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Research Article

Synthesis, Characterization and Catalytic Activity of Cu/Cu_2O Nanoparticles Prepared in Aqueous Medium

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Abstract

Copper/Copper oxide (Cu/Cu_2O) nanoparticles were synthesized by modified chemical reduction method in an aqueous medium using hydrazine as reducing agent and copper sulfate pentahydrate as precursor. The Cu/Cu_2O nanoparticles were characterized by X-ray Diffraction (XRD), Energy Dispersive X-ray Fluorescence (EDXRF), Scanning Electron Microscope (SEM), and Transmission Electron Microscope (TEM). The analysis revealed the pattern of face-centered cubic (fcc) crystal structure of copper Cu metal and cubic cuprites structure for Cu_2O. The SEM result showed monodispersed and agglomerated particles with two micron sizes of about 180 nm and 800 nm, respectively. The TEM result showed few single crystal particles of face-centered cubic structures with average particle size about 11-14 nm. The catalytic activity of Cu/Cu_2O nanoparticles for the decomposition of hydrogen peroxide was investigated and compared with manganese oxide MnO_2. The results showed that the second-order equation provides the best correlation for the catalytic decomposition of H_2O_2 on Cu/Cu_2O. The catalytic activity of hydrogen peroxide by Cu/Cu_2O is less than the catalytic activity of MnO_2 due to the presence of copper metal Cu with cuprous oxide Cu_2O. © 2015 BCREC UNDIP. All rights reserved.

Keywords: Cu/Cu_2O Nanoparticles; Copper/Copper oxide; Nanoparticles; hydrogen peroxide

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1. Introduction

Nano-materials involved transition metals and metal oxides become one of the hottest topics in materials science due to their special properties and potential applications [1-3]. Amongst these materials, the supported and unsupported copper and copper oxide nanoparticles are of great interest due to their advantages such as nontoxicity, abundance, high optical absorption coefficient and low band gap energies [4,5]. These characteristics make them prospective candidates for different applications such as catalysis, semiconductor equipment, solar/photovoltaic energy conversion, gas sensing, antimicrobial materials, luminescence sources field, emission devices, lithium-ion electrode materials and dye-sensitized solar cells [6-9]. Copper nanoparticles have a high antimicrobial activity against *Bacillus Subtilis*. Copper ions released may also interact with DNA molecules and intercalate with nucleic acid

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strands. Copper ions inside bacterial cells also disrupt biochemical processes [10].

CuO is a *p*-type semiconductor with a narrow band gap (1.2 eV) and exhibits a number of interesting properties [11]. Copper oxide based materials have widespread applications [12, 14]. CuO crystal also has photocatalytic or photovoltaic properties and photoconductive functionalities [15]. As CuO is cheaper than silver, easily mixes with polymers and relatively stable in terms of both chemical and physical properties, it finds a wide application [16]. The synthesis of metallic copper nanoparticles surrounded by amorphous CuO, in the presence of poly(vinylpyrrolidone) as a protecting agent, via a polyol method in ambient atmosphere was described in previous works [17].

The novel synthesis of copper and copper oxide nanoparticles using the chemical reduction method and its physicochemical characterization were reported [18]. The nanoparticles have been prepared using copper(II) succinate as precursor. Copper nanoparticles are initially formed and subsequently oxidized to copper oxide. The copper nanoparticles showed excellent activity against Escherichia coli and Staphylococcus aureus, with excellent inhibition zones [18].

Copper based nano-material containing different phases of copper, $CuO/Cu_2O/Cu$, was prepared by the glycine assisted combustion method [19]. The results of X-ray diffraction (XRD) and scanning electron micrographs (SEM) revealed that the investigated method led to formation of mixture of $CuO/Cu_2O/Cu$ by using a certain amount of glycine as a fuel. CuO, Cu_2O nanoparticles and Cu/Cu_2O composite nanoparticles of different sizes have been hydrothermally synthesized by varying the reaction temperature and in the presence of biocompatible surfactants; polyoxyethylene, sorbitan laurate, polyethylene glycol 1000 and polyethylene glycol 8000 [20]. The copper-containing phases - copper oxide (CuO), cuprous oxide (Cu_2O), copper aluminate ($CuAl_2O_4$), zinc oxide (ZnO) and zinc aluminate ($ZnAl_2O_4$) were prepared by thermal reactions [21]. Capture of CO_2 and conversion to syn-gas by the samples of copper and zinc aluminates at higher temperatures were observed.

In the present work, the synthesis of Cu nanoparticles was studied using a modified reducing method in aqueous medium. Cuprous oxide (Cu_2O), which was later confirmed in XRD, may be produced via partial oxidation of Cu in aqueous or acid medium. Cu_2O may be also formed by reduction of copper ions Cu^{2+} to cuprous ions Cu^{2+}. Then the cuprous ions react with hydroxyl in the aqueous medium to form cuprous oxide. For synthesis of pure Cu, such a finding consider a non-aqueous system to avoid the formation of copper oxide. Further chemical and morphology structures were investigated for Cu/Cu_2O nanoparticles. The catalytic activity of Cu/Cu_2O nanoparticles for the decomposition of hydrogen peroxide, in comparison with manganese oxide MnO_2, was investigated and analyzed by fitting various kinetic order equations.

2. Materials and Methods

2.1. Synthesis of Cu/Cu_2O Nanoparticles

Cu/Cu_2O powder was obtained by reaction of an aqueous solution of copper sulfate pentahydrate (Fluka) with hydrazine hydrate (Sigma-Aldrich) in ammonia chloride solution. In a modification of preparation of copper powder [22], 100 ml solution containing 50 g (80%) hydrazine hydrate was added dropwise for 40 min to 200 ml aqueous mixture of $CuSO_4 \cdot 5H_2O$ (40g), NH_4Cl (15 g) and aqueous ammonia (70 ml, 28%) with stirring. The temperature was kept below 30 °C. Then, the solution was heated to 80 °C for 2 h to carry out the reaction sufficiently, to reduce the copper ion in the solution to metallic copper. The Cu/Cu_2O powder was recovered from the solution by filtration, washed and dried under vacuum.

2.2. Characterizations

X-ray diffraction pattern was recorded in the continues scanning mode at room temperature on an EMPYREAN Diffractometer system operated at 45 kV and a current of 30 mA using Cu tube with Cu Kα radiation (λ = 1.5406 Å). The diffraction intensities were recorded from 10^o to 80^o, in 2θ angles. The diffraction intensity was compared with the standard ICSD collection files. Elemental analysis was performed using Energy Dispersive X-ray Fluorescence system (Jeol JSX - 3222 element analyzer) system. The scanning electron microscope for samples was performed using SEM (Quanta 250 Field Emission Gun), with accelerating voltage 30 kV and magnification 14X up to 1000000. The morphological analysis was analyzed using transmission electron microscopy (JEOL JEM-2100).

2.3. Catalytic decomposition of hydrogen peroxide

To investigate the catalytic activity of Cu/Cu_2O nanoparticles for the decomposition of hydrogen peroxide (0.09 M H_2O_2), different Cu/Cu_2O concentrations, 0.08, 0.20 and 0.40 g/l, at 25 °C were used. The solution was stirred uniformly. After an interval time; 5ml of the reaction mixture was withdrawn by pipette from the beaker and was rapidly added to 5 ml of 1.0 M H_2SO_4 solutions and then titrated against 0.02 M of $KMnO_4$ solution until color disappearance.

3. Results and discussion

3.1. Synthesis of Cu/Cu₂O nanoparticles

Hydrazine hydrate and $NH_4Cl/NH_3 \cdot H_2O$ were used as reductant and buffer agent, respectively [22]. Hydrazine (N_2H_4) is a powerfully strong reductant widely used in various chemical operations. The optimum reduction of Cu can be achieved at pH > 11 [23]. The solution of Cu^{2+} was blue before being reduced, and became yellow after reduction. In this process, the following chemical reaction occurred:

$$Cu^{2+} + 4NH_3 \longrightarrow [Cu(NH_3)_4]^{2+} \quad (1)$$

$$2[Cu(NH_3)_4]^{2+} + N_2H_4 \longrightarrow 2Cu + N_2 + 4NH_3 + 4NH_4^{+} \quad (2)$$

In aqueous ammonia media, ammonia reacts with Cu^{2+} according to the reaction (1) and $[Cu(NH_3)_4]^{2+}$ complex was reduced to obtain fine copper powder as being seen in Equation (2). The copper ions Cu^{2+} may be reduced to cuprous ions. Then the cuprous ions react with hydroxyl in the system to form cuprous oxide [24]:

$$Cu^{2+} + e^{-} \longrightarrow Cu^{+} \quad (3)$$

$$2Cu^{+} + 2OH^{-} \longrightarrow Cu_2O + H_2O \quad (4)$$

Cuprous oxide may be produced via oxidation of Cu as follow:

$$4Cu + O_2 \longrightarrow 2Cu_2O \quad (5)$$

Additives, such as: water and acids, affect the rate of this process as the further oxidation to copper(II) oxides [25].

3.2. Characterizations

The characterization techniques that are commonly used to study the crystal structure and chemical composition of products include X-ray diffraction and Energy dispersive X-ray fluorescence (EDXRF). Figure 1 showed the XRD pattern of the product prepared by the solution containing $CuSO_4 \cdot 5H_2O$ and hydrazine hydrate. The diffractogram exhibits the characteristic peaks of two phases; crystalline metallic copper (cubic) and Cu_2O (cubic). This means that Cu^{2+} ions were reduced to Cu and Cu^{+1}. The spectrum of Cu shows the peaks corresponding to 2θ = 43.23, 50.51, 74.30 with d-spacing = 2.09, 1.81, 1.28, respectively. All peaks can be attributed to the cubic form of metallic copper [26]. The spectrum of Cu_2O shows the peaks corresponding to 2θ = 29.63, 36.37, 42.45, 61.64, 73.75 with d-spacing = 3.02, 2.46, 2.13, 1.51, 1.28, respectively. These peaks are

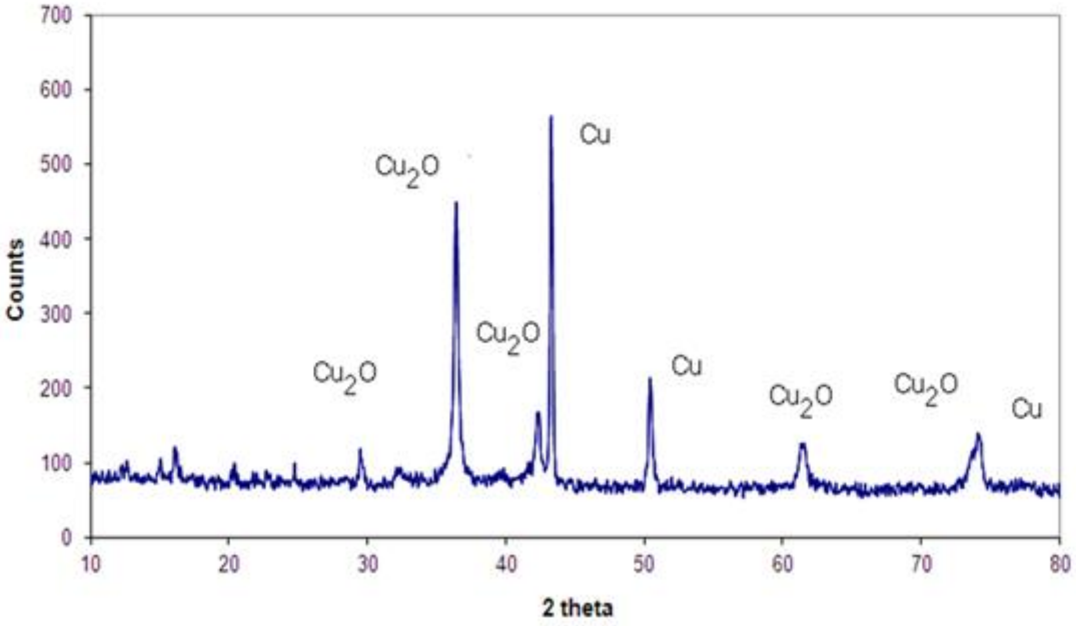

Figure 1. XRD of Cu/Cu_2O nanoparticles

very close to that given by JCPDS data of XRD for copper (cubic) and Cu_2O (cubic). No other diffraction peaks arising from metal CuO appear in the XRD patterns.

Energy dispersive X-ray fluorescence (XRF) was carried out to determine elemental composition of nanoparticles. The spectrum (Figure 2) shows two peaks CuKα (8.06 keV) and CuKβ (8.93 keV) characteristic of copper with 97.25% element content. The impurities calculated from XRF are 2.75% element of sulfur.

Figure 3 shows the TEM image of Cu/Cu_2O nanoparticles synthesized by chemical reduction with hydrazine hydrate. It shows that higher tendency of agglomerations of nanoparticles in agglomerated bulks. On the edges, few particles are single crystals of face-centered cubic structures. The actual size of nanoparticles is estimated from TEM micrograph. The average particle size is about 11-14 nm.

The morphology of the prepared particles was studied by SEM as shown in Figure 4. From SEM photographs, we can distinctly find monodispersed and agglomerated particles of two micron sizes. The particles are spherical-like and have uniform sizes of about 18 µm and 0.80 µm (Figure 4). These results confirm the analysis by XRD for the formation of copper and cuprous oxide nanoparticles by chemical reduction with hydrazine hydrate.

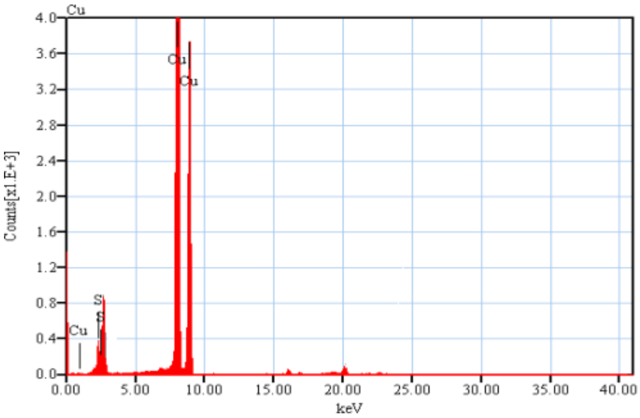

Figure 2. XRF of Cu/Cu_2O nanoparticles

3.3. Catalytic decomposition of H_2O_2

The decomposition of hydrogen peroxide (H_2O_2) has been used as a model reaction for the investigation of the catalytic activity of various metal complexes [27] as follow:

$$H_2O_2 \longrightarrow H_2O + 1/2O_2 \tag{6}$$

The rate of decomposition can be accelerated by transition metal compounds due to their higher activity. Manganese oxide is considered as an active catalyst for decomposition of hydrogen peroxide. The amount of the decomposed H_2O_2 % was estimated against the time of catalytic reaction using different Cu/Cu_2O concentrations, 0.08, 0.20 and 0.40 g/l, at room temperature as shown in Figure 5. The decomposition increases and then slows with reaction time. The decomposition of hydrogen peroxide can be described by the second order kinetic expression as follow:

$$d[H_2O_2]/dt = k\,[catalase][H_2O_2] \tag{7}$$

The kinetic of the catalytic activity of Cu/Cu_2O nanoparticles for the decomposition of hydrogen peroxide was analyzed by fitting various kinetic order equations. Figure (6) indicates that the decomposition of H_2O_2 on

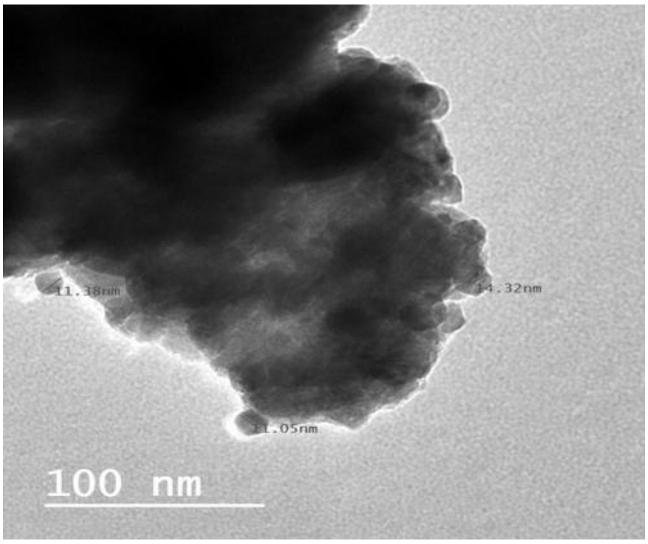

Figure 3. TEM of Cu/Cu_2O nanoparticles

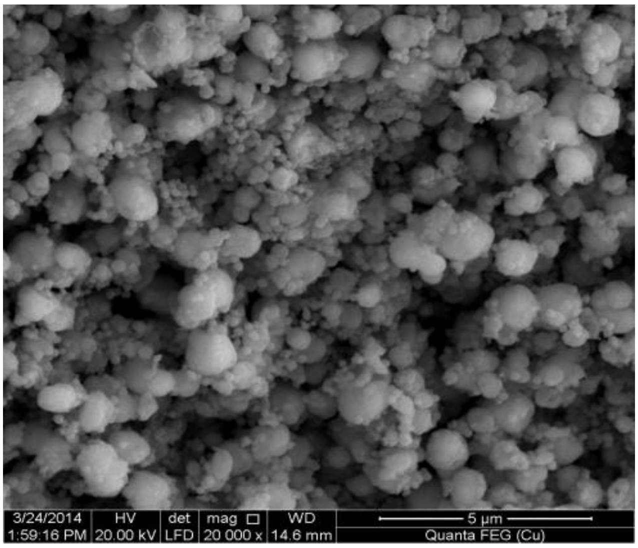

Figure 4. SEM of Cu/Cu_2O nanoparticles

Cu/Cu_2O is in a second-order reaction with rate constants of 0.013, 0.076 and 0.145 $M^{-1}.min^{-1}$ for Cu/Cu_2O concentrations of 0.08, 0.20 and 0.40 g/l, respectively.

The catalytic effect of Cu/Cu_2O was compared to that of manganese oxide for the decomposition of hydrogen peroxide at catalyst concentration of 0.08 g/l. Figure 7 shows that the reaction rate of Cu/Cu_2O (0.013 $M^{-1}.min^{-1}$) is less than the reaction rate of MnO_2 (0.26 $M^{-1}.min^{-1}$). The catalytic activity of hydrogen peroxide by Cu/Cu_2O is less than the catalytic activity of MnO_2 due to the presence of copper metal Cu with cuprous oxide Cu_2O. The affinity of $HO^{\bullet}$ towards the surfaces of the oxides, depends on the type of oxide. The obtained trend for adsorption energies of $HO^{\bullet}$ onto the different metal oxides is inversely proportional to the variation in ionization potential of the metal cation [28].

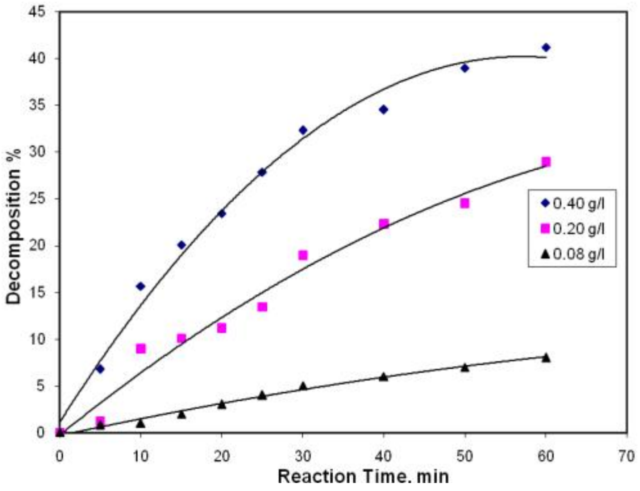

Figure 5. Decomposition of H_2O_2 % (percentage of the reacted H_2O_2) against reaction time, min

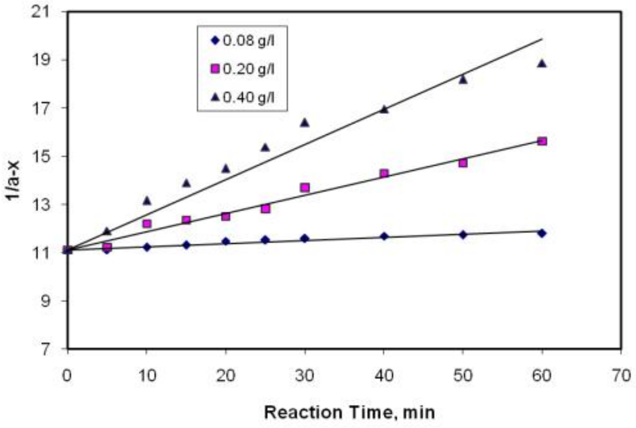

Figure 6. $1/(a\text{-}x)$ against time of reaction, min, for decomposition of H_2O_2 on Cu/Cu_2O, where a and x are the initial and the reacted concentrations of H_2O_2, respectively.

4. Conclusion

Copper/Copper oxide Cu/Cu_2O nanoparticles were synthesized by the chemical reduction method using hydrazine as reducing agent and copper sulfate pentahydrate as precursor. Copper nanoparticles were initially formed and subsequently partially oxidized to copper oxide. Cu_2O may be formed by reduction of copper ions Cu^{2+} to cuprous ions Cu^{2+}. Then the cuprous ions react with hydroxyl in the aqueous medium to form cuprous oxide. For synthesis of pure Cu, unaqueous system is considered to avoid the formation of copper oxide. The XRD analysis revealed the pattern of the fcc crystal structure of copper Cu metal and cubic cuprites structure for copper oxide Cu_2O. The SEM showed monodispersed and agglomerated particles with two micron sizes of about 180 nm and 800 nm, respectively. The TEM showed few single crystal particles of face-centered cubic structures with average particle size about 11-14 nm. The second-order equation provides the best correlation for the catalytic decomposition of H_2O_2 on Cu/Cu_2O. The catalytic activity of hydrogen peroxide by Cu/Cu_2O is less than the catalytic activity of MnO_2 due to the presence of copper metal Cu with cuprous oxide Cu_2O.

Acknowledgments

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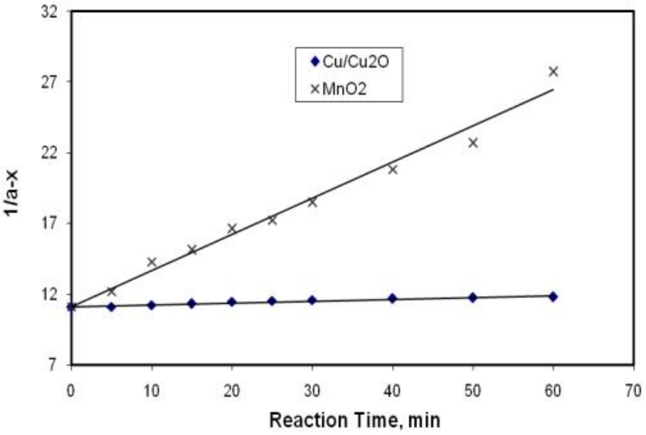

Figure 7. Comparison between Cu/Cu_2O and MnO_2 for the decomposition of hydrogen peroxide, where a and x are the initial and the reacted concentrations of H_2O_2, respectively

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