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PREPARATION OF CuO NANOPARTICLES VIA REFLUX METHOD AND THEIR PHOTOCATALYTIC BEHAVIOUR

D. Magimai Antoni Raj[1]*, Amal George[2], S. Rahul[2], Dominic Savio C[2], A. Dhayal Raj[2], G. Jayakumar[2], D. Daniel Lawrence[2]

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Abstract

Among the various oxides of transition metals, CuO has attracted a lot of interest because of its variety of uses. This work reports on the simple synthesis of CuO nanoparticles to be used as photocatalyst through the use of urea and copper nitrate as precursors via reflux process. CuO sample was prepared at six-hour reaction timing. To assure the formation of copper oxide, the samples were calcined at 500ºC for about an hour. The end product was examined using UV-Vis, Scanning Electron Microscopy (SEM), XRD, and FT-IR spectroscopy to study the characteristics of the produced copper oxide nanoparticles. The CuO nanoparticles thus produced was tested for its organic dye degradation capability by utilizing methylene blue as a model dye under the irradiation of light.

Keywords: CuO nanoparticles, reflux method, Methylene blue, Photocatalytic activity.

1. Introduction

A wide range of frequently used products are now produced on a big industrial scale with the help of remarkable technological advancements [1-3]. Dyes are essential to the textile and fashion sectors among these products. However, after extensive use, dyes become harmful pollutants that represent a major risk to the environment and public health if not managed and disposed of appropriately [4]. The leftover dyes in the dyeing bath are a regular issue for the textile industry. These sectors use cutting-edge, expedient, and environmentally friendly treatment techniques to improve wastewater's ability to remove color [5]. Additionally, laws and regulations pertaining to discharge limitations and color removal reduction are becoming more and more strict [6]. Consequently, in order to lessen dye contamination as well as organic and inorganic pollutants, effective treatment techniques such membrane filtering and physical separation are required. On the other hand, these approaches' operating and maintenance costs are thought to be the fundamental and decisive elements for large-scale applications [7]. Therefore, to reduce the issues associated with treating liquid dye wastes, alternative methods that are affordable, effective, eco-friendly, and cost-effective are desired [4]. Due to its lack of secondary pollutants and environmental friendliness, photocatalytic degradation has emerged as a potential method for the optical catalyst-assisted removal of organic dye pollutants [8, 9]. Due to their low cost, chemical and biological inertness, and superior capacity to remove organic pollutants, colors, and toxins from wastewater, semiconductor materials are a viable candidate for photocatalysis [10–12]. The ability of semiconductors to produce charge carriers in the presence of sunlight, together with the subsequent generation of free radicals like OH, which in turn triggers other reactions and finally forms CO2 and H2O, is what essentially defines the mechanism of photocatalysis [13, 14]. For effective photocatalytic degradation of organic molecules, a variety of materials and agents are available, including nitrides, transition metal oxides, complex oxides, and simple metal oxides. [15-20]. Among these, CuO is a very good choice as a semiconductor photocatalyst because of its easy and cheap synthesis and non-toxicity.

P-type CuO is an imperative semiconductor with a band gap of 1.2 eV and low electrical resistance values, and exhibits usable properties such as minimal effort, non-poisonous, environmentally friendly and high steadiness.

*** Corresponding author: e-mail** magimaiantoniraj@gmail.com
[1]Department of Physics, St. Charles College of Arts and Science, Eraiyur, Kallakurichi District, Tamil Nadu, India.
[2]PG & Research Department of Physics, Sacred Heart College (Autonomous), Tirupattur-635601, Tirupattur District, Tamil Nadu, India.

Moreover, CuO is considered as a standout amongst the most prominent materials in a wide assortment of uses of electronic and optical fields, similar to gas sensors, Super conductor high temperature, optical switch, sun powered cells, and electron field emitter, and so on [21-23]. Regarding to potential commercial values, CuO nanostructures with high rates of surface-size exploited on a large-scale sensitive material gas and make offers excellent sensing [24-28].

In this work, CuO nanoparticles with good crystallinity was synthesized by simple Reflux method in the absence of surfactants and capping agent. The resulting nanoparticles was analyzed by XRD, SEM, FTIR, UV-Vis transmittance and Photocatalytic behaviour.

2. Experimental Procedure

2.1 Preparation of CuO nanoparticles

CuO nanoparticles was prepared by simple reflux method at different reaction timings in the presence of Ammonia solution. All the chemical reagents used in this research were analytical grade and these reagents were used in experiments without further purification. In a typical synthesis of CuO nanostructures, Copper nitrate (0.1 M) solution was mixed with urea and stirred well for half an hour. Afterwhich, ammonia solution was added drop by drop inorder to fix the pH level of the precursor solution at 5. Now, the as-prepared solution was heated to about 120°C and stirred constantly in a reflux apparatus for 6 hours. The precipitate was collected, washed, dried and calcinated at 500°C for 1 hour.

2.2 Testing of Photocatalytic performance

Methylene blue degradation was used as a model in this case to investigate the photocatalytic property of the CuO nanoparticles to be used as photocatalyst in organic dye degradation. To ascertain the manufactured semiconductor material's capacity for dye degradation, it is exposed along with the dye solution to Xenon lamp radiation. The test solution is prepared by mixing with 0.2g of CuO nanoparticles with the appropriate amount of Methylene blue dye solution using a magnetic stirrer. The test solution was continually stirred in the absence of light for 30 min in order to guarantee the achievement of adsorption-equilibrium. A Xenon lamp was used to illuminate the test solution that has been produced with the prepared photocatalyst and dye. Sampling was done at an interval of 15 min each and the withdrawn solution is characterized for its absorption analysis with the help of UV-Vis spectrophotometer. By monitoring the intensity of the absorbance peak at λ max = 665.2 nm corresponding to the absorption of methylene blue dye, the quantity of Methylene blue dye in the test solution at the given time can be ascertained in the irradiated solution that is extracted at regular intervals.

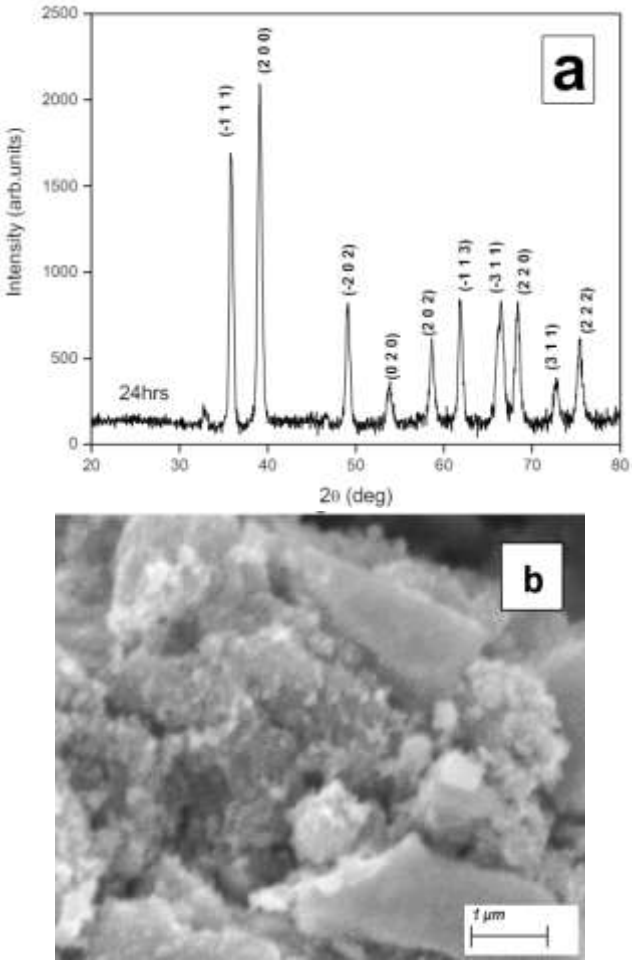

Figure 1. a) XRD patterns of CuO sample b) SEM image of CuO nanoparticles

The XRD patterns of CuO nanoparticles prepared with a reaction time of 6 hours is presented in figure 1. The broadening of all recorded peaks in the spectrum indicates the presence of nanoscale crystallites and the peaks match well with the standard JCPDS card 05-0661, suggesting the formation of CuO. All the peaks are indexed to the monoclinic phase of CuO with lattice constants a = 4.684Å, b = 3.425 Å, and c = 5.129 Å. The crystallite size (D) is calculated by using Debye-Scherer's formula,

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

Where β - is the broadening of diffraction line measured at half of its maximum intensity (FWHM) in radians, λ - is the wavelength of x-ray used (λ=1.5418Å), K - is a constant (taken as 1), θ - is the Bragg's angle. The average crystallite size of CuO samples prepared with a reaction time of 6 hours is 9.8 nm.

The CuO nanoparticles were obtained by calcinating the as-prepared samples at 500 °C for 1 hour. The Morphology

of the prepared CuO nanoparticles was analyzed using SEM. It is found that the samples prepared with a reaction time of 6 hours (Figure 1 (b)) shows formation of nanoparticles with agglomerations. The image shows that fine particles are formed through this synthesis. However, the particle size could not be calculated due to agglomeration.

3.2 Vibrational and optical analysis of CuO nanoparticles

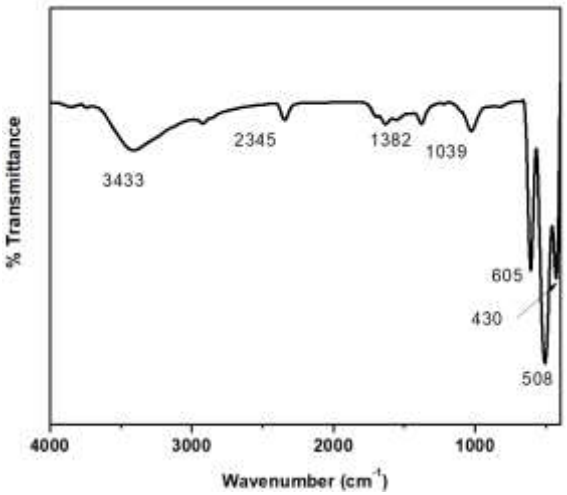

Figure 2. FTIR Spectrum of CuO samples

The functional groups present in the prepared samples were identified using FTIR spectrophotometer. FTIR spectrum for the samples prepared with a reaction time of 6 hours is presented in figure 2. At 2345, the N=C=O Stretching became visible. On the other hand, the prepared sample's O-H stretching vibrations are measured at 3433 and 1348 cm-1. However, the XRD data show no evidence of Cu(OH). Thus, during sample preparation, the KBr may have absorbed moisture from the ambient, which might account for the O-H vibrations [26,27]. The low intensity of the peak is in support with this assumption. Cu-O stretching vibrations appeared at 596, 520and 444 cm^{-1} confirming the formation of CuO. Also, the high peak intensity of these peaks suggest that the sample is CuO [28]. A comparison of vibrational frequencies has been provided in table 1.

Table 1. Assignments of IR band frequencies (cm^{-1}) of CuO nanoparticle

Vibrational assignment	FTIR peaks positions
O-H stretching	3433
N=C=O Stretching	2345
O-H Stretching	1382
C-N Stretching	1029
Cu-O stretching	605
Cu-O Stretching	508
Cu-O Stretching	430

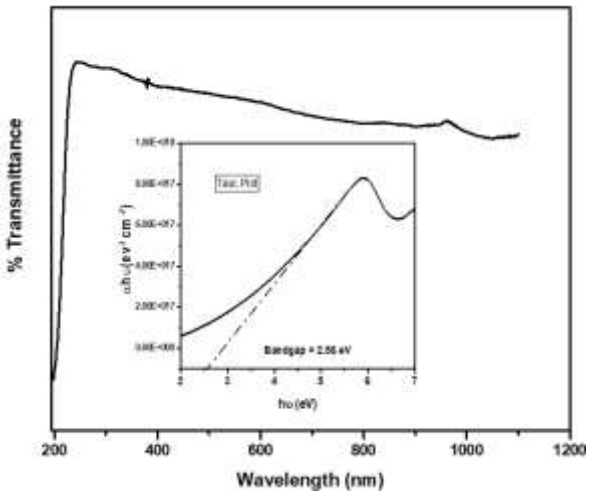

Figure 3. UV-Vis Spectrum of CuO nanoparticles prepared with a reaction time of 6 hrs.

Using a Perkin Elmer Lambda 35 UV-Visible Spectrometer, the UV-Vis transmission spectra of CuO was recorded between 190 and 1100 nm. Figure 3 displays the observed spectrum of CuO. The produced CuO nanoparticles had a lower cut-off wavelength of 198 nm and a maximum transparency of almost 85%.

The bandgap of the prepared CuO sample has been calculated through a tauc *plot* using an equation relating absorption co-efficient (α), bandgap energy (E_g), and photon energy (hν). The tauc plot formula is $\alpha h\nu = (h\nu - Eg)^n$, where n denotes the electronic transition having values 2 and ½ for indirect and direct transitions respectively. The band gap of the CuO nanoparticles was estimated through tauc plot and was found to be 2.56 eV.

3.3 Photocatalytic performance of CuO nanoparticles

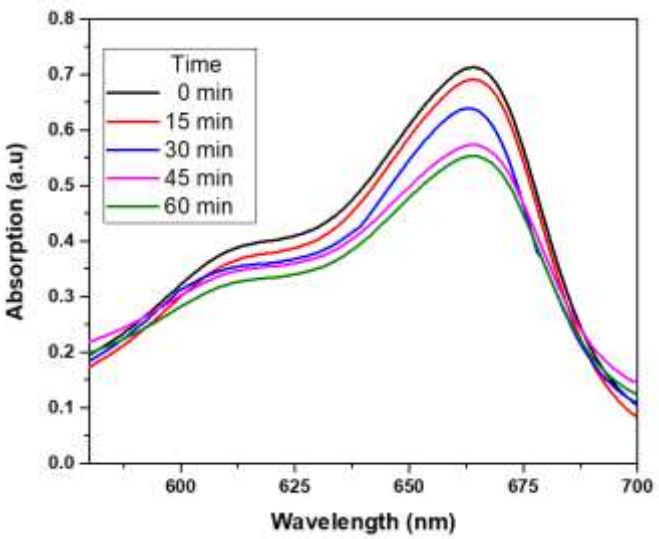

Figure 4. Photocatalytic activity of CuO nanoparticles

As can be seen from the time dependent absorption spectra of Methylene blue solution with catalyst presented in figure.4, the absorption peak intensity at λ max= 665.2 nm pertaining to the MB dye reduces considerable with in-

creasing exposure time [29 – 31]. However, complete degradation of the dye is not witnessed even after exposing the dye solution containing the photocatalyst to light for one hour. Approximately, 50% degradation is obtained within an hour which is in agreement with earlier reports. Manoranjan et.al has reported that MB dye decreases non-linearly with Cu2O contents and it reaches a value of 90 % after light exposure for 120 min [32]. This confirms that the CuO nanoparticles can be used as photocatalyst to degrade organic dyes such as MB.

4. Conclusion

Copper oxide nanoparticles were produced using a straight forward reflux method. This is an easy, low-cost method that encourages young researchers to pursue study and promotes research. SEM results show many agglomerations that can be related to the low reaction time. However, the broad peaks appearing in the XRD pattern confirms the formation of CuO nanoparticles. The band gap calculated from the transmittance spectra by plotting Tauc plot was found to be was 2.56 eV. The prepared CuO nanoparticles degraded the methylene blue dye to half its concentration within one hour of exposure to Xenon lamp. Thus, the prepared CuO nanoparticles can be utilized as photocatalyst to degrade organic dyes.

Reference

[1] S. Maity, D. Sinha, A. Sarkar, Wastewater and industrial effluent treatment by using nanotechnology, in: I. Bhushan, V.K. Singh, D.K. Tripathi (Eds.), J. Environ. Nanotechnol., Springer International Publishing, (2020) 299–313.

[2] M.F. Hamza, F.Y. Ahmed, I. El-Aassy, A. Fouda, E. Guibal, Groundwater purification in a polymetallic mining area (SW Sinai, Egypt) using functionalized magnetic chitosan particles, Water Air Soil Pollut. 229 (2018) 360.

[3] K.N. Yogalakshmi, A. Das, G. Rani, V. Jaswal, J.S. Randhawa, Nano-bioremediation: a new age technology for the treatment of dyes in textile effluents, Biorem. Ind. Waste Environ. Saf. Springer (2020) 313–347.

[4] A.A.M. Sakib, S.M. Masum, J. Hoinkis, R. Islam, M. Molla, A. Islam, Synthesis of CuO/ZnO nanocomposites and their application in photodegradation of toxic textile dye, J. Compos. Sci. 3 (2019) 91.

[5] S.S. Salem, A. Mohamed, M. El-Gamal, M. Talat, A. Fouda, Biological decolorization and degradation of azo dyes from textile wastewater effluent by Aspergillus niger, Egypt. J. Chem. 62 (2019) 1799–1813.

[6] G. Iervolino, I. Zammit, V. Vaiano, L. Rizzo, Limitations and prospects for wastewater treatment by UV and visible-light-active heterogeneous photocatalysis: a critical review, Top. Curr. Chem. 378 (2019) 7.

[7] A.S. Adeleye, J.R. Conway, K. Garner, Y. Huang, Y. Su, A.A. Keller, Engineered nanomaterials for water treatment and remediation: costs, benefits, and applicability, Chem. Eng. J. 286 (2016) 640–662.

[8] A.S. Elfeky, S.S. Salem, A.S. Elzaref, M.E. Owda, H.A. Eladawy, A.M. Saeed, et al., Multifunctional cellulose nanocrystal/metal oxide hybrid, photodegradation, antibacterial and larvicidal activities, Carbohydr. Polym. 230 (2020) 115711.

[9] D. Chen, Y. Cheng, N. Zhou, P. Chen, Y. Wang, K. Li, et al., Photocatalytic degradation of organic pollutants using TiO2-based photocatalysts: a review, J. Clean. Prod. (2020) 121725.

[10] B. Qiu, M. Xing, J. Zhang, Mesoporous TiO2 nanocrystals grown in situ on graphene aerogels for high photocatalysis and lithium-ion batteries. J. Am. Chem. Soc. 136, (2014) 5852–5855.

[11] J.C. Colmenares, R. Luque, Heterogeneous photocatalytic nanomaterials: prospects and challenges in selective transformations of biomass-derived compounds. Chem. Soc. Rev. 43, (2014) 765–778.

[12] Z. Xie, Y. Zhou, L. Guan, S. Muhammad, Y. Jiang, S. Zhang, C. Yu, Y. Jiao, S. Zhang, Y. Ren, X. Zhou, Z. Liu, Efect of impurity in Cu2O nanowires on the degradation of methyl orange. J. Mater. Sci.: Mater. Electron. 31, (2020) 3817–3824.

[13] P. Verma, S.K. Samanta, Facile synthesis of TiO2–PC composites for enhanced photocatalytic abatement of multiple pollutant dye mixtures: a comprehensive study on the kinetics, mechanism, and efects of environmental factors. Res. Chem. Intermed. 44, (2018) 1963–1988.

[14] M. Waqas, S. Iqbal, A. Bahadur, A. Saeed, M. Raheel, M. Javed, Designing of a spatially separated hetero-junction pseudobrookite (Fe2TiO5-TiO2) yolk-shell hollow spheres as efcient photocatalyst for water oxidation reaction. Appl. Catal. B 219, (2017) 30–35.

[15] W. Raza, D. Bahnemann, M. Muneer, A green approach for degradation of organic pollutants using rare earth metal doped bismuth oxide. Catal. Today 300, (2018) 89–98.

[16] A. George, D. M. A. Raj, X. Venci, A. D. Raj, A. A. Irudayaraj, R.L. Josephine, S. J. Sundaram, A. M. Al-Mohaimeed, D. A. A. Farraj, T. W. Chen, K. Kaviyarasu, Photocatalytic effect of CuO nanoparticles

flower-like 3D nanostructures under visible light irradiation with the degradation of methylene blue (MB) dye for environmental application, Environ. Res., 203, (2022) 111880.

[17] A. George, D. M. A. Raj, A. D. Raj, B.S. Nguyen, T.P. Phan, T. Pazhanivel, K. Sivashanmugan, R. L. Josephine, A. A. Irudayaraj, J. Arumugam, V. H. Nguyen, Morphologically tailored CuO nanostructures toward visible-light-driven photocatalysis, Mater. Lett., 281, (2020) 128603.

[18] J Madona, C Sridevi, G Velraj, A Dhayal Raj, Amal George,
Surfactant assisted morphology controlled CuO nanostructures for enhanced photocatalytic performance and bacterial growth inhibition, Mater. Sci. Eng. B., 294 (2023) 116562.

[19] X Venci, A George, A Dhayal Raj, A Albert Irudayaraj, RL Josephine, S John Sundaram, K Kaviyarasu, Self-assembly of CdSe 3D urchins and their photocatalytic response, Environ. Res., 214, (2022) 113804.

[20] Y. Chen, F. Meng, H. Yua, C. Zhu, T. Wang, P. Gao, Q. Ouyang, Sonochemical synthesis and ppb H2S sensing performances of CuO nanobelts, Sens. Actuators B 176, (2013) 15–21.

[21] G. Eranna, Metal oxide nanostructures as gas sensing devices, in: B. Jones, H.Huang (Eds.), Sensors, CRC Press, Boca Raton, (2011) 291.

[22] Steinhauer, E. Brunet, T. Maier, G.C. Mutinati, A. Köck, O. Freudenberg, C.Gspan, W. Grogger, A. Neuhold, R. Resel, Gas sensing properties of novel CuOnanowire devices, Sens. Actuators B 187, (2013) 50–57.

[23] X. hen, C.K.Y. Wong, C.A. Yuan, G. Zhang, Nanowire-based gas sensors, Sens. Actuators B 177, (2013) 178–195.

[24] Zhu, H. Xu, Y. Xiao, Y. Liu, A. Yuan, X. Shen, Facile fabrication and enhanced sensing properties of hierarchically porous CuO architectures, ACS Appl. Mater. Interfaces 4, (2012) 744–751.

[25] Amal George, S. Rahul, A. Dhayal Raj, A. Albert Irudayaraj, M. Senthilkumar, B. Natarajan, S. John Sundaram, K. Kaviyarasu, Surfactant assisted synthesis of nickel vanadium oxide nanostructures with strong visible-light-induced photocatalytic activity, Results in Surfaces and Interfaces 12 (2023) 100129.

[26] D. Magimai Antoni Raj, A. Dhayal Raj, A. Albert Irudayaraj, Facile synthesis of rice shaped CuO nanostructures for battery application, J Mater Sci: Mater Electron., 25, (2014) 1441–1445.

[27] C. Li, Y. Yin, H. Hou, N. Fan, F. Yuan, Y. Shi, Q. Meng, Solid State Communications 150, (2010) 585.

Manoranjan Behera, Gitisudha Giri, Int. J. Ind. Chem., 7, (2016) 157–166.