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Copper(II) oxide nanocatalyst preparation and characterization: green chemistry route

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Abstract

Background: Green synthesis as a technique of preparation of metal/metal oxide nanomaterials is becoming an important and competitive method of preparation replacing the conventional method of preparation. Among metal oxides, nanocatalyst copper(II) oxide is considered as a very important and potent catalyst/photocatalyst with a very wide range of applications.

Results: In this work, copper(II) oxide nanoparticles were prepared with the assist of aqueous spinach extract from copper metal powder. Spinach extract catalyzes the formation of copper oxide nanoparticles with manipulation of chlorophyll that exists in the extract. The produced copper(II) oxide nanoparticles were characterized using scanning electron microscopy (SEM), energy dispersive X-ray (EDX), and X-ray diffraction (XRD).

Conclusions: It was proved that spinach extract catalyzes the preparation of copper(II) oxide nanocatalyst. It was elucidated from the characterization technique that the produced nanoparticles are pure copper oxide with particle size range of 60–100 nm.

Keywords: Chlorophyll, Copper(II) oxide, Green chemistry, Photocatalysis

Background

Recently, green chemistry routes of preparation of different metal/metal oxide nanomaterials have been attracting increasing attention due to their advantages being operating under mild conditions, environmentally safe, and assist in manipulating the reaction condition toward the production of desired engineered nanomaterials. These green synthesis routes could be achieved by using microbial micro-organism, plant-related materials, and plant extract. As it is well known, nanomaterials are effectively existed in the scientific research market due to their marvelous wide range of applications as well as their outstanding optical, chemical, and physical properties which affect to a great extent their activity. Preparation of metal oxide nanoparticles has been extensively investigated using conventional methods as sonochemical method (Chen and Mao 2007; Xu et al. 2013), hydrothermal/

solvothermal synthesis (Khan et al. 2011), sol-gel method (Macwan et al. 2011), combustion (Patil et al. 1997; Patil et al. 2002), chemical precipitation (Rakhshani 1986), and metal reduction (Dang et al. 2011; Phoka et al. 2009). Also, green synthesis methods of preparation of metal oxides have been investigated extensively (Parsons et al. 2009; Klaus et al. 1999; Phumying et al. 2013; Munshi et al. n.d.). Green chemistry synthesis involves two distinguished principle roles which served as a reaction medium (could be stabilizers or capping agents) and environmentally and biologically safe reducing agents (could help in medical and biological applications). Among metal oxide nanomaterials, copper oxide represents a very important and potent candidate in a wide range of applications as magnetic storage media (Li et al. 2004), sensors (Shishiyanu et al. 2006; Kim et al. 2008), catalytic applications (de Jongh et al. 1999; Zhang et al. 2014), and many other fields of application. Cu₂O is considered as a p-type semiconductor with a narrow bandgap of 1.4–1.9 eV (Grozdanov 1994), so it has a potent role in photoconductive and photothermal applications (Rakhshani 1986). In this work, CuO preparation—in a green chemistry method with the assistance of spinach extract—was studied. The obtained CuO nanoparticles

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were characterized using scanning electron microscopy, energy dispersive X-ray, and X-ray diffraction.

Experimental

Materials

Copper powder (Ranbaxy Chemicals, $> 5 \mu\text{m}$) has been used without any preheated producer or any further purification, and de-ionized water has been prepared in the laboratory. For the synthesis of nanomaterials, a closed cylindrical Teflon-lined stainless steel chamber of 100 ml capacity (autoclave, Latech Scientific Supply Pte. Ltd. Company) was used.

Characterization

The structural properties of ZnO nanoparticles were characterized using scanning electron microscopy (SEM) (NOVA NANOSEM-600) coupled with energy dispersive X-ray spectrometer (EDX). The powders were characterized by X-ray diffraction (XRD) using Cu $K\alpha$ radiation ($\lambda = 0.15141 \text{ nm}$) in the 2θ range from 25 to 65° with $0.02^\circ/\text{min}$ performed in King Abdulaziz University labs.

Methods

An aqueous solution of fresh spinach extract in deionized (DI) water (Munshi et al. *n.d.*) 80 ml together with 0.2 g copper metal (powder) was placed in a stainless-steel

Teflon-lined metallic autoclave of 100 ml capacity and sealed under ambient conditions. A blank sample with copper metal aqueous solution free from spinach extract was processed at the same conditions. The autoclaved reaction mixture is heated to 180°C ($2^\circ\text{C}/\text{min}$) in a preheated furnace and left for 72 h under the same conditions. After being cooled, the produced powder was centrifuged, washed, and vacuum dried.

Results

Scanning Electron microscopy

The morphology of the obtained CuO nanoparticles was studied using scanning electron microscopy technique Fig. 1.

Energy-dispersive X-ray spectroscopy

The EDX analysis result of CuO NPs was illustrated in Fig. 2. It can be concluded that the sample mainly consists of copper and oxygen as a major constituent besides some other minor by-product that coexists from the organic precursor such as carbon beak that exists at 0.25 keV. The molecular ratio of Cu:O was 1:1. Meanwhile, the blank sample EDX showed almost no reaction with mainly Cu peaks with very minor oxygen beak Fig. 3.

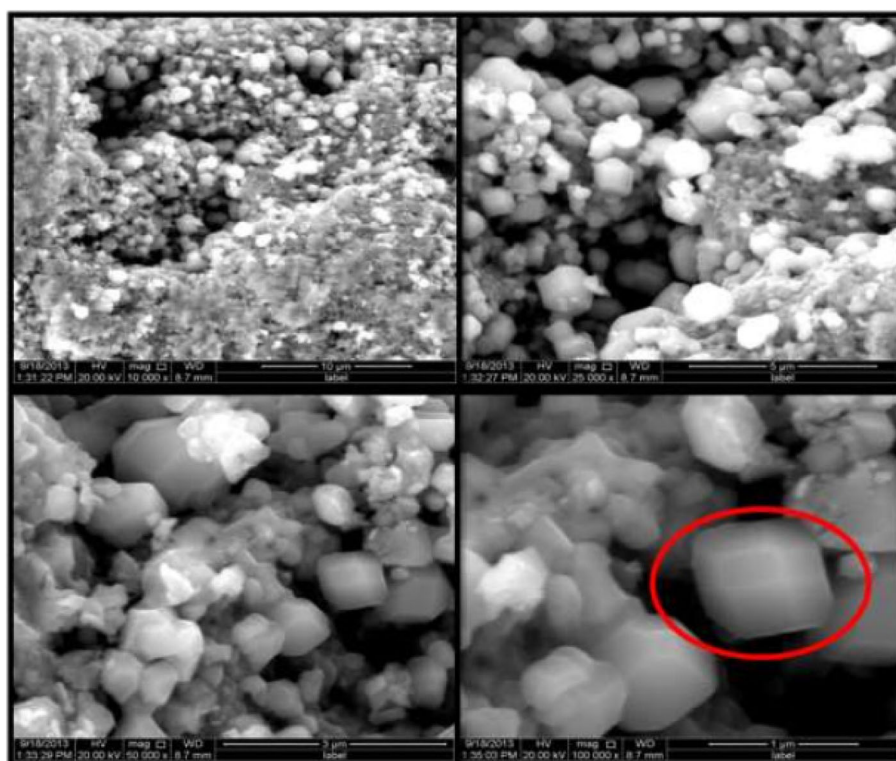


Fig. 1 SEM images of copper oxide sample at different magnification

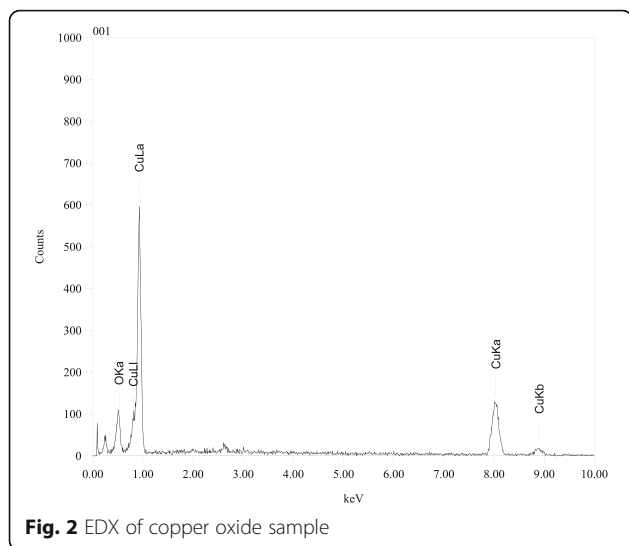


Fig. 2 EDX of copper oxide sample

X-ray diffraction spectroscopy

X-ray diffraction technique not only confirms the identity of the products but also determines the crystal structure and the crystallite size of the obtained product. The XRD pattern of the obtained CuO NPs Fig. 2 showed the strongest three peaks at 2θ values of 35.5074° , 38.7954° , and 61.3445° corresponding to $(1, 1, -1)$, $(1, 1)$, and $(1, 1, -3)$ planes of copper(II) oxide, respectively (Fig. 4).

Discussion

Spinach green extract—like any green plant—contains chlorophyll which is considered as the first known photocatalyst from the beginning of the universe. Chlorophyll in photosynthesis process catalyzes the splitting of water molecules into hydroxyl ions OH^- and hydrogen ions H^+ ¹³. The first step in chlorophyll photocatalytic action is the oxidation of chlorophyll to produce electron which carried

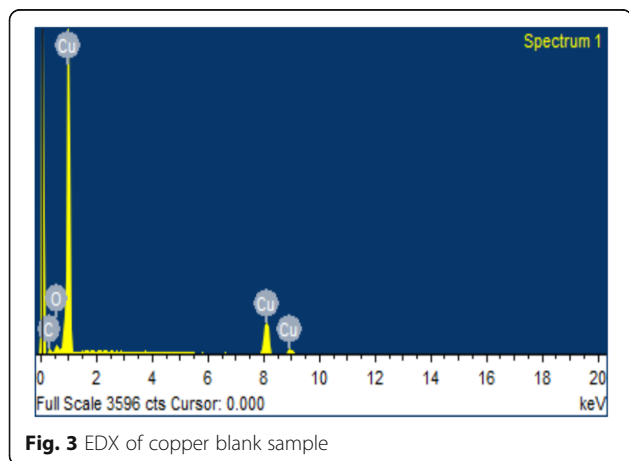


Fig. 3 EDX of copper blank sample

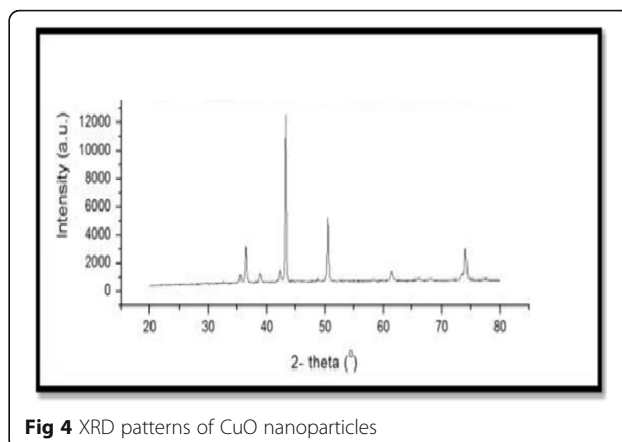


Fig 4 XRD patterns of CuO nanoparticles

out the catalytic process through the attack of water molecules. The hydroxyl ions in subsequent step react with copper metal to produce copper II hydroxide which transformed into copper(II) oxide by the effect of heat as it was illustrated in Scheme 1.

X-ray diffraction studies prove that the obtained CuO NPs is a face-centered cubic phase in agreement with standard powder diffraction card JCPD file No. 48-1548. No diffraction peaks arising from any impurity can be detected, and the pattern confirms that the products are pure CuO. The average crystallite size of copper oxide nanoparticles was determined using Debye Scherrer formula (Cullity 2001).

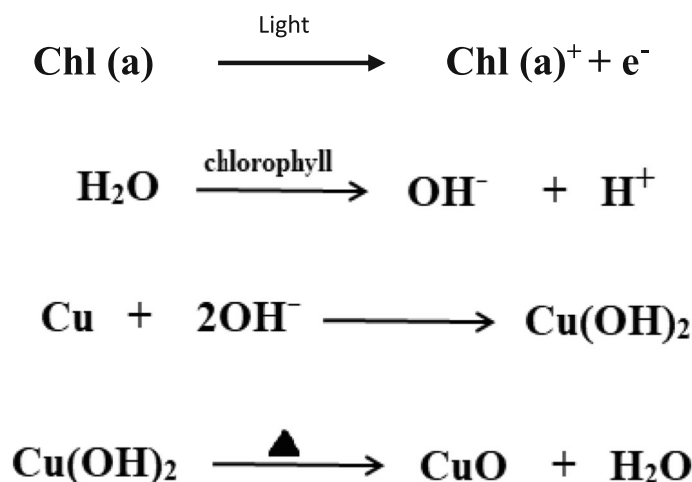
$$D = \frac{0.9\lambda}{\beta \cos\theta}$$

The particle size of the sample was calculated using the above formula, and the small average grain size of copper oxide nanoparticles was 0.58 nm.

From SEM, it was obvious that CuO nanoparticles appear as irregular spherical particles, with predominant tetrahedron structure with dimensions ranging from 60 to 100 nm.

Conclusions

Chlorophyll as the main constituent of any green plant represents a potent photocatalyst to initiate and catalyze the preparation of metal oxide nanoparticles under milder conditions than that of the conventional method of preparation. Herein, it was concluded that chlorophyll that exists in spinach aqueous catalyzed the preparation of CuO NPs in a process simulating the way of action of chlorophyll in the photosynthesis process. The produced CuO NPs were found to have a particle size ranging from 60 to 100 nm.

**Scheme 1** Chlorophyll photocatalytic action**Acknowledgements**

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Availability of data and materials

All data generated or analyzed during this study are included in this published article [and its supplementary information files].

Authors' contributions

All authors contribute in the work and in writing the manuscript. All authors read and approved the final manuscript.

Ethics approval and consent to participate

The manuscript does not contain studies involving human participants, human data, or human tissue.

Consent for publication

Not applicable

Competing interests

The authors declare that they have no competing interests.

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