

Preparation, Characterization and Catalytic Activity of Copper(II) Oxide Nanoparticles

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Abstract

An environmental benign synthetic route was used for preparation of copper(II) oxide nanoparticles from copper(II) sulphate precursor. Precipitates of copper(II) hydroxide were prepared from $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and NaOH. The product was then calcined at 350°C to get the expected copper(II) oxide nanoparticles. Characterization of prepared sample was carried out by scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), FTIR spectroscopy, X-ray powder diffractometry and reflectance measurement. SEM images show that the particle size was less than 100 nm. It is evident from the EDS analysis that the prepared sample was pure and contains only the atoms of Cu and O. XRD pattern confirmed the presence of only CuO in the sample. This result was supported by FTIR spectrum. The prepared CuO was used to study the adsorption and photodegradation of brilliant red (BR) in aqueous medium. The catalytic activity of CuO was investigated and compared with that of commercial CuO.

Keywords: Copper(II) oxide, Brilliant Red, Adsorptive activity and Photocatalytic activity.

I. Introduction

Introduction of nano-technology in the field of material science gives a new dimension in the development of solid state chemistry. Increase in surface area with decrease in particle size is the unique property of particle. Semiconductor nanoparticles are attracting more interest due to their vast application in the field of photocatalysis, optoelectronics, solar cell, water purification, H_2 production etc¹⁻³.

The oxides of transition metals are an important class of semiconductors, which have applications in magnetic storage media, solar energy transformation, electronics and catalysis⁴⁻⁶. Among the oxides of transition metals, copper(II) oxide nanoparticles are of special interest because of their low band gap energy which is in visible range in the electromagnetic spectrum of light. CuO is a semiconducting compound with a narrow band gap and used for photoconductive and photo thermal applications.⁷ However, the reports on the preparation and characterization of nanocrystalline CuO are relatively few to some other transition metal oxides such as zinc oxide, titanium dioxide, tin dioxide and iron oxide. Some methods for the preparation of nanocrystalline CuO have been reported recently such as the sonochemical method⁸, sol gel technique⁹, one step solid state reaction method at room temperature¹⁰, electrochemical method¹¹, thermal decomposition of precursors and co-implantation of metal and oxygen ions and so on. In 1993 Hai-Yan, Yu-Ling, Jing-Kui, and Si-Shen published a preparative method for ultrafine CuO particles utilizing deposition of an aqueous CuO sol onto a SrTiO_3 substrate.¹² In 1997 Kakihata, Usami, Yamamoto and Shibata published a route to CuO powder from copper chloride by a precipitation stripping method. The average particle size for the resultant CuO was found by laser light scattering to be about 600 nm. In 1998 Dianzeng, Jianqun, and Xi reported on a solid-state reaction between copper chloride and sodium hydroxide to prepare copper(II) oxide.¹³

II. Experimental

Preparation of copper(II) oxide from copper(II) sulphate

A solution of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was prepared in a beaker and 1M solution of NaOH was added to it with continuous stirring. A blue precipitate was formed. The solution was kept for half an hour and a few more drops of NaOH were added for complete precipitation. Finally the blue precipitate of $\text{Cu}(\text{OH})_2$ was separated by filtration and washed several times by deionized water to make it neutral. The precipitate was collected in a watch glass and dried in an oven at about 95°C . After that, it was grained into powder by a mortar. The powder was taken in a dry, empty porcelain dish. To calcine the powder the dish was put in a muffle furnace and the temperature of the furnace was maintained in the range of 350°C – 360°C for three hours.

Characterization of prepared copper(II) oxide

Surface morphology, particle size, stoichiometry, functional groups, crystallinity and band gap energy of the prepared copper(II) oxide were investigated by scanning electron microscopy, energy dispersive X-Ray spectrometer, Fourier transform infrared spectrophotometer, X-ray diffractometer and reflectance measurement.

Adsorptive and photocatalytic activity of oxide

0.10 g prepared CuO was added to the 90.0 mL water to prepare suspension and it was kept overnight so that particles can soak water. 10.0 mL of brilliant red (BR) solution was to the suspension in a 100 mL beaker. To study the adsorption, in absence of light the beaker containing suspension was placed on a magnetic stirrer in the lamp house. Initial concentration of BR was determined by taking little amount of suspension in a semi-micro test tube just after mixing. After that, suspensions were collected in test tubes at different times and centrifuged at a constant speed for 30 minutes to obtain clear solution. The absorbance of these centrifugates was measured at λ_{max} of BR using deionized water as reference. The pH of deionized water was kept same as pH of suspension. Experiments were carried out in ambient temperature. Amount of BR adsorbed on copper(II) oxide was calculated using the following equation

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$$q_t = (C_i - C_t) \times \frac{V}{W}$$

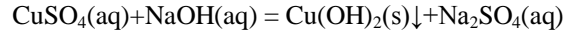
where, C_i and C_t are the concentrations of BR (mg. L^{-1}) at zero time and at time t . V is the volume of the suspension in liter and W is the weight of CuO in g. Concentration of BR in suspension was calculated using Beer- Lambert Law. The amount adsorbed was plotted as a function of time in Fig. 6(a).

The photocatalytic activity of the prepared copper(II) oxide was investigated by irradiating the suspension with ultra-violet light (wavelength ~ 254 nm) in a closed lamp house, inner walls of which were covered with aluminium foil to

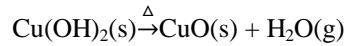
prevent the loss of light by absorption. Before irradiation the suspension was agitated for an hour to reach the equilibrium of adsorption in dark. The suspension was collected and investigated in the same way as done during adsorption study.

III. Results and Discussion

The formation of copper(II) oxide follows simple chemical reactions;



Precipitate



SEM image and EDS spectrum of copper(II) oxide

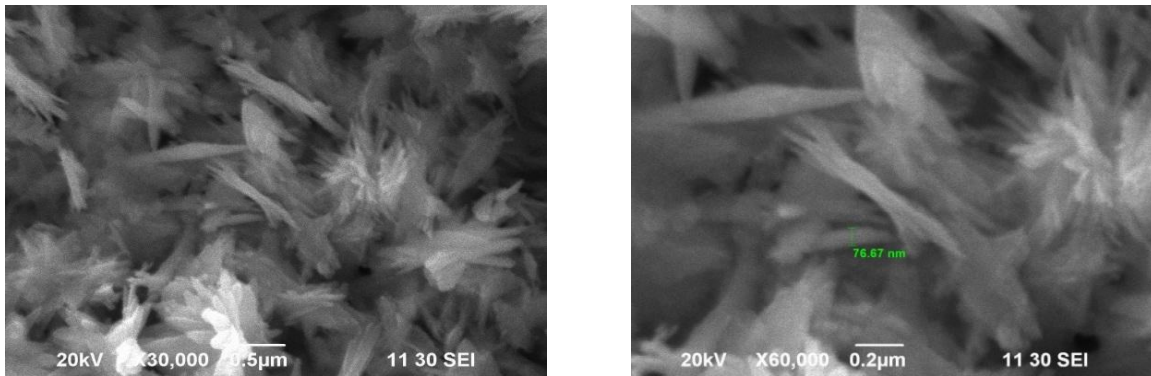


Fig. 1(a). SEM image of prepared copper(II) oxide at 30000 and 60000 magnification.

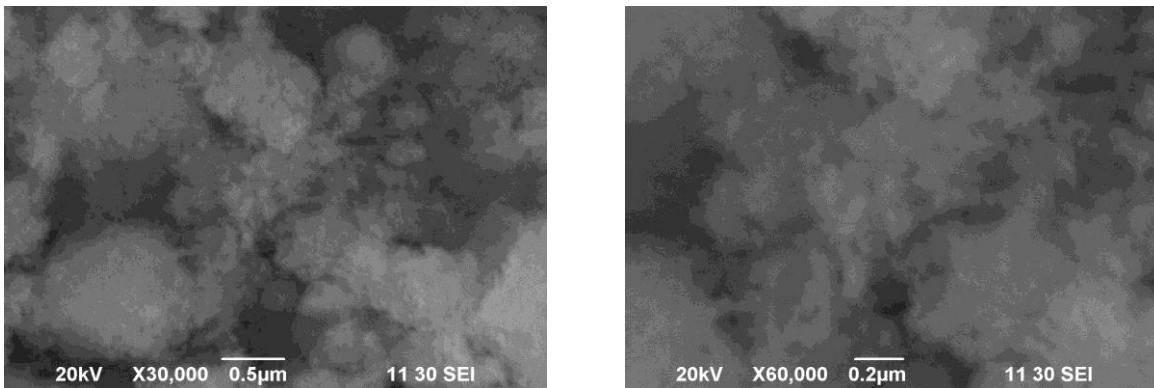


Fig. 1(b). SEM image of commercial copper(II) oxide at 30000 and 60000 magnification.

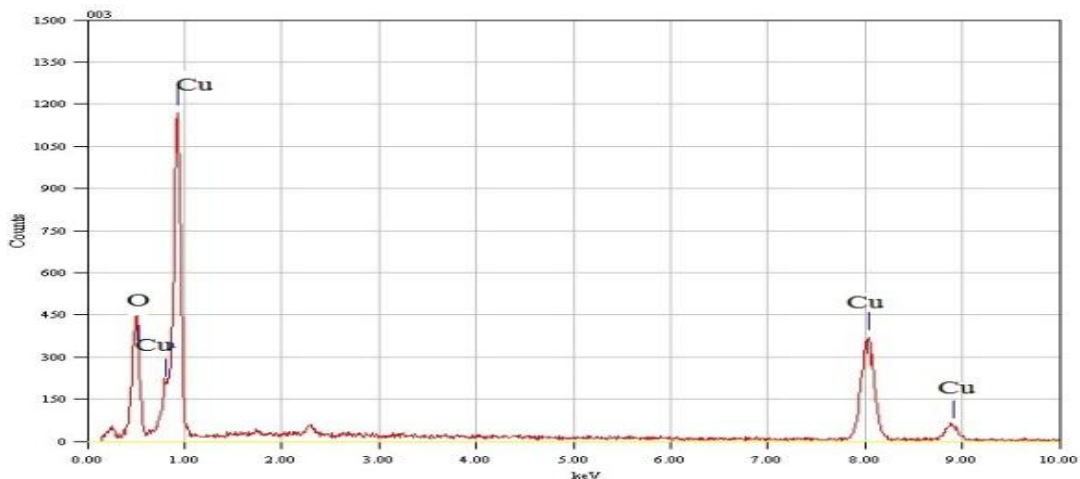


Fig. 2. EDS spectrum of copper(II) oxide

The morphology of the CuO powder was examined by SEM. The SEM images in Fig. 1(a) show the fibrous shape of particles and the diameter of the particle of CuO has been estimated to be 76.67 nm approximately at 60000 magnification. SEM images in Fig. 1(b) of commercial copper(II) oxide indicate that particles are mostly coagulated and form lumps.

The EDS spectrum shows the peaks only for Cu and O atoms which bear the evidence of purity of the oxide sample (Fig. 2). The abundance of Cu and O atoms in the sample was shown to be 52.84 and 47.16 respectively by the ZAF standerless method. This result suggests that the sample is CuO.

FTIR spectrum of copper(II) oxide

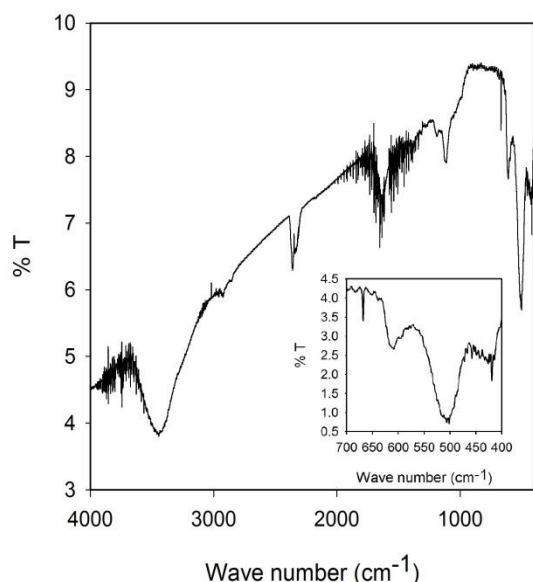


Fig. 3. FTIR spectrum of copper(II) oxide.

The peaks at 1650 cm^{-1} and 3438 cm^{-1} in FTIR spectrum were due to H-O-H bending and O-H stretching vibration (Fig. 3). Due to the presence of atmospheric CO_2 , a weak band appeared at about 2300 cm^{-1} .¹⁴ The stretching mode of vibration of C=O is observed at 1640 cm^{-1} . The bands at about 419.3 cm^{-1} , 506.8 cm^{-1} and 612.6 cm^{-1} have been assigned to the stretching mode of vibrations of Cu-O.¹⁵⁻¹⁷ Absorption bands at 668.7 cm^{-1} and 1114.5 cm^{-1} were due to the SO_4^{2-} bending and stretching vibration respectively.^{18,19} Hence the prepared copper(II) oxide sample contains trace amount of impurities.

XRD pattern of copper(II) oxide

The XRD peaks can be indexed as monoclinic CuO (Fig. 4) (space group C2/c; JCPDS cards no. 48-1548). According to the standard XRD pattern of the CuO powder, the peaks at 35.5498° , 38.7624° , 48.7916° and 58.354° can be endorsed to the Miller indexes of (-111), (200), (-202) and (202).²⁰ No reflections from impurities ($\text{Cu}(\text{OH})_2$ or Cu_2O) were detected in the sample. In this case, the indexed diffraction rings can be again attributed to (-111), (200), (-202) and

(202) planes of monoclinic CuO.

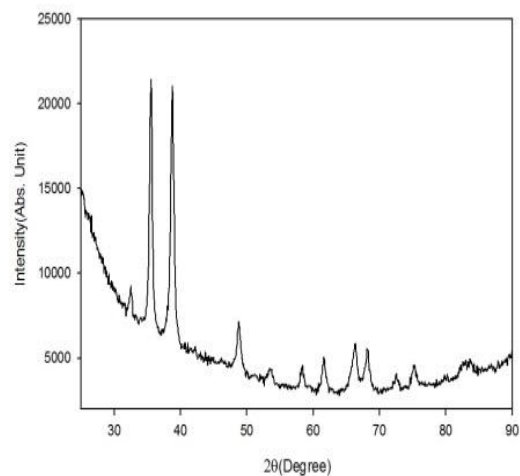


Fig. 4. XRD pattern of CuO.

Reflectance spectrum of copper(II) oxide

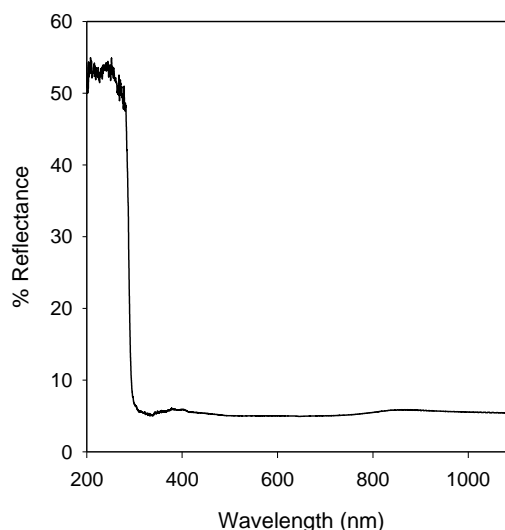


Fig. 5. Reflectance measurement of the prepared copper(II) oxide.

Fig. 5 shows a sharp increase of the reflectance at 300 nm. This characteristics of reflectance spectrum may be attributed to the band gap energy of the prepared copper(II) oxide.²¹

Adsorptive activity

Adsorption is the major prerequisite condition for any heterogeneous catalytic reaction. The extent of adsorption greatly depends on the particle size of the catalyst and the degree of interaction between the catalyst surface and the dye molecules. It was found from SEM images that CuO nanoparticles are fiber in shape and the average diameter of CuO nanoparticles was determined to be 76.67 nm. Adsorption of BR on prepared copper(II) oxide and commercial copper(II) oxide at pH 6.20 under same experimental conditions is shown in Fig. 6(a). Comparative

catalytic activity of prepared copper(II) oxide and commercial copper(II) oxide is shown in Fig. 6(b). Amount adsorbed of BR on prepared copper(II) oxide at experimental conditions is 32.23 mg/g and for commercial copper(II) oxide is 28.15 mg/g.

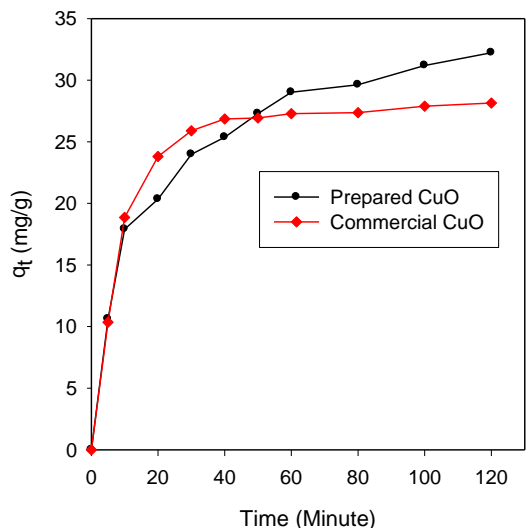


Fig. 6(a). Change of amount adsorbed of BR on CuO with time for the initial concentration of 36.92 mgL^{-1} at pH 6.20.

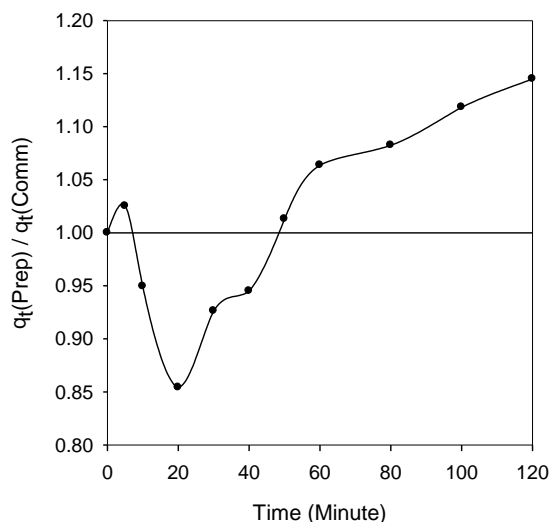


Fig. 6(b). Ratio of amount adsorbed of BR on prepared and commercial CuO with time at same conditions.

Adsorptive activity of prepared copper(II) oxide is about 1.15 times higher than that of commercial copper(II) oxide. This enhanced adsorptive activity of prepared copper(II) oxide is mainly due to the particle size of the prepared oxide and which is in nano-scale. Adsorptive activity of adsorbent increases with the decrease of particle size because with the decrease of particle size effective surface area increases. In Fig. 6(b), the ratio $q_t(\text{prep.})/q_t(\text{comm.})$ is plotted against time interval to understand the way of changing the adsorptive activity of both the samples. At the beginning the $q_t(\text{prep.})$ is slightly higher than $q_t(\text{comm.})$ but soon after nearly ten minutes the ratio becomes unity suggesting that the

adsorptive activity of both the samples becomes equal. During next twenty minutes the sharp decrease of the ratio suggests the increased adsorption on commercial oxide which is due to the adsorption of BR molecules on heterogeneous surface of the lumps of commercial oxide. Soon after twenty minutes the ratio starts increasing and becomes unity again after fifty minutes. Finally beyond fifty minutes adsorptive activity of prepared oxide increases and overcomes that of commercial oxide and sharp increase is observed with time. The slow adsorption of BR on prepared oxide in the beginning is due to its fibrous shape of particles. As the time passes adsorption increases because of smaller size and higher surface area of particles.

Photocatalytic activity

From the spectrum of Fig. 7, it is evident that absorbance does not change significantly with the irradiation time of the degradation of BR in the suspension of prepared copper(II) oxide. The result shows that the BR undergoes only 4% degradation during one hour irradiation. It means CuO is not advisable to use as photocatalyst to the degradation of dye unless the experimental conditions are changed or surface of the oxide is modified.

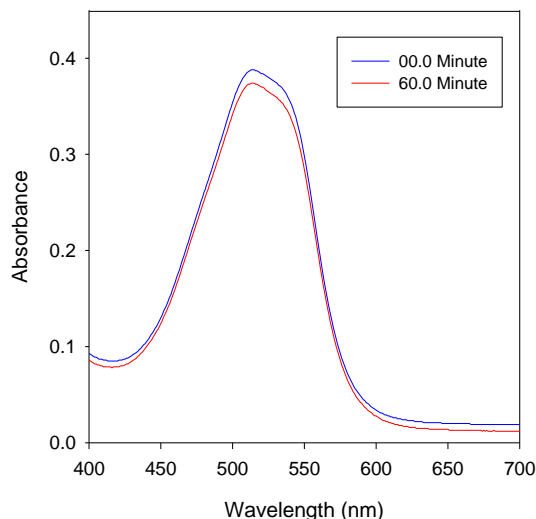


Fig. 7. Spectrum for the degradation of BR in the suspension of prepared copper(II) oxide at pH 6.20 in different times in presence of ultra-violet light.

Tajmeri S. A. Islam et al.²² has investigated that the composite of CuO and Cu_2O is an efficient photocatalyst for Methylene blue. 95.5% of Methylene blue has been found to be degraded in presence of visible light during three hours irradiation. The CuO aerogel (80% Cu^{I} + 15% Cu^{II} + 5% Cu^0) mediated degradation of nitrophenols by irradiation under solar simulator was also investigated by J. Bandara, J. Kiwi.²³

IV. Conclusion

In the present investigation CuO have been prepared from copper(II) sulphate and characterized by different techniques e.g. SEM, EDX, XRD FTIR and also by reflectance measurement. SEM image of the prepared

copper(II) oxide shows that diameter of the particle is about 76.67 nm. EDS result suggests that copper(II) oxide is quite pure. FTIR and XRD pattern are also consistent with literature value.

Adsorption of BR on copper(II) oxide shows that adsorptive activity of prepared copper(II) oxide is about 1.15 times higher than that of commercial copper(II) oxide. This enhanced adsorptive activity is mainly due to the nano-size particles of the prepared copper(II) oxide, which has larger surface area.

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