

SYNTHESIS AND CHARACTERIZATION OF COPPER OXIDE NANOPARTICLES BY SOLUTION COMBUSTION METHOD: PHOTOCATALYTIC ACTIVITY UNDER VISIBLE LIGHT IRRADIATION

K. THARANI, L.C. NEHRU[#]

Department of Medical Physics, School of Physics, Bharathidasan University, Tiruchirappalli-24, Tamil Nadu, India, [#]e-mail: lcnehr@bdu.ac.in

Abstract. Copper oxide nanoparticles (CuO-NPs) have been prepared by solution combustion method by using copper nitrate and glycine. The prepared powder was characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), UV-Vis spectroscopy, scanning electron microscopy (SEM), energy-dispersive spectroscopy (EDX) and fluorescence spectroscopy. The synthesized powder were monoclinic phase and the average particle size was in the range of 20–30 nm. The FTIR results showed the functional groups required for the reduction of copper ions. The UV-Vis and fluorescence spectroscopy showed the optical property and the result shows the band gap energy of CuO nanoparticles were 6 eV. The SEM result shows a uniform spherical nanostructures and particle size is 48 nm. The photocatalytic activity of CuO nanoparticles were studied by the rhodamine B under visible light irradiation.

Keywords: CuO, combustion, XRD, photocatalytic activity.

INTRODUCTION

Copper oxide nanoparticles are technologically interesting due to their physical and chemical properties, and they can be applied in high temperature super conductors, catalysis, batteries, gas sensors, solar energy conversion. Copper (II) oxide, CuO, also known as cupric oxide, is a p type semiconductor with a band gap of 1.2–1.9 eV. It is a black transition metal oxide with monoclinic crystal structure and many interesting characteristics, *e.g.*, high thermal conductivity, photovoltaic properties, high stability and antimicrobial activity. Because same useful properties, CuO has been investigated extensively for its wide range of potential applications, such as, electrochemical cell, gas sensors, magnetic storage devices, field emitters and in catalysis [1, 3]. In the past decades different methods have been proposed as to how to synthesize CuO nanoparticles. Through great efforts by many researches many methods were found conducive to produce

Received: December 2019;
in final form April 2020.

well-dispersed nanoparticles with varying with size and shapes, such as thermal oxidation, sol-gel technique, sonochemical method, electrochemical method, microwave irradiation, wet chemical/alcothermal method [7], electro deposition [6], hydrothermal treatment [8], high temperature combustion [5], gas-phase oxidation [2], quick precipitation [9], etc. But of these methods only hydrothermal and quick precipitation are of importance because they involve safe and environmentally friendly synthesis methods at moderate temperatures and easily preparation. According to the latest research, varying reaction microscopic environment using oil-water mixed solvent as medium may result in the different shape and size of the nanoparticles. In this article we discuss CuO nanoparticles prepared by low temperature combustion method by using fuel glycine.

MATERIALS AND METHODS

All the reagents used in the experiments were analytically pure and were purchased from MERCK Company, and were used as received without further purification. Nanocrystalline CuO was synthesized by a solution combustion method using glycine as fuel. Stoichiometric amounts of copper nitrate and glycine were dissolved in deionized water and poured into a quartz container can be mixed well by magnetic stirring for 1/2 h, which makes them almost as homogeneous mixtures, which was placed in a muffle furnace. Initially, the solution boils and undergoes dehydration followed by decomposition with the evolution of large amount of gases with white fumes coming out. After the solution reaches the point of spontaneous combustion, it begins burning and releases a large amount of heat, vaporizes all the solution instantly and becomes a foamy white solid powder.

The synthesized CuO powders identified the phase formation by powder X-ray diffraction (PXRD) method using a “X” Pert PRO PAN analytical diffractometer using nickel-filtered Cu-K α radiation ($\lambda = 0.15418$ nm) as source and operated at 40 kV and 30 mA. The sample was scanned in the 2θ ranging from 10 to 80 ° for 2 s in the step scan mode. The observed peak positions were compared with the standard ICDD data and Miller indices were assigned to the Bragg peaks. The composition analyses of samples were obtained on a Hitachi S4800 scanning electron microscope equipped with an energy-dispersive X-ray spectrometer (EDX). SEM measurements were mounted on aluminum studs using adhesive graphite tape and sputter coated with gold before analysis. Infrared spectra were recorded on a Nicolet Avatar 360 FTIR spectrometer using KBr pellets. UV–Vis absorption spectra were recorded on a Shimadzu UV-2550 spectrophotometer.

PHOTOCATALYTIC DEGRADATION OF RHODAMINE B

The photocatalytic activity of the CuO-NPs was investigated for the degradation of RhB under visible light irradiation. The photo reactor Heber Visible

Annular Type Photo Reactor equipped with 300 W tungsten halogen lamp (8,500 lumen) was used for the investigation. The photo reactor was comprised of a borosilicate immersion jacketed tube to hold the lamp with inlet an outlet for water circulation to cancel the IR radiation. The immersion well is held at the centre of a reaction chamber. The inner surface of reaction chamber is fitted with highly polished anodized aluminum reflector. The depth of the solution was 8 cm and the internal diameter of test tube was 1.6 cm. The distance from test tubes to lamp was 10 cm. The photoreactor was kept open to air to get sufficient oxygen for photochemical reaction. The dye with concentration of 1.0×10^{-5} M was used in the present study. In each experiment, 10 mg of the prepared photocatalyst (CuO-NPs) was mixed with 50 mL of above dye solution and then sonicated for about 15 minutes in a sonicator. The above reaction mixture was loaded in the photoreactor and again stirred well for about 30 minutes in dark to attain adsorption–desorption equilibrium condition, then exposed to light. To see the catalytic activity of as prepared CuO-NPs, RhB degradation was carried out for both photocatalyst. At regular time intervals, 5 mL of sample have been collected from the reactor and then centrifuged to remove photocatalyst. After centrifugation UV-Vis absorption spectra have been taken to monitor the degradation of RhB dye by monitoring the characteristic absorption peak intensity at ~ 554 nm. The centrifuged solution was used to monitor and the concentration of RhB and obtained by UV-Vis spectrophotometer (UV–3600, Shimadzu).

The reaction time ranged from 0 to 40 min. The degradation (η) of RhB was calculated by the formula:

$$\eta = (A_0 - A_t) / A_0 \times 100, \quad (1)$$

where A_0 is the initial absorbance at time $t = 0$, A_t is the absorbance at time t .

RESULTS

The XRD pattern shows (Fig. 1a) that the synthesized fuel-deficient composition powder was not a single-phase and some additional peaks are obtained due to incomplete combustion reaction. When the fuel is Stoichiometric, the oxygen content of copper nitrate is exactly sufficient to consume/oxidize the fuel), single-phase CuO powder was obtained. The phase identification of the as-prepared CuO was determined by X-ray diffraction (XRD). It is indicated in the reflecting planes (1 1 0), (1 1 1), (2 0 0), (2 0 2), and (1 1 3) in the patterns, which can be perfectly indexed to the monoclinic phase. Also, no diffraction peaks corresponding to Cu and other impurities are observed in these patterns. The value of lattice parameters ($a = 4.6$ Å, $b = 3.4$ Å, and $c = 5.1$ Å) was good agreement with the standard diffraction patterns (48–1548).

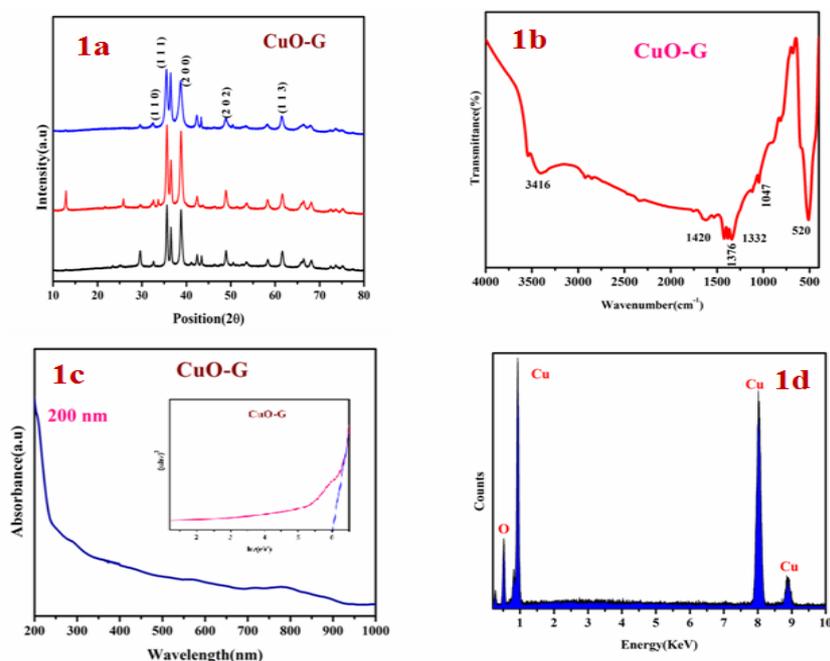


Fig. 1. Spectrum of CuO nanoparticles by solution combustion method using glycine; 1a – XRD, 1b – FTIR, 1c – UV-Vis and 1d – EDX.

The nanoparticle crystallite size was calculated from X-ray line broadening using Debye-Scherrer equation.

$$D = 0.94\lambda / (\beta_{1/2} \cos \theta) \quad (2)$$

where, D is the average crystallite size of the particles, λ is the wavelength of the Cu-K α -radiation (1.54 Å), $\beta_{1/2}$ is the full width half maximum (FWHM) of the peak, θ is the Bragg's angle. The average particle size of CuO is estimated to be around 20–30 nm.

The FTIR Spectrum of CuO nanoparticle is as shown in Fig. 1b in the range of 400–4000 cm^{-1} . The peak 520 cm^{-1} denotes Cu-O metal ions. The peak 1047 cm^{-1} represents C–O stretching. The peak 1332 cm^{-1} represents C–N stretching. The peaks 1376 and 1420 cm^{-1} represents C–H bending vibration for CuO nanoparticles. The peak 3416 cm^{-1} denoted to a –OH group present water molecules present in the sample at a surfactant of moisture absorbance in a sample. The UV–Vis spectrum of nanocrystalline CuO is as shown in Fig. 1c. The absorption peak shoulder onset peaks are located at 200 nm. In general, the monoclinic phase CuO structure has a direct band gap (E_g) can be determined using Tauc's relation. In addition, the EDX spectrum confirms that the as-prepared nanocrystalline CuO is composed of copper and oxygen elements. The EDX

spectrum of CuO nanoparticles is as shown in Fig. 1d. The elemental composition of synthesized nanoparticles was found from energy dispersive spectroscopy. It shows 70 % of Cu and 30 % O present in the sample.

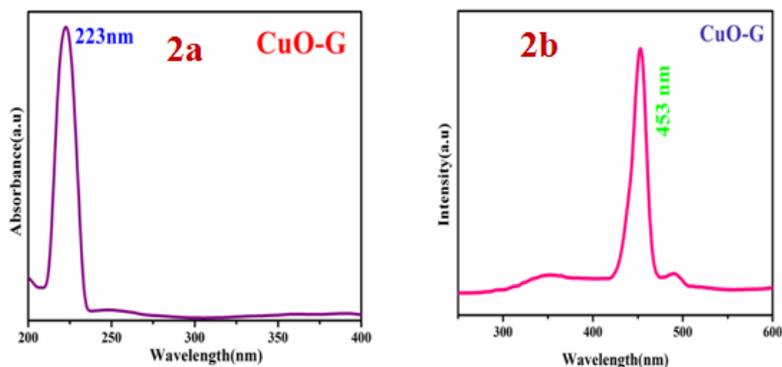


Fig. 2. The fluorescence excitation and emission spectrum of CuO nanoparticles.

The fluorescence emission and excitation spectrum of CuO nanoparticles is as shown in Figs 2a and 2b. The excitation wavelength of fluorescence spectrum is 223 nm (5.5 eV). The wavelength was fixed at 750 nm. The fluorescence emission spectrum of CuO nanoparticles shows excitation wavelength of 453 nm. The wavelength was fixed at 200 nm.

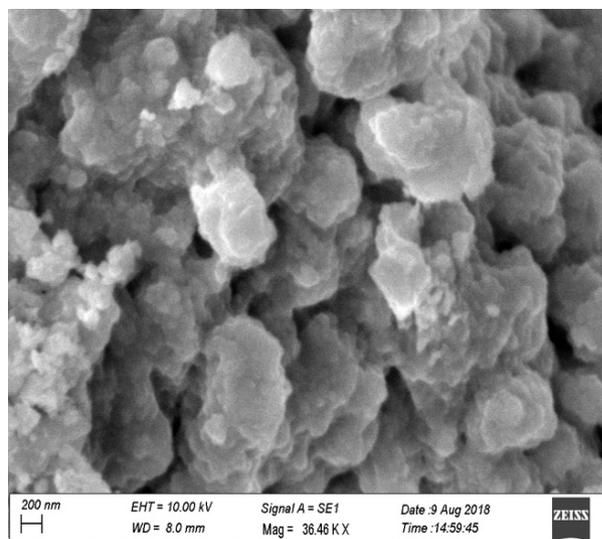


Fig. 3. SEM micrograph of CuO nanoparticles.

The SEM micrograph of the as-prepared CuO synthesized by a solution combustion process is as shown in Fig. 3. The product is foamy porous in nature formed by the escaping gases during the combustion process. The particle size of CuO nanoparticles observed in SEM images is smaller than its average particle size which is 50 nm with more regular spherical shape produced in processes with glycine as a fuel. It is found that the porous ball CuO nanoparticle consists of small nanocrystals and micropores.

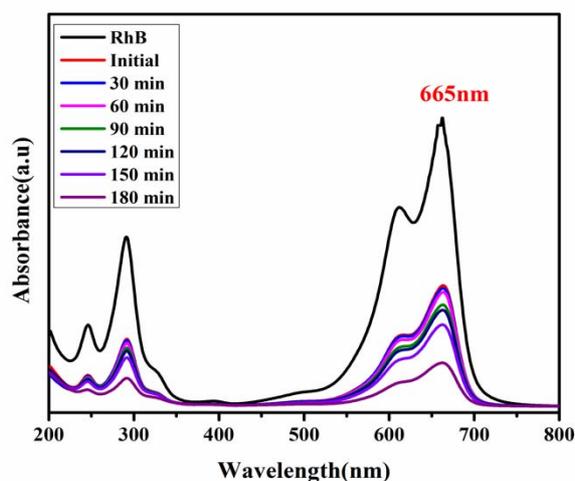


Fig. 4. Photocatalytic activity of prepared CuO nanoparticles using glycine as a fuel.

The photocatalytic activity of copper oxide nanoparticles was observed under visible light irradiation. The time dependent absorption spectrum for the degradation of RhB is as shown in Fig. 4. This figure shows visible light decomposed by RhB with various time interval from 0 to 180 min and the maximum absorbance wavelength occurred at 665 nm. A decrease in RhB dye concentration by increasing concentration of the copper oxide nanoparticles. Because the absorbance intensities of RhB are gradually decreased in the presence of copper oxide nanoparticles with the increase of exposed time. The percentage of dye degrade value is 97.6 %.

CONCLUSION

CuO nanoparticles with monoclinic structure were successfully synthesized by combustion method. The morphology of the CuO nanoparticles was found in XRD spectrum, monoclinic phase and particle size around 30 nm and SEM spectrum indicates porous ball like structure that particle size is around

40–50 nm. FTIR spectrum confirmation of CuO functional groups. The optical properties were studied by using UV-Vis and fluorescence spectrum. The band gap energy of the synthesized CuO nanoparticles was around 6 eV by UV-Vis spectrum. CuO nanoparticles have good photocatalytic material proved by photocatalytic studies. Therefore, combustion method of CuO nanoparticles has extensive applications in future in many fields.

Acknowledgements. This work was financially supported by DST-PURSE.

REFERENCES

1. AHAMED, M., H.A. ALHADLAQ, M. KHAN, P. KARUPPIAH, N.A. AL-DHABI, Synthesis, characterization, and antimicrobial activity of copper oxide nanoparticles, *Journal of Nanomaterials*, 2014, **3**, 33–42.
2. ALBADI, J, A. MANSOURNEHAD, H. ABBASZAEH, CuO-CeO₂ nanocomposite: A highly efficient recyclable catalyst for the green synthesis of 1-dioxooctahydroxanthenes in water, *Journal of the Chinese Chemical Society*, 2013, **60**, 1193–1206.
3. APARNA, Y., K.V. ENKATESWARA RAO, P. SRINIVASA SUBBARAO, Synthesis and characterization of CuO nano-particles by novel sol-gel method, *2nd International Conference on Environment Science and Biotechnology IPCBEE*, IACSIT Press, Singapore, 2012, **48**, pp. 156–160.
4. JOSHUA, J.P., S. KRISHNAN, D. RAJ, R. UTHRAKUMAR., S. LAXMI, S.J. DAS, Novel synthesis of tenorite (CuO) nanoparticles by wet chemical method, *International Journal of Chem. Tech. Research*, 2014, **6**, 22–33.
5. MANIMARAN, R., K. PALANIRAJA, N. ALAGUMURTHI, S. SENHILNATHAN, J. HUSSAIN, Preparation and characterization of copper oxide nanofluid for heat transfer applications, *Applied Nanoscience*, 2014, **4**, 163–167.
6. MUSTAFA, G., H. TAHIR., M. SULTAN, N. AKHTAR, Synthesis and characterization of cupric oxide (CuO) nanoparticles and their application for the removal of dyes, *African Journal of Biotechnology*, 2013, **12**, 6650–6662.
7. SAITO, G., S. HOSOKAI, M. TSUBOTA, T. AKIYAMA, Synthesis of copper/copper oxide nanoparticles by solution plasma, *J. Appl. Phys.*, 2011, **110**, Doi: 10.1063/1.3610496.
8. SULEIMAN, M., M. MOUSA, A. HUSSEIN, B. HAMMOUTI, T.B. HADDA, I. WARAD, Copper (II)-oxide nanostructures: Synthesis, characterizations and their applications – Review, *Journal of Materials and Environmental Science*, 2013, **5**, 792–807.
9. ZHOU, Z., C. LU, X. WU, X. ZHANG, Cellulose nanocrystals as a novel support for CuO nanoparticles catalysts: facile synthesis and their application to 4-nitrophenol reduction, *RSC Advances*, 2013, **48**, 26066–26073.

