar{1}$11), (111), ($\bar{2}$02), (202), ($\bar{1}$13) and ($\bar{3}$11) planes of pure monoclinic structure (JCPDS No. 89-5895). The ($\bar{1}$11) peak is more intense than (111) peak, which confirmed

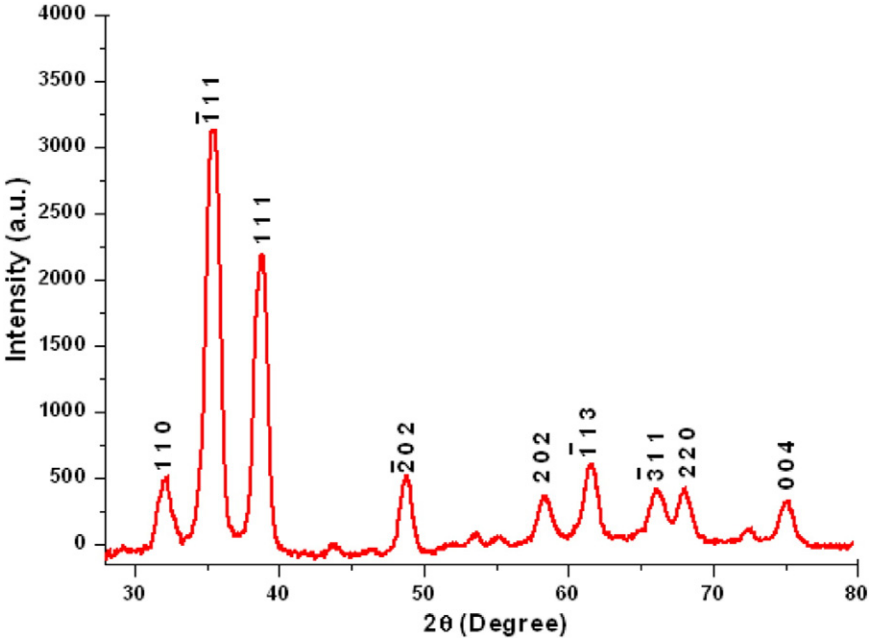

Fig. 1. XRD pattern of CuO at 25 °C.

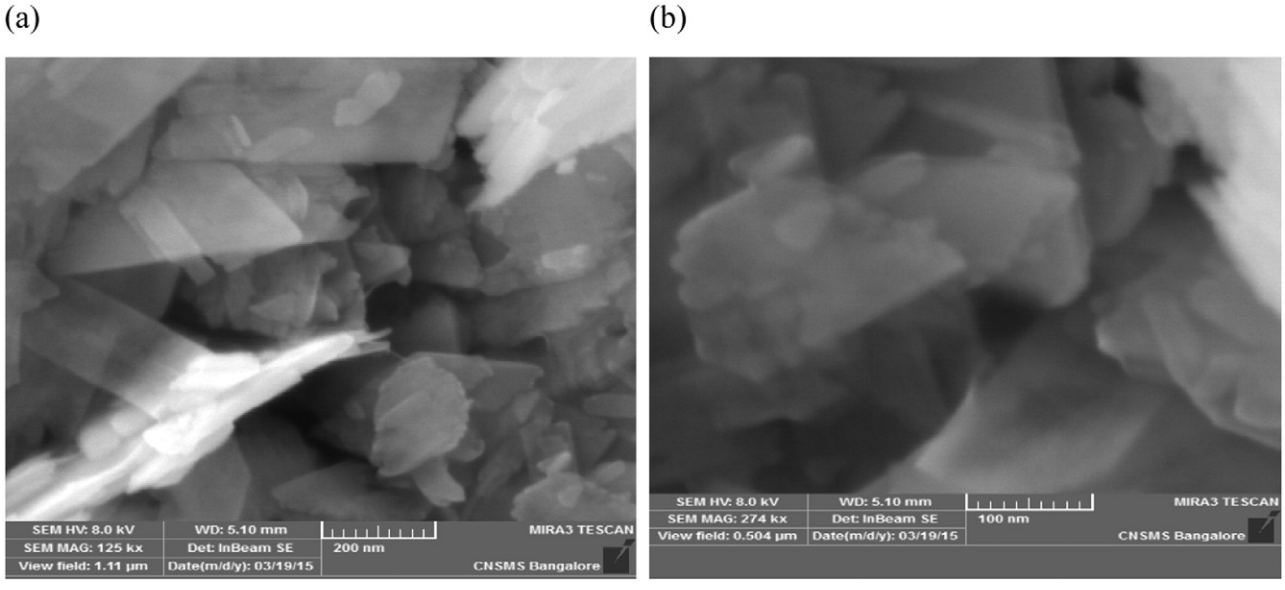

Fig. 2. FESEM images of CuO.