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ZnO/CuO nanocomposite prepared in one-pot green synthesis using seed bark extract of *Theobroma cacao*

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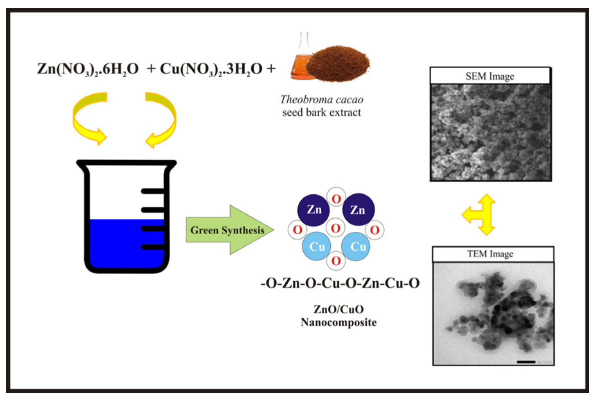
HIGHLIGHTS

- ZnO/CuO nanocomposite was prepared in one-pot green synthesis using *Theobroma cacao* seed bark extract (TBE).
- TBE acts as the weak base source material in the formation of ZnO/CuO nanocomposite.
- The nanocomposite was characterized by UV–Vis DRS, Fluorescence Spectrophotometer, FT-IR, SEM-EDX, TEM and XRD.
- ZnO/CuO has particle size in nanometer scale and decreased energy band gap.

GRAPHICAL ABSTRACT



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ABSTRACT

A method for green synthesis of ZnO/CuO nanocomposite using *Theobroma cacao* seed bark extract (TBE) has been investigated. ZnO/CuO nanocomposite synthesis aims to decrease a high band gap energy of ZnO. $Zn(NO_3)_2$ and $Cu(NO_3)_2$ solutions were used as a precursors. TBE can substitute NaOH as the base source material which contained alkaloids as shown from the phytochemical test. Identification of nanocomposite was characterized by UV–Vis diffuse reflectance spectrophotometry (DRS), Fourier-transform infrared (FT-IR) spectroscopy, scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX), transmission electron microscopy (TEM), X-ray diffraction analysis (XRD) and Fluorescence Spectrophotometer. ZnO/CuO nanocomposite had the band gap energy of 2.3 eV. TEM result showed the size of ZnO/CuO nanocomposite was 20–50 nm.

1. Introduction

Metal oxide nanocomposites have attracted an attention some researchers for several applications such as fuel cells, photocatalysis, sensors, antibacterials and UV protections [1–5]. Nowadays, metal oxide nanocomposites have been synthesized such as ZnO–MgO [4], CeO_2-MnOx [6], CuO–ZnO [7,8], ZnO–NiO [9], TiO_2-WO_3 [10], Co_3O_4-ZnO [11,12], MgO–CuO [13], Dy_2O_3-CuO [14], and CeO_2-ZnO [15]. Among of various nanocomposites metal oxide, researchers are more interested in ZnO/CuO. Zinc oxide (ZnO) is a non-toxic material, low cost, and abundant availability. It has a high energy density, electrical and piezoelectric properties [16–19]. ZnO is a n-type semiconductor with a conductivity of about 10^{-7}-10^{-3} S/cm, and has a relatively large binding energy of 60 meV, but it has a high band energy of about 3.37 eV. The high band gap (3.0–3.9 eV) limits the use of ZnO for wider applications, because it is only active in UV light area. UV rays contains about 3%–5% of photon flux which reaches the earth's surface, and about 45% are in visible light area. The doping or coupling process is a

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Table 1
Comparison result related to synthesis of ZnO-CuO nanocomposite.

Materials	Precursor	Methods	Stabilizing and capping agent	Particle size result
ZnO NPs [30]	$Zn(NO_3)_2$	Green synthesis	*Imperata cylindrical*	11.9 nm
ZnO NPs [31]	$Zn(NO_3)_2$	Green synthesis	*Moringa oleifera*	12.27–30.51 nm
ZnO NPs [33]	$Zn(NO_3)_2$	Green synthesis	*Vitex trifolia*	15–46 nm
ZnO NPs [34]	$Zn(NO_3)_2$	Green synthesis	*Tabernaemontana divaricata*	20–50 nm
CuO NPs [35]	$CuSO_4$	Green synthesis	*Callistemon viminalis*	3.8–42.4 nm
CuO NPs [36]	$Cu(NO_3)_2$	Green synthesis	*Calotropis gigantea*	20 nm
CuO NPs [37]	$CuCl_2$	Green synthesis	*Theobroma cacao*	40 nm
CuO NPs [46]	$CuCl_2$	Chemical precipitation	palmetic acid and stearic acid	22 nm
CuO–ZnO Nanocomposite [44]	$ZnCl_2$ $CuSO_4$	Co-precipitation	Oxalic acid	20 nm
CuO–ZnO Nanocomposite [43]	$Zn(CH_3COO)_2$ $Cu(CO_2CH_3)_2$	Spray pyrolisis	Perfume	25–45 nm
CuO–ZnO core shell Nanocomposite [42]	ZnO NPs $CuCl_2$,	Green synthesis	*Melissa officinalis*	10–20 nm
CuO–ZnO Nanocomposite (this work)	$Zn(NO_3)_2$ $Cu(NO_3)_2$	Green synthesis	*Theobroma cacao* seed bark	20–50 nm

modification process to displace the absorption area of a material [20]. The enhancement of ZnO photocatalytic activity can be performed by modifying ZnO with the transition metals [21]. These process can decrease the band gap energy value and extend the absorbance range to the visible light areas [22]. On the other hand, CuO is a natural p-type semiconductor with a narrow band gap of 1.2 eV and a conductivity of 10^{-4} s/cm. CuO is widely applied in various catalysis reactions [23]. CuO nanoparticle also shows photocatalytic activity in the degradation of some dyes.

Several methods are used for metal oxide nanocomposite synthesis such as hydrothermal [7], electrochemistry [8], wet chemical [13], microwave method [24] coprecipitation, sol–gel, wet impregnation, and thermal decomposition [25–28]. The classical method to synthesis of metal oxide nanoparticles using hazardous chemicals and has a negative effect for the environment. Green synthesis of metal oxide nanocomposite has received special attention due to a cheaper and environmentally friendly method. It can refer to the formation of nanoparticle structures which capped by organic materials from living organisms or plants [29]. The plant which has been ever used to prepare ZnO nanoparticle was *Imperata cylindrical*, *Moringa oleifera*, *Adansonia Digitata*, *Vitex trifolia*, and *Tabernaemontana divaricata* [30–34], *while Callistemon viminalis* [35], Calotropis gigantea [36], and *Theobroma cacao* [37] were used to synthesis CuO nanoparticle. *Theobroma cacao* is the natural plants from Indonesia which has antioxidant activity. *Theobroma cacao* seed bark contains some secondary metabolite compounds such as flavan-3-ol and derivatives (including procyanidins), flavonols, N-phenylpropenoyl-L-amino acids, and alkaloid theobromine [38]. These compounds are used to synthesis the metal nanoparticle [39].

Zinc and copper material have been investigated as Cu–Zn alloy [40], core shell CuO–ZnO nanoparticle [41,42], ZnO/CuO nanocomposite by chemical method [24,43,44] and Cu@ZnO core shell nanoparticle [45]. However, ZnO/CuO nanocomposite by one-pot green synthesis method has not been ever investigated yet in the previous research. Moreover, ZnO/CuO nanocomposite has been known as a good photocatalyst that can work in the visible light area. The following researches related to this work about synthesis ZnO-CuO nanocomposite can be seen in Table 1.

In this study, ZnO/CuO nanocomposite was prepared for the first time by one-pot green synthesis method using the reaction of $Zn(NO_3)_2$ and $Cu(NO_3)_2$ solutions with the seed bark of *Theobroma cacao* extract and the calcinations of precipitate at 400 °C for 4 h. Herein, we investigate a simple and an environmentally friendly method to synthesis ZnO/CuO nanocomposite. To the best of our knowledge, there is no study about one-pot green synthesis of ZnO/CuO nanocomposite using *Theobroma cacao* seed bark extract (TBE) in the previous research. The modification of ZnO nanoparticle with CuO nanoparticle produces the framework structure of zinc, oxygen and copper in the nanocomposite. ZnO/CuO nanocomposite decrease the band gap energy of ZnO as a photocatalyst in the visible light area.

2. Materials and methods

2.1. Materials and methods

All precursors of $Zn(NO_3)_2.6H_2O$ and $Cu(NO_3)_2.3H_2O$ were used from Merck. *Theobroma cacao* seed bark (TB) was obtained from Bandar Lampung, Indonesia. TB was completely washed with distilled water, and dried at the room temperature for a week. Dried TB was grinded to get the fine powder. The 50 g powder was macerated in 250 ml methanol for a week by stirring continuously every day, then filtrated, and evaporated using vacuum rotary evaporator. The concentrated extract was fractionated with water and n-hexane. Each fraction was separated and phytochemically tested for the secondary metabolite presence of flavonoids, polyphenols, tannins, saponosides, steroids, terpenoids and alkaloids [47]. Furthermore, the aqueous fraction of *Theobroma cacao* seed bark extract (TBE) was used to prepare of ZnO/CuO nanocomposite by one-pot green synthesis method.

2.2. ZnO/CuO nanocomposite synthesis

Synthesis of ZnO/CuO nanocomposite was performed by adding TBE into 0.03 M $Zn(NO_3)_2$ and 0.01 M $Cu(NO_3)_2$ solutions to obtain mixed $Zn(OH)_2$ and $Cu(OH)_2$ colloids at room temperature. The colloid was separated using ultra centrifuge and dried, then calcined at 400 °C for 4 h. ZnO/CuO nanocomposite formation was detected by observing dark blue color of powder. The same method was done for green synthesis of ZnO and CuO for comparison, respectively.

2.3. ZnO/CuO nanocomposite characterization

Shimadzu 7000 X-ray diffraction was used to get a crystallinity of ZnO/CuO nanocomposite. Identification of functional groups of biocompounds in TBE was carried out using FTIR spectrophotometer (Perkin-Elmer). UV–Vis DRS (Shimadzu 2450) was used to determine the band gap energy of ZnO/CuO nanocomposite. SEM-EDX (Evo MA10-ZEISS instrument) was used to investigate the morphology and elements content of ZnO/CuO. TEM (JEM 1400) was used to observe the particle size and shape of nanocomposite. Fluorescence Spectrophotometer F-2700 was used to investigate the emission of ZnO/CuO nanocomposite.