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Original Research Article

Synthesis of CuO and CuO/ZnO Composite Powders for Antibacterial, Photocatalytic, and Pigment-Related Applications

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A B S T R A C T

Incorporation of CuO into ZnO contributes to the formation of CuO/ZnO composite, thus enhancing some properties of individual oxides such as antibacterial and photocatalytic activities. The current study evaluated the effect of both synthesis and in-situ syntheses of copper oxide on the zinc oxide particles using Copper(II) nitrate trihydrate as the starting material as well as acetic acid, D200, SHMP, PVP, CTAB, SDS, urea, and M2P surfactants. The impact of surfactants on the microstructure and chromatic properties of the samples was also investigated. The results from scanning electron micrographs showed different morphologies of copper oxide particles in the forms of needle, round, and flake depending on the type of surfactant. Moreover, the chromatic properties of the powders showed that the pigment synthesized in the presence of SHMP was in a better and darker black color than the others. Further, copper oxide powders exhibited more proper anti-bacterial behavior than the copper oxide/zinc oxide composite powders. In addition, copper oxide/zinc oxide particles had higher photocatalytic activity (up to 95 %) than copper oxide powders (about 65 %).

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1. INTRODUCTION

The increasing growth of population has negatively affected water quality by releasing a variety of pollutants into water sources. It is predicted that more than 50 % of the countries around the globe will face water crisis by 2025 [1]. Different pollutants such as heavy metal ions, organic dyes, industrial wastes, pesticides, and pharmaceutical wastes are considered seious threats to water quality. This is the reason why application of efficient water purification technologies such as photocatalysis, electrochemical treatment, membrane filtration, ozonation, and flocculation for water treatment have gained significance. For a long time, photocatalysis has used as a simple and efficient technique for water purification. Nowadays, using composite materials has

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significantly contributed to developing highly efficient materials and removing a wide range of pollutants [2].

Synthesis, coating, and fabrication of copper (II) oxide and copper (I) oxide materials have considerably drawn researchers' attention in the last decades due to their numerous applications. They are employed in different fields of ceramic applications such as producing inks for FET transistors [3], antibacterial materials for medical and biological applications [4-6], solar cells [7-9], gas sensors [10,11], electrochemical sensors [12,13], photocatalysts [14-16], and pigments [17].

Copper oxide was synthesized through several methods such as thermal decomposition [18,19], sonochemical [20,21] and hydrothermal [22,23], milling [24,25], electrodeposition [26,27], ultrasonic spray pyrolysis [25,28], solution combustion [25,29], electrochemical oxidation [30], and precipitation [28,31]. The precipitation method as an easy-eco route was employed to prepare copper oxide particles in many studies. Several investigations evaluated the effects of different surfactants on the microstructure and properties of copper oxide particles [32]. Of note, addition of CuO to ZnO can form CuO-ZnO composite that increases the particle size and decreases the bandgap energy. In other words, the higher the concentration of CuO in the composite, the smaller the bandgap energy. It can also increase the stability of the photocatalytic reaction and radical species such as superoxide anion radical ($^{\bullet}O^{2-}$), ($HO_2^{\bullet}$) and (HO_2^{-}) which can inhibit the growth of bacteria [33]. Some researchers have evaluated the effects of antibacterial and photocatalytic properties of CuO/ZnO composites on different pollutants under UV or visible irradiation [2].

The main objective of the current study was to synthesize copper oxide and copper oxide/zinc oxide composite particles based on the precipitation method in the presence of different surfactants. To the best of the authors' knowledge, the effect of these surfactants on the morphology of CuO/ZnO particles was investigated for the first time. In this regard, the structure, microstructure, and antibacterial and optical properties of the powders were examined. In addition, the photocatalytic properties of the synthesized composite were studied on DR23 dye for the first time.

2. MATERIALS AND METHODS

CuO and CuO/ZnO composite powders were synthesized using Copper (II) nitrate trihydrate ($Cu(NO_3)_2.3H_2O$, Merck), Manganese (II) acetate tetrahydrate ($Mn(CH_3COO)_2{\cdot}4H_2O$, Merck), Zinc nitrate hexa-hydrate ($Zn(NO_3)_2.6H_2O$, Merck) as the starting materials. In addition, Glycine ($C_2H_5NO_2$, Merck) and Glucose ($C_6H_{12}O_6$, Merck) were used as the fuels. Moreover, Cetyl trimethyl ammonium bromide ($(C_{16}H_{33})N(CH_3)_3]Br$, CTAB, Merck), Polyvinyl-pyrrolidone ($(C_6H_9NO)_n$, PVP, Rahavard Tamin Pharmaceutical Co.), Sodium hexametaphosphate ($(NaPO_3)_6$, SHMP, Dai Viet Chem), Sodium dodecyl sulfate ($NaC_{12}H_{25}SO_4$, SDS, Merck), acetic acid (CH_3COOH, Merck), Urea (CH_4N_2O, Merck), Acrylic homopolymer (D200, MW=5000, Simab Rezin Co.), dispersants (MP, ICST), Anionic PEG acrylate homopolymer dispersants (M2P, ICST) were used as the surfactants.

Copper oxide powders were synthesized through the precipitation method in the presence of different surfactants. To this end, first, 0.97 g copper nitrate tri-hydrated and 0.0194 g Manganese acetate tetra-hydrate (0.02 wt. % of Cu precursor) were dissolved in 250 mL water. Then, the surfactants were added to the solution and agitated under magnetic stirring to dissolve completely. The weight ratio of the surfactant to copper precursor was assumed to be 1:2. Next, NaOH solution (1 molar, Merck) was added drop wise to the solution up to the pH adjustment of 9 and mixed for 15 min followed by more heating at 100 °C for an hour until a black precipitate was obtained. Finally, the obtained sample was washed three times and dried at 100 °C in an electric oven for one hour.

Zinc oxide particles were synthesized through solution combustion synthesis method. To this end, first, 5 g zinc nitrate hexahydrate, 1.15 g glucose, and 0.1 g glycine were dissolved in 20 mL deionized water under magnetic stirring. The transparent solutions were heated at 80 °C under magnetic stirring until yellowish gel-like precipitates were obtained.

The combustion reaction of samples occurred in a commercial microwave oven (SAMSUNG) with the frequency of 50 Hz and power of 900 W for one min, and spongy-foam like agglomerated particles were obtained. To complete the reaction and remove the residual organic matters, the samples were transferred to an electric furnace and calcined (post-heated) at 500 °C at the soaking time of one hour and heating rate of 10 °C min^{-1}.

The mentioned CuO synthesis process was repeated in the presence of synthesized ZnO particles to obtain CuO/ZnO composite. All other synthesized processes are similar to those of CuO synthesis.

The microstructure and structural characteristcs of the samples were identified using Scanning Electron Microscopy (SEM, LEO 1455 VP) and XRD (Siemens D-500) methods. The mean particle size of the powder samples was determined using an image processing software, i.e., ImageJ 1.44p.

The mean diameter ($d_{Scherrer}$) of zinc aluminate (gahnite) crystallite was determined considering the half-height width (β) of the (311) diffraction peak of gahnite using Scherrer equation ($d_{Scherrer}=0.9\lambda/\beta\cos\theta$). In addition, WQF-510 FT-IR (RAYLEIGH) Spectrometer was used to study the bonding structures. Photoluminescence (PL) studies were conducted using a

PerkinElmer LS 55 Fluorescence Spectrometer (phosphorescence mode) with the exciting wavelength of 360 nm. Chromaticity color index (CIE) calculations were performed based on the photoluminescence spectra using MATLAB programming.

Broth microdilution method was used in the anti-bacterial tests with E. coli and S. aureus bacteria which were Gram-negative and Gram-positive, respectively.

The photocatalytic activities of the prepared CuO and CuO/ZnO powders were evaluated based on the degradation of Direct Red 23 (RD23) under UV light source in a prototype photocatalytic agitated reactor. Suspensions were prepared by adding 0.4 g of the synthesized powders to 500 mL standard solution of DR23 with the concentration of 20 mg/L. First, suspensions were kept in a dark medium under agitating for 30 min to complete the absorption/desorption process. Then, the DR23 photodegradation yield was obtained during 210 min of suspension irradiation. Photodegradation reactions occured in a 500 mL volumetric glass where a transparent silica glass tube containing a 15 Watt UV lamp was located. The suspension was agitated by a magnet stirrer rotating at 500 rpm during the test. Two mL of suspensions were obtained at each 15 min interval, and their absorbency was measured using a UV–vis spectrophotometer (Perkin-Elmer Lambda 25) at the maximum absorption wavelength of 503 nm.

3. RESULTS AND DISCUSSION

Figure 1 depicts the XRD patterns of the synthesized copper oxide and copper oxide/zinc oxide powder samples. As shown in this figure, copper oxide powder contained CuO phase characterized by a monoclinic structure (card no. 01-080-1916). Apparently, NaOH and surfactant function locally as a redox in the synthesis process that leads to the Cu_2O minor phase. Moreover, ZnO with wurtzite structure (card no.01-076-0704) was formed in addition to these phases in copper oxide/zinc oxide composite powder samples.

Figures 2 (a-h) show the SEM micrographs of copper oxide particles synthesized in the presence of different surfactants. As shown in Figures 2 (a-b), the presence of acetic acid and D200 surfactants contributes to the formation of highly agglomerated particles. Moreover, some spherical nanoparticles of the particle sizes of 50-70 nm were formed.

In comparison with the synthesis of case in the presence of acetic acid and D200, synthesis in the presence of Sodium Hexametaphosphate (SHMP) led to formation of very fine spherical particles with less agglomeration (Figure 2(c)). In addition, PVP and CTAB surfactants made the synthesis of particles with flake-like microstructures (Figures 2 (d-e)) feasible. Moreover, synthesis in the presence of amine containing surfactants, i.e., SDS, urea, and M2P, resulted in a combination of needle- and flake-shaped morphologies, as illustrated in Figures 2 (f-h), respectively.

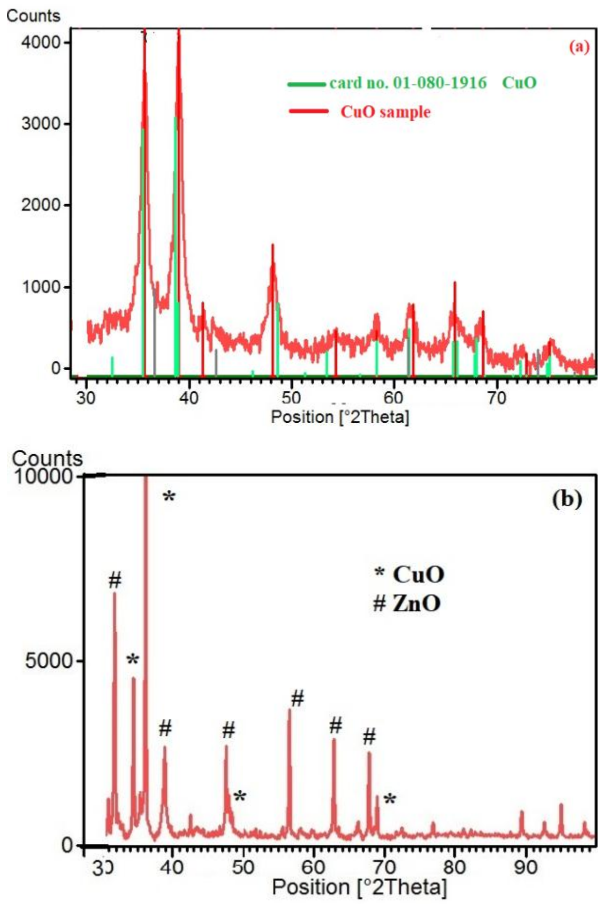


Figure 1. XRD pattern of the synthesized copper oxide (a) and (b) copper oxide/zinc oxide powders

Figure 3 presents the macro images of the synthesized particles using different surfactants. Based on these images, darker powders were selected for chromatic characterization (Table 1). Powder samples synthesized in the presence of SHMP surfactant are shown in darker colors than the other ones.

The anti-bacterial properties of ZnO/CuO composite and CuO powders synthesized in the presence of SHMP surfactant were studied using two E. coli and S. aureus bacteria. Table 2 lists the MBC values where both CuO and CuO/ZnO composite materials affect the S. aureus bacteria. However, the CuO samples failed in properly elimintaing the E. coli bacteria. Malwal et al. pointed out to the effect of ZnO/CuO composite on S. aureus instead of E. coli [2]. Sakib et al. reported that upon increasing the amount of CuO in ZnO/CuO composites, the antibacterial activities of both bacteria would increase [34].

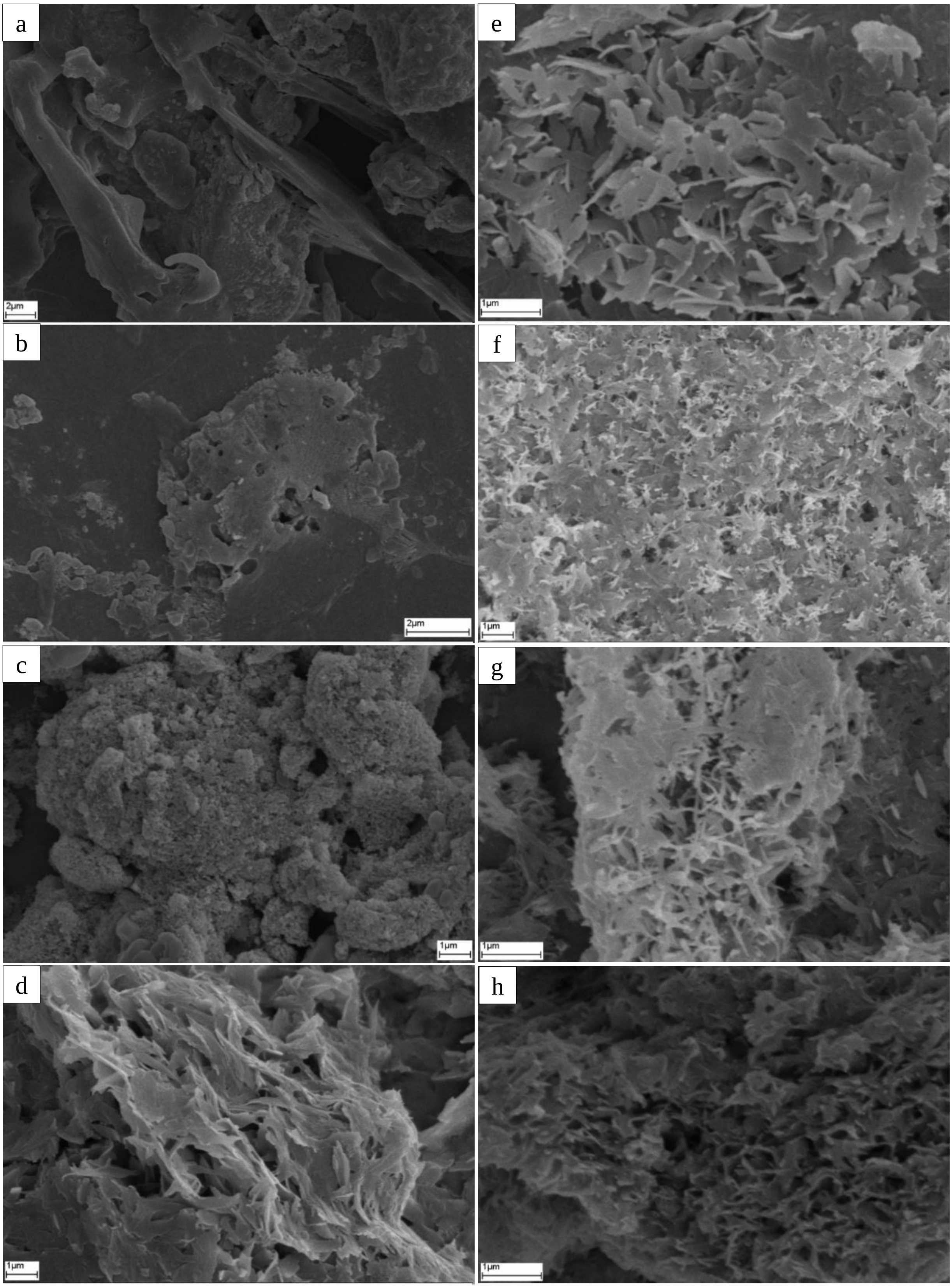


Figure 2. SEM micrographs of the copper oxide particles synthesized in the presence of different surfactants: a) acetic acid, b) D200, c) SHMP, d) PVP, e) CTAB, f) SDS, g) urea, and h) M2P

The composite samples exhibted better performance in terms of removing bacteria than the individual oxide [35]. He et al. remarked that the antibacterial properties of CZ-ESM indicated improvement in their activity against S. aureus and E. coli, compared to single components, mainly due to the synergistic interaction of Zn^{2+} and Cu^{2+} ions [36].

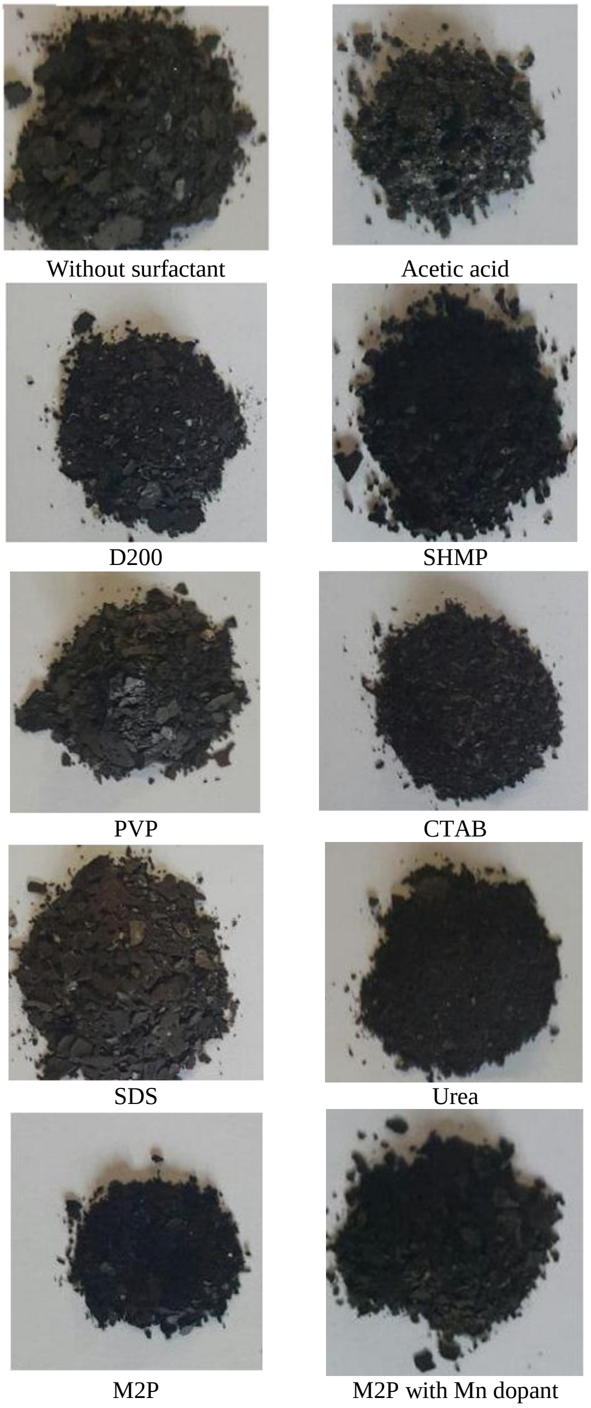


Figure 3. Macro images of synthesized particles synthesized with different surfactants

TABLE 1. Chromatic properties of the samples synthesized in the presence of different surfactants

	L*	a*	b*	c*	h*
M2P with Mn dopant	37.26	-0.34	-0.25	0.43	216.21
M2P	36.31	-0.24	-0.21	0.32	220.37
D200	36.01	-0.34	-0.25	0.42	215.98
SHMP	35.26	-0.06	0.38	-0.38	99.24

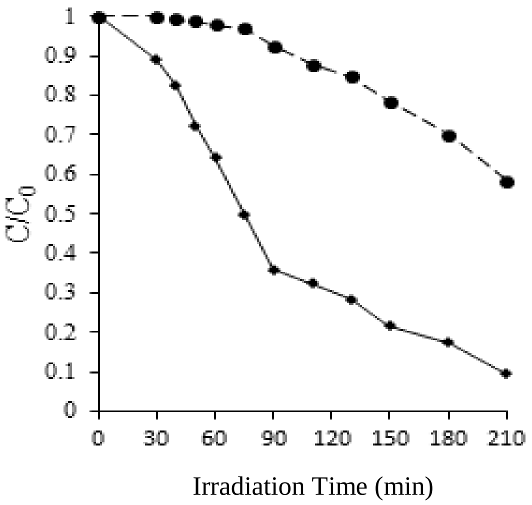
TABLE 2. Chromatic properties of the samples synthesized in the presence of different surfactants

Bacteria	S. aureus		E. coli	
	Remained	Yield (%)	Remained	Yield (%)
ZnO/CuO	0	100	0	100
	3.5×10^4	99.5	0	100
	0	100	0	100
CuO	0	100	3.5×10^4	99
	0	100	3.5×10^4	97
	0	100	5.5×10^4	92

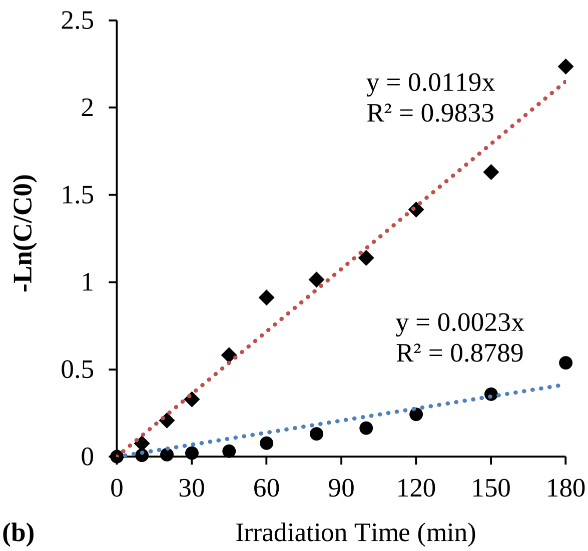
Figure 4a shows the concentration changes (C/C_0) of DR23 with pH=9 as a function of illumination time in the reactor under UV irradiation for ZnO/CuO composite and CuO powders synthesized in the presence of SHMP surfactants. The initial 30 min was considered as the dark interval. As illustrated, photocatlitic yield of ZnO/CuO composite powder (about 90 %) was more than that of CuO particles (about 64 %) mainly due to the narrower band gap of CuO (1.2-1.7) than that of ZnO (3.7 eV) [37]. ZnO with a wide band gap can absorb UV irradiation properly and increase photocatalytic activity. The decrease in the DR23 concentration resulting from degradation was taken into account in the kinetic study. Given the low initial concentration of the DR23 solution, the reaction rate can be considered apparently first-ordered, as presented in following equation:

$$\text{Rate} = -dC/dt = K_\alpha C \tag{1}$$

where K_α is the apparent rate constant, and C the concentration of DR23. The kinetic degradation order for the process using CuO and CuO–ZnO composite powders as photocatalysts was calculated by plotting ($Ln(C/C_0)$) versus irradiation time (Fig. 4b). The rate constants of the CuO–ZnO and CuO photocatalysis processes were calculated from the slopes which fitted the first-order kinetic equation ($-Ln(C/C_0)=kt$). According to the findings, CuO and CuO–ZnO samples under UV irradiation represented the constant photocatalytic activity values equal to 0.23×10^{-2} and 1.2×10^{-2} min^{-1}, respectively. P. Muhambihai et al. reported that NiO/CuO composite showed a higher degradation ability on Direct Red 80 dyes than that of ZnO/CuO [38]. Wei et al. also reported that the photocatalytic reduction of Cr(VI) was obtained over the composite films with 0.73 atomic Cu/Zn ratios. The enhanced activity of CuO/ZnO composite films could be mainly attributed to the efficient separation of charges photogenerated in CuO/ZnO heterostructures [39]. Zhu et al. remarked that the photocatalytic removal efficiency of phenol, in comaparison to that of the CuO/ZnO composite, was up to 78 % under the irradiation of the light, which was ~2 and ~4 times higher than those of the pristine ZnO and CuO, respectively [40].



(a)



(b)

Figure 4. a) concentration changes (C/C_0) and b) -Ln(C/C_0) versus irradiation time of DR23 with pH=9 versus irradiation time UV irradiation for ZnO/CuO composite and CuO powders synthesized in the presence of SHMP surfactants

4. CONCLUSIONS

In the present study, copper oxide and copper oxide/zinc oxide particles were successfully synthesized in the presence of different surfactants to investigate their effect on the morphology of particles. The main results are suammarized in the following:

1) Copper oxide powders with different morphologies in the forms of needle, round, and flake were synthesized in the presence of acetic acid, D200, SHMP, PVP, CTAB, SDS, urea, and M2P surfactants.
2) The chromatic properties of the powders indicated that the pigment synthesized in the presence of SHMP had a better and darker black color than that of the others. Therefore, it could be a suitable candidate for the black pigment in the ceramic industry.
3) Copper oxide powders exhibited a more proper anti-bacterial behavior than copper oxide/zinc oxide powders in dealing with S. aureus bacteria. However, ZnO/CuO composite was more effective than CuO in removing E. coli bacteria.
4) Copper oxide/zinc oxide particles demonstrated higher photocatalytic activity than copper oxide powders.

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REFERENCES

1. Thavasi, V., Singh, G., Ramakrishna, S., “Electrospun nanofibers in energy and environmental applications”, ***Energy & Environmental Science***, Vol. 1, No. 2, (2008), 205–221. https://doi.org/10.1039/B809074M
2. Malwal, D., Gopinath, P., “Efficient adsorption and antibacterial properties of electrospun CuO-ZnO composite nanofibers for water remediation”, ***Journal of Hazardous Materials***, Vol. 321, (2017), 611–621. https://doi.org/10.1016/j.jhazmat.2016.09.050
3. Vaseem, M., Hong, A. R., Kim, R. T., Hahn, Y. B., “Copper oxide quantum dot ink for inkjet-driven digitally controlled high mobility field effect transistors”, ***Journal of Materials Chemistry C***, Vol. 1, No. 11, (2013), 2112–2120. https://doi.org/10.1039/C3TC00869J
4. Dadi, R., Azouani, R., Traore, M., Mielcarek, C., Kanaev, A., “Antibacterial activity of ZnO and CuO nanoparticles against gram positive and gram negative strains”, ***Materials Science and Engineering: C***, Vol. 104, (2019), 109968. https://doi.org/10.1016/j.msec.2019.109968
5. Mirhosseini, M., Houshmand Marvasti, S., “Antibacterial Activities of Copper Oxide (CuO) Nanoparticles in Combination With Nisin and Ultrasound Against Foodborne Pathogens”, ***Iranian Journal of Medical Microbiology***, Vol. 11, No. 5, (2017), 125–135. http://ijmm.ir/article-1-742-en.html
6. Bezza, F. A., Tichapondwa, S. M., Chirwa, E., “Fabrication of monodispersed copper oxide nanoparticles with potential application as antimicrobial agents”, ***Scientific Reports***, Vol. 10, No. 1, (2020), 1–18. https://doi.org/10.1038/s41598-020-73497-z
7. Kumar, N., Parui, S. S., Limbu, S., Mahato, D. K., Tiwari, N., Chauhan, R. N., “Structural and optical properties of sol–gel

derived CuO and Cu_2O nanoparticles", ***Materials Today: Proceedings***, Vol. 41, (2021), 237–241. https://doi.org/10.1016/j.matpr.2020.08.800

8. Masudy-Panah, S., Dalapati, G. K., Radhakrishnan, K., Kumar, A., Tan, H. R., "Reduction of Cu-rich interfacial layer and improvement of bulk CuO property through two-step sputtering for p-CuO/n-Si heterojunction solar cell", ***Journal of Applied Physics***, Vol. 116, No. 7, (2014), 074501. https://doi.org/10.1063/1.4893321
9. Iqbal, K., Ikram, M., Afzal, M., Ali, S., "Efficient, low-dimensional nanocomposite bilayer CuO/ZnO solar cell at various annealing temperatures", ***Materials for Renewable and Sustainable Energy***, Vol. 7, No. 2, (2018), 1–7. https://doi.org/10.1007/s40243-018-0111-2
10. Steinhauer, S., "Gas sensors based on copper oxide nanomaterials: A review", ***Chemosensors***, Vol. 9, No. 3, (2021), 51. https://doi.org/10.3390/chemosensors9030051
11. Peng, G., Wu, S., Ellis, J. E., Xu, X., Xu, G., Yu, C., Star, A., "Single-walled carbon nanotubes templated CuO networks for gas sensing", ***Journal of Materials Chemistry C***, Vol. 4, No. 27, (2016), 6575–6580. https://doi.org/10.1039/C6TC01722C
12. Avinash, B., Ravikumar, C. R., Kumar, M. A., Nagaswarupa, H. P., Santosh, M. S., Bhatt, A. S., Kuznetsov, D., "Nano CuO: Electrochemical sensor for the determination of paracetamol and D-glucose", ***Journal of Physics and Chemistry of Solids***, Vol. 134, (2019), 193–200. https://doi.org/10.1016/j.jpcs.2019.06.012
13. Buledi, J. A., Ameen, S., Memon, S. A., Fatima, A., Solangi, A. R., Mallah, A., Karimi, F., Malakmohammadi, S., Agarwal, S., Gupta, V. K., "An improved non-enzymatic electrochemical sensor amplified with CuO nanostructures for sensitive determination of uric acid. Open Chemistry", ***Open Chemistry***, Vol. 19, No. 1, (2021), 481–491. https://doi.org/10.1515/chem-2021-0029
14. Tadjarodi, A., Akhavan, O., Bijanzad, K., "Photocatalytic activity of CuO nanoparticles incorporated in mesoporous structure prepared from bis (2-aminonicotinato) copper (II) microflakes", ***Transactions of Nonferrous Metals Society of China***, Vol. 25, No. 11, (2015), 3634–3642. https://doi.org/10.1016/S1003-6326(15)64004-3
15. Senobari, S., Nezamzadeh-Ejhieh, A., "A comprehensive study on the photocatalytic activity of coupled copper oxide-cadmium sulfide nanoparticles", ***Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy***, Vol. 196, (2018), 334–343. https://doi.org/10.1016/j.saa.2018.02.043
16. Aminzadeh, H., Shahabi Nejad, M., Mohammadzadeh, I., Sheibani, H., "Assembly of CuO nanorods onto poly (glycidylmethacrylate)@ polyaniline core–shell microspheres: Photocatalytic degradation of paracetamol", ***Applied Organometallic Chemistry***, Vol. 35, No. 12, (2021), e6423. https://doi.org/10.1002/aoc.6423
17. Wu, S., Reddy, G. K., Banerjee, D., "Pitch-Black Nanostructured Copper Oxide as an Alternative to Carbon Black for Autonomous Environments", ***Advanced Intelligent Systems***, Vol. 3, No. 9, (2021), 2100049. https://doi.org/10.1002/aisy.202100049
18. Fukuda, M., Koga, N., "Kinetics and mechanisms of the thermal decomposition of copper (II) hydroxide: A consecutive process comprising induction period, surface reaction, and phase boundary-controlled reaction", ***The Journal of Physical Chemistry C***, Vol. 122, No. 24, (2018), 12869–12879. https://doi.org/10.1021/acs.jpcc.8b03260
19. Al-Gaashani, R., Radiman, S., Tabet, N., Daud, A. R., "Synthesis and optical properties of CuO nanostructures obtained via a novel thermal decomposition method", ***Journal of Alloys and Compounds***, Vol. 509, No. 35, (2011), 8761–8769. https://doi.org/10.1016/j.jallcom.2011.06.056
20. Ranjbar-Karimi, R., Bazmandegan-Shamili, A., Aslani, A., Kaviani, K., "Sonochemical synthesis, characterization and thermal and optical analysis of CuO nanoparticles", ***Physica B: Condensed Matter. Matter***, Vol. 405, No. 15, (2010), 3096–3100. https://doi.org/10.1016/j.physb.2010.04.021
21. Pandiyarajan, T., Saravanan, R., Karthikeyan, B., Gracia, F., Mansilla, H. D., Gracia-Pinilla, M. A., Mangalaraja, R. V., "Sonochemical synthesis of CuO nanostructures and their morphology dependent optical and visible light driven photocatalytic properties", ***Journal of Materials Science: Materials in Electronics***, Vol. 28, No. 3, (2017), 2448–2457. https://doi.org/10.1007/s10854-016-5817-2
22. Sonia, S., Poongodi, S., Kumar, P.S., Mangalaraj, D., Ponpandian, N. and Viswanathan, C., "Hydrothermal synthesis of highly stable CuO nanostructures for efficient photocatalytic degradation of organic dyes", ***Materials Science in Semiconductor Processing***, Vol. 30, (2015), 585–591. https://doi.org/10.1016/j.mssp.2014.10.012
23. Bosigo, R., Lepodise, L. M., Kuvarega, A., Muiva, C., "Hydrothermal synthesis of CuO and CeO2/CuO nanostructures: spectroscopic and temperature dependent electrical properties", ***Journal of Materials Science: Materials in Electronics***, Vol. 32, No. 6, (2021), 7136–7152. https://doi.org/10.1007/s10854-021-05423-6
24. Zheng, X. G., Xu, C. N., Nishikubo, K., Nishiyama, K., Higemoto, W., Moon, W. J., Tanaka, E., Otabe, E. S., "Finite-size effect on Néel temperature in antiferromagnetic nanoparticles", ***Physical Review B***, Vol. 72, No. 1, (2005), 014464. https://doi.org/10.1103/PhysRevB.72.014464
25. Wang, Y., Jiang, T., Meng, D., Yang, J., Li, Y., Ma, Q., Han, J., "Fabrication of nanostructured CuO films by electrodeposition and their photocatalytic properties", ***Applied Surface Science***, Vol. 317, (2014), 414–421. https://doi.org/10.1016/j.apsusc.2014.08.144
26. Yang, Y., Xu, D., Wu, Q., Diao, P., "Cu_2O/CuO bilayered composite as a high-efficiency photocathode for photoelectrochemical hydrogen evolution reaction", ***Scientific Reports***, Vol. 6, No. 1, (2016), 1–13. https://doi.org/10.1038/srep35158
27. Sadabadi, H., Aftabtalab, A., Zafarian, S., Chakra, S., Rao, K. V., Shaker, S., "Influence of fuel and condition in combustion synthesis on properties of copper (II) oxide nanoparticle", ***Advanced Materials Research***, Vol. 829, (2013), 152-156. https://doi.org/10.4028/www.scientific.net/AMR.829.152
28. Xu, C., Manukyan, K. V., Adams, R. A., Pol, V. G., Chen, P., Varma, A., "One-step solution combustion synthesis of CuO/Cu2O/C anode for long cycle life Li-ion batteries", ***Carbon***, Vol. 142, (2019), 51–59. https://doi.org/10.1016/j.carbon.2018.10.016
29. Zuo, Y., Liu, Y., Li, J., Du, R., Han, X., Zhang, T., Arbiol, J., Divins, N. J., Llorca, J., Guijarro, N., Sivula, K., "In situ electrochemical oxidation of Cu2S into CuO nanowires as a durable and efficient electrocatalyst for oxygen evolution reaction", ***Chemistry of Materials***, Vol. 31, No. 18, (2019), 7732–7743. https://doi.org/10.1021/acs.chemmater.9b02790
30. Luna, I. Z., Bangladesh Atomic Energy Commission, "Preparation and characterization of copper oxide nanoparticles synthesized via chemical precipitation method", ***Open Access Library Journal***, Vol. 2, No. 03, (2015), 1. http://doi.org/10.4236/oalib.1101409
31. Rahnama, A., Gharagozlou, M., "Preparation and properties of semiconductor CuO nanoparticles via a simple precipitation method at different reaction temperatures", ***Optical and Quantum Electronics***, Vol. 44, No. 6, (2012), 313–322. https://doi.org/10.1007/s11082-011-9540-1
32. Siddiqui, H., Qureshi, M. S., Haque, F. Z., "Surfactant assisted wet chemical synthesis of copper oxide (CuO) nanostructures and their spectroscopic analysis", ***Optik***, Vol. 127, No. 5, (2016), 2740–2747. https://doi.org/10.1016/j.ijleo.2015.11.220
33. Widiarti, N., Sae, J. K., Wahyuni, S., "Synthesis CuO-ZnO nanocomposite and its application as an antibacterial agent", In

IOP Conference Series: Materials Science and Engineering, February 2017, IOP Publishing, Vol. 172, No. 1, (2017), 012036. https://doi.org/10.1088/1757-899X/172/1/012036

34. Sakib, A. A. M., Masum, S. M., Hoinkis, J., Islam, R., Molla, M., Islam, A., "Synthesis of CuO/ZnO nanocomposites and their application in photodegradation of toxic textile dye", ***Journal of Composites Science***, Vol. 3, No. 3, (2019), 91. https://doi.org/10.3390/jcs3030091
35. Raizada, P., Sudhaik, A., Patial, S., Hasija, V., Khan, A. A. P., Singh, P., Gautam, S., Kaur, M., Nguyen, V. H., "Engineering nanostructures of CuO-based photocatalysts for water treatment: current progress and future challenges", ***Arabian Journal of Chemistry***, Vol. 13, No. 11, (2020), 8424–8457. https://doi.org/10.1016/j.arabjc.2020.06.031
36. He, X., Yang, D. P., Zhang, X., Liu, M., Kang, Z., Lin, C., Jia, N., Luque, R., "Waste eggshell membrane-templated CuO-ZnO nanocomposites with enhanced adsorption, catalysis and antibacterial properties for water purification", ***Chemical Engineering Journal***, Vol. 369, (2019), 621-633. https://doi.org/10.1016/j.cej.2019.03.047
37. Kumaresan, N., Sinthiya, M. M. A., Ramamurthi, K., Babu, R. R., Sethuraman, K., "Visible light driven photocatalytic activity of ZnO/CuO nanocomposites coupled with rGO heterostructures synthesized by solid-state method for RhB dye degradation", ***Arabian Journal of Chemistry***, Vol. 13, No. 2, (2020), 3910–3928. https://doi.org/10.1016/j.arabjc.2019.03.002
38. Muhambihai, P., Rama, V., Subramaniam, P., "Photocatalytic degradation of aniline blue, brilliant green and direct red 80 using NiO/CuO, CuO/ZnO and ZnO/NiO nanocomposites", ***Environmental Nanotechnology, Monitoring & Management***, Vol. 14, (2020), 100360. https://doi.org/10.1016/j.enmm.2020.100360
39. Wei, S., Chen, Y., Ma, Y., Shao, Z., "Fabrication of CuO/ZnO composite films with cathodic co-electrodeposition and their photocatalytic performance", ***Journal of Molecular Catalysis A: Chemical***, Vol. 331, No. 1–2, (2010), 112-116. https://doi.org/10.1016/j.molcata.2010.08.011
40. Zhu, L., Li, H., Liu, Z., Xia, P., Xie, Y., Xiong, D., "Synthesis of the 0D/3D CuO/ZnO heterojunction with enhanced photocatalytic activity", ***The Journal of Physical Chemistry C***, Vol. 122, No. 17, (2018), 9531–9539. https://doi.org/10.1021/acs.jpcc.8b01933