Chemistry and Materials

The Center for Science Innovation

Research Article

Chem. Mater. 4(2) 2025, 66-71

Synthesis of Co-doped Cu_2O via Photoelectrodeposition

Muhammad Raihan Rauf[1,2], Jumaeda Jatmika[3], Mohammad Hamzah Fauzi[3], Suci Winarsih[3,*]

[1]The Center for Science Innovation, Arva Building, Jl. RP. Soeroso, Jakarta Pusat 10350, Indonesia

[2]Department of Chemistry, Faculty of Mathematics and Naturals Sciences, Universitas Negeri Jakarta, Jl. Rawamangun Muka, Jakarta 13220, Indonesia

[3]Research Center for Quantum Physics, National Research, and Innovation Agency (BRIN), South Tangerang 15314, Indonesia

*Corresponding author: suci.winarsih@brin.go.id

Received
29 April 2025

Received in revised form
22 May 2025

Accepted
2 June 2025

Published online
30 June 2025

DOI
https://doi.org/10.56425/t1s07623

Abstract

The superior optical and electronic properties of Cu_2O make it a promising semiconductor material for various applications. To enhance its performance, several approaches have been explored, including cobalt (Co) doping, which has been reported to improve light absorption, reduce crystal size, and enhance the crystallinity of Cu_2O. Moreover, the morphology of the material plays a crucial role in determining its functional performance. Photoelectrodeposition offers a unique advantage in tailoring material morphology through light-assisted deposition processes. Therefore, this study aims to investigate the effect of Co concentration on the crystallinity, structure, and morphology of Cu_2O synthesized via photoelectrodeposition. The results demonstrate the successful synthesis of pure Cu_2O and Co-doped Cu_2O phases. X-ray diffraction analysis indicates that Co atoms successfully substitute Cu atoms, leading to a reduction in crystal size. Raman spectroscopy further confirms an increase in oxygen vacancies in the doped samples. In addition, the particle morphology undergoes significant changes attributed to the influence of illumination during the deposition process.

Keywords: Cu_2O doped Co, crystallinity, photoelectrodeposition

1. Introduction

Copper(I) oxide (Cu_2O), as a p-type semiconductor with a narrow band gap of 2.17 eV, is an attractive material for various applications [1]. Cu_2O has been developed as a material for efficient solar cells [2]. Furthermore, Cu_2O exhibits photocatalytic activity under visible light, making it a promising candidate for the degradation of synthetic dye[3–5], CO_2 reduction [6], and hydrogen production via photoelectrochemical water splitting [7,8]. Due to its unique electrical properties also opens up opportunities for the utilization of Cu_2O in the development of supercapacitors and Li-ion batteries [9]. In addition, Cu_2O has also been used in H_2S gas detection [10].

The electronic and optical characteristics of Cu_2O can be adjusted to meet specific functional requirements through heterojunction formation [11], composite development [12], and doping either metal or non-metal [13]. Among these strategies, metal doping is particularly notable. This technique can induce structural and electronic modifications in the host lattice, potentially altering the bandgap energy [14]. The incorporation of dopant ions also created defects, which can modify diffusion behavior and enhance charge transport and carrier mobility [15]. Transition metals, including cobalt (Co), have been extensively investigated as Cu_2O dopants. Co-doping has been reported to influence the crystal structure of Cu_2O and modulate its bandgap, thereby enhancing visible light absorption [16].

Beyond electronic and optical enhancements, the performance of Cu_2O for any application can also be improved by modifying its physical attributes, such as morphological particle [17]. In electrodeposition techniques, morphological control is achieved by adjusting various synthesis parameters, including changing applied voltage and current, adding additives, and modulated

precursor concentration [18]. Nevertheless, a particularly promising approach involves the utilization of light during synthesis, commonly referred to as photoelectrodeposition. Light irradiation during deposition can influence the morphological evolution of Cu_2O by generating photoexcited electrons within the growing film, which participate in the reduction of precursor ions [19]. This process may alter particle growth dynamics and lead to the formation of unique morphologies with enhanced surface activity.

In this study, Cu_2O and Co-doped Cu_2O were synthesized via photoelectrodeposition. The aim of this study is to investigate the effects of varying Co ion concentrations on the crystallinity, structural properties, and morphology of the resulting Cu_2O thin films. The findings are expected to contribute to the development of optimized Co-doped Cu_2O materials tailored for advanced functional applications.

2. Materials and Methods

2.1 Materials

The materials used in this study were copper(II) sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$), sodium sulfate (Na_2SO_4), sodium hydroxide (NaOH), and lactic acid ($C_3H_6O_3$), supplied by PT. Merck Tbk, Indonesia. The substrate was indium tin oxide (ITO) coated onto a polyethylene terephthalate (PET) film.

2.2 Methods

2.2.1 Synthesize of Cu_2O and Co-doped Cu_2O

The electrolyte solution was prepared with the following composition: 0.025 M $CuSO_4 \cdot 5H_2O$, 0.2 M Na_2SO_4, and 2 M $C_3H_6O_3$. $CoSO_4 \cdot 7H_2O$ was added with varying concentrations as detailed in Table 1.

Table 1. Concentrations of the electrolyte solution.

Sample	$CoSO_4.7H_2O$ (M)
Cu_2O	0
Co-doped Cu_2O 1	0.002
Co-doped Cu_2O 2	0.005
Co-doped Cu_2O 3	0.01
Co-doped Cu_2O 4	0.02

The pH of the electrolyte solution was adjusted to 10 by the dropwise addition of 10 M NaOH. Subsequently, electrodeposition was performed at a constant potential of -0.3 V for a duration of 30 minutes under illumination from a solar simulator.

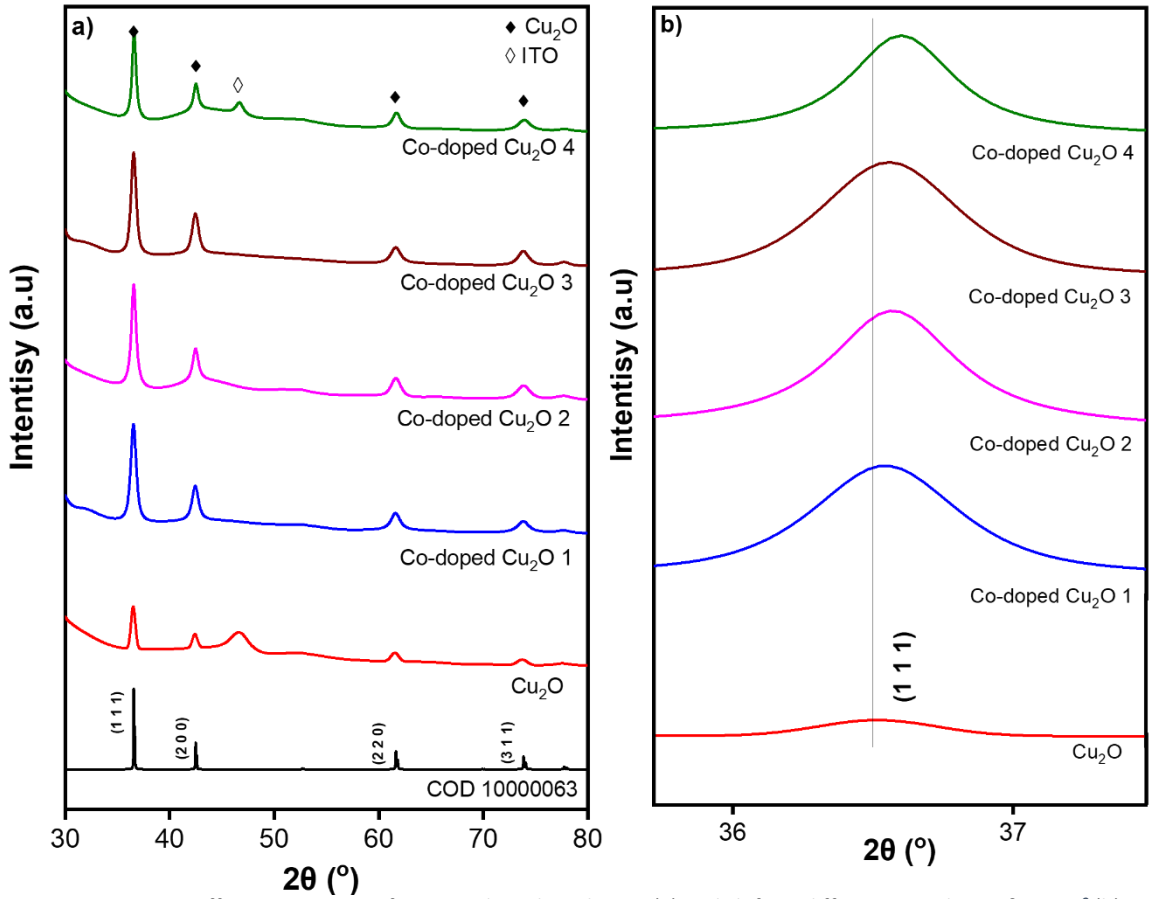

Figure 1. Diffraction pattern of Cu_2O and Co-doped Cu_2O (a) and shifting diffraction angle at 2θ 36.52° (b).

2.2.2 Phase and structural characterization

Phase analysis was conducted using an X-ray diffractometer (XRD, SmartLab Rigaku). Raman spectrometer (Horiba Scientific, yexc 532) with a wavelength of 532 nm was illuminated, and the Raman shift was recorded in the range of 50-1000 cm^{-1}.

2.2.3 Morphological characterization

Scanning electron microscopy (SEM, JIB-4610F equipped with a Schottky electron gun, accelerating voltage ranging from 0.1 to 30 kV) was employed to characterize the particle morphology.

3. Results and Discussion

The presence of Cu_2O in the synthesized samples was confirmed by XRD analysis, as presented in Fig. 1a. The diffraction pattern exhibits characteristic peaks corresponding to the cubic phase of Cu_2O at 2θ 36.52°, 42.4°, 61.52°, and 73.72°, which are associated with the (111), (200), (220), and (311) planes, respectively, and match the reference data COD 10000063. A noticeable shift in the diffraction peak of the (111) plane, as illustrated in Fig. 1b, indicates successful doping, attributed to lattice strain caused by the substitution of Co atoms into the Cu_2O lattice [20]. Moreover, the Co-doped Cu_2Osample generated sharper diffraction peaks compared to undoped Cu_2O, suggesting improved crystallinity [21].

The full width at half maximum (FWHM) of the (111) diffraction peak was employed to estimate the crystallite size using the Debye-Scherrer equation, as shown in equation 1 [22].

$$D = \frac{K\lambda}{B_{(hkl)}\mathrm{Cos}\theta} \quad (1)$$

where D is the crystallite size, K is the shape factor, λ represents the wavelength of the CuKα radiation, $B_{(hkl)}$ is the FWHM of the diffraction peak, and Cos θ is the Bragg angle. The calculated crystallite sizes for Cu_2O and Co-doped Cu_2O samples are summarized in Table 2.

Table 2. Crystallite size of Cu_2O and Co-doped Cu_2O.

Sample	Crystallite size (nm)
Cu_2O	18.3
Co-doped Cu_2O 1	14.4
Co-doped Cu_2O 2	15.0
Co-doped Cu_2O 3	15.0
Co-doped Cu_2O 4	16.0

Incorporating Co dopant influences the crystallite size of Cu_2O. Specifically, the dopant leads to a reduction in crystallite size, attributed to lattice distortion arising from the disparity in atomic radius between Cu and Co [16]. Conversely, an increase in dopant concentration generally promotes the growth of Co-doped Cu_2Ocrystallites. This phenomenon is associated with heightened lattice strain and the generation of interstitial atoms, ultimately contributing to an expansion in crystallite dimensions [23,24].

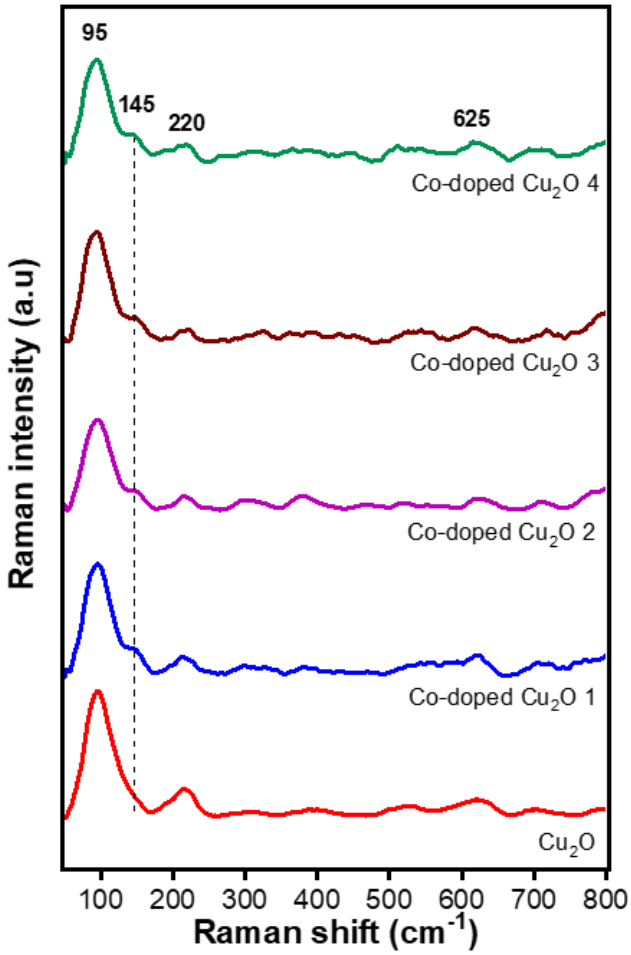

Figure 2. Raman shift of Cu_2O and Co-doped Cu_2O with different doping concentrations.

To further analyze cobalt doping, Raman spectra were obtained, as shown in Fig. 2. Raman analysis revealed characteristic Raman shifts corresponding to Cu_2O crystal vibrations at 95 and 220 cm^{-1}, which are attributed to the Γ_{15}^- and $2\Gamma_{12}^-$ modes, respectively [25,26]. Furthermore, peaks at 145 and 625 cm^{-1} are characteristic of infrared-active Γ_{15}^- vibrational modes induced by oxygen vacancies [25,27]. Notably, the peak at a Raman shift of 145 cm^{-1} was absent in the pure Cu_2O sample. This observation indicates the successful incorporation of the Co dopant. The introduction of Co atoms into the Cu_2O crystal lattice likely

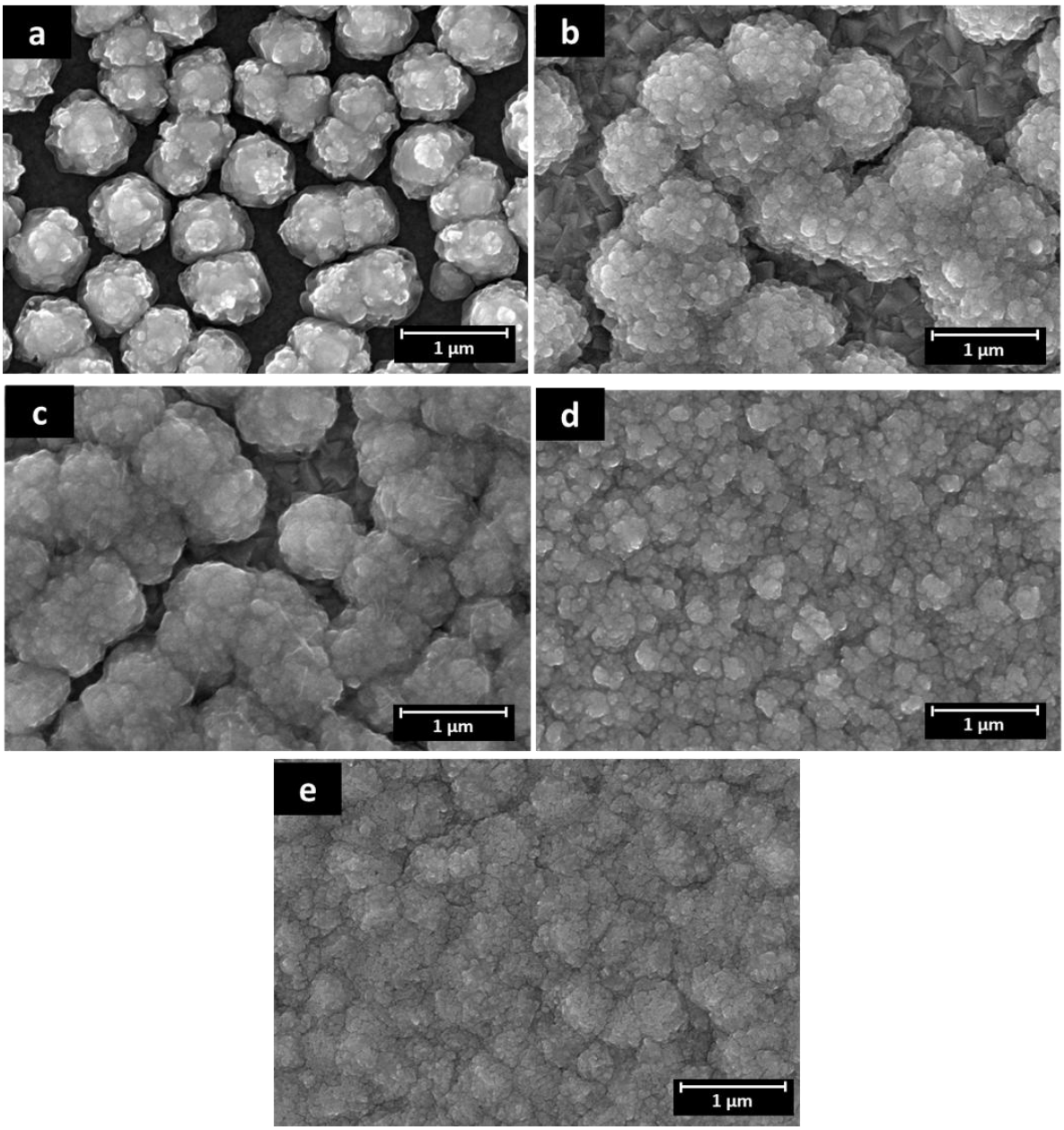

Figure 3. SEM micrograph top surface of Cu_2O and Co-doped Cu_2O with different doping concentration, 0 M (a), 0.00 2M (b), 0.005 M (c), 0.01 M(d), and 0.02 (d).

perturbs the lattice stability, potentially leading to the formation of defects, specifically oxygen vacancies.

Significant morphological changes were observed in the Cu_2O samples upon Co doping, as clearly shown in Fig. 3. The pristine Cu_2O sample exhibited a spherical structure with random orientation. Both the Co-doped Cu_2O 1 and Co-doped Cu_2O 2 samples displayed an identical structure, appearing to be composed of two layers: a pyramidal structure coated with a spherical structure. The finest particle morphology was observed in the Co-doped Cu_2O 3 sample. The morphology of Co-doped Cu_2O 3 and Co-doped Cu_2O 4 showed spherical particle shapes with less distinct grain boundaries. This irregular morphology could be influenced by illumination during electrodeposition. As the Cu_2O layer forms, it actively generates photogenerated electrons that can be utilized to reduce precursor ions [19,28]. These active sites may lead to rapid particle growth compared to less active sites, potentially resulting in the observed random orientation of particle shapes.

Table 3 presents the results of the EDS elemental percentage measurements. The atomic percentages of the constituent elements of the ITO substrate decreased with increasing Co doping. This indicates the influence of Co doping in enhancing the particle growth rate. The absence of detectable monometallic Co in samples Co-doped Cu_2O 1 to 3 suggests the successful incorporation of the dopant.

However, the higher doping percentage in sample Co-doped Cu_2O 4 resulted in a trace amount of monometallic Co, measuring 0.2%. This quantity is relatively smaller compared to findings in previous studies [26].

Table 3. Compositions of elements contained in Cu_2O and Co-doped Cu_2O coated on the ITO substrate.

Element	Cu_2O	Co-doped Cu_2O 1	Co-doped Cu_2O 2	Co-doped Cu_2O 3	Co-doped Cu_2O 4
Cu	54.1	68.4	72.1	71.3	75.8
O	41.8	29.5	26.8	27.6	23.3
In	3.9	2.0	1.0	1.0	0.7
Sn	0.3	0.1	0.1	0.1	0.1
Co	0	0	0	0	0.2

4. Conclusion

The synthesis of Co-doped Cu_2O was successfully achieved via a photoelectrodeposition method at room temperature. XRD analysis indicated the incorporation of Co atoms into the Cu_2O crystal lattice, as evidenced by a shift in the (111) diffraction peak. Cobalt doping initially led to a decrease in the Cu_2O crystallite size. In addition, the crystallite size subsequently increased with higher doping concentrations. Raman spectroscopy results corroborated the XRD findings, revealing an increase in oxygen vacancies upon Co doping. The irregular morphology of the Cu_2O potentially arises from the illumination during the deposition. Future studies could focus on optimizing the doping concentration and illumination parameters to further enhance the structural and optical properties of Co-doped Cu_2O for potential applications in photoelectrochemical devices.

Author contributions

Muhammad Raihan Rauf: Writing Original Draft and Investigation. Jumaeda Jatmika: Writing Review Editing and Supervision. Mohamad Hamzah Fauzi: Writing Review Editing and Supervision. Suci Winarsih: Writing Review Editing, Formal Analysis and Supervision.

Conflicts of interest

There are no conflicts to declare.

Acknowledgement

The authors thank DRTPM Kemendikbudristek of the Republic of Indonesia for supporting this work under Penelitian Terapan Kompetitif Nasional (PTKN) research scheme (6/PG.02.00.PT/LPPM/V/2022). The authors also thank the Advanced Characterization Laboratories Serpong, National Research and Innovation Agency (BRIN), for technical support and facility access through E-Layanan Sains for X-ray diffraction, Raman spectroscopy, and scanning electron microscopy. The Center for Science Innovation is also acknowledged for access to the electrochemical workstation during sample preparation.

References

[1] Q. Su, C. Zuo, M. Liu, X. Tai, A Review on Cu_2O-Based Composites in Photocatalysis: Synthesis, Modification, and Applications, *Molecules*. **28** (2023) 5576. https://doi.org/10.3390/molecules28145576.

[2] S. Zulqarnain Haider, S. Iqbal, H. Anwar, A. Ghadafi Ismail, J. Ali, Theoretical study on performance of heterojunction solar cell using wide bandgap metal oxide semiconductors, n.d.

[3] S. Budi, M. Gladiani Sutrisno, T. Hadinugrahaningsih, Synergistic enhancement of photocatalytic efficiency and durability in CoNi-decorated Cu_2O/Cu films for superior synthetic dye degradation, *Cleaner Materials*. **12** (2024) 100250. https://doi.org/10.1016/j.clema.2024.100250.

[4] S. Budi, M. Takahashi, M.G. Sutrisno, W.A. Adi, Z. Fairuza, B. Kurniawan, S. Maenosono, A.A. Umar, Phases evolution and photocatalytic activity of Cu_2O films electrodeposited from a non-pH-adjusted solution, *R Soc Open Sci*. **10** (2023). https://doi.org/10.1098/rsos.230247.

[5] Muhamad Athariq, Muhammad Raihan Rauf, Ikhfa Wiqoy Khairany, Intan Fadia Adani, Mega Gladiani Sutrisno, Synthesis and Characterization of Nanocube Cu_2O Thin Film at Room Temperature for Methylene Blue Photodegradation Application, *Chemistry and Materials*. **2** (2023) 67–71. https://doi.org/10.56425/cma.v2i3.65.

[6] S. Mohan, B. Honnappa, A. Augustin, M. Shanmugam, C. Chuaicham, K. Sasaki, B. Ramasamy, K. Sekar, A Critical Study of Cu_2O: Synthesis and Its Application in CO_2 Reduction by Photochemical and Electrochemical Approaches, *Catalysts*. **12** (2022). https://doi.org/10.3390/catal12040445.

[7] S.D. Tilley, Will Cuprous Oxide Really Make It in Water-Splitting Applications?, *ACS Energy Lett*. **8** (2023) 2338–2344. https://doi.org/10.1021/acsenergylett.3c00578.

[8] H. Lu, S. Song, Q. Jia, G. Liu, L. Jiang, Advances in Cu2O-based Photocathodes for Photoelectrochemical Water Splitting, *Acta Physico-Chimica Sinica*. **40** (2024) 2304035. https://doi.org/10.3866/PKU.WHXB202304035.

[9] H. Zhou, H. Zhao, X. Zhang, H. Cheng, X. Lu, Q. Xu, Facile one-step synthesis of Cu_2O@Cu sub-microspheres composites as anode materials for

lithium ion batteries, *J Mater Sci Technol*. **34** (2018) 1085–1090. https://doi.org/10.1016/j.jmst.2017.12.010.

[10] M. Lu, J. Chi, H. Chen, Z. Liu, P. Shi, Z. Lu, L. Yin, L. Du, L. Lv, P. Zhang, K. Xue, G. Cui, Ultrasensitive Bio-H2S Gas Sensor Based on Cu_2O-MWCNT Heterostructures, *ACS Sens*. (2023). https://doi.org/10.1021/acssensors.3c01594.

[11] A.M. Mohammed, S.S. Mohtar, F. Aziz, S.A. Mhamad, M. Aziz, Review of various strategies to boost the photocatalytic activity of the cuprous oxide-based photocatalyst, *J Environ Chem Eng*. **9** (2021). https://doi.org/10.1016/j.jece.2021.105138.

[12] Y.-H. Zhang, M.-M. Liu, J.-L. Chen, S.-M. Fang, P.-P. Zhou, Recent advances in Cu_2O-based composites for photocatalysis: a review, *Dalton Transactions*. **50** (2021) 4091–4111. https://doi.org/10.1039/D0DT04434B.

[13] P.C. Okoye, S.O. Azi, T.F. Qahtan, T.O. Owolabi, T.A. Saleh, Synthesis, properties, and applications of doped and undoped CuO and Cu_2O nanomaterials, *Mater Today Chem*. **30** (2023) 101513. https://doi.org/10.1016/j.mtchem.2023.101513.

[14] Y. Wang, J. Yang, Z. Zhang, P. Zhao, Y. Chen, Y. Guo, X. Luo, Highly stable Ag-doped Cu_2O immobilized cellulose-derived carbon beads with enhanced visible-light photocatalytic degradation of levofloxacin, *Int J Biol Macromol*. **269** (2024) 131885. https://doi.org/10.1016/j.ijbiomac.2024.131885.

[15] R. Medhi, M.D. Marquez, T.R. Lee, Visible-Light-Active Doped Metal Oxide Nanoparticles: Review of their Synthesis, Properties, and Applications, *ACS Appl Nano Mater*. **3** (2020) 6156–6185. https://doi.org/10.1021/acsanm.0c01035.

[16] E.F. Rakotonarivo, C.N. Abouloula, A. Narjis, L. Nkhaili, F. Brouillette, A. Oueriagli, Optimization of the electrodeposition of the pure and cobalt doped copper oxide for solar cells and other applications, *Physica B Condens Matter*. **609** (2021). https://doi.org/10.1016/j.physb.2020.412783.

[17] S. Sun, X. Zhang, Q. Yang, S. Liang, X. Zhang, Z. Yang, Cuprous oxide (Cu_2O) crystals with tailored architectures: A comprehensive review on synthesis, fundamental properties, functional modifications and applications, *Prog Mater Sci*. **96** (2018) 111–173. https://doi.org/10.1016/j.pmatsci.2018.03.006.

[18] K.-R. Yeo, J. Eo, M.J. Kim, S.-K. Kim, Shape Control of Metal Nanostructures by Electrodeposition and their Applications in Electrocatalysis, *J Electrochem Soc*. **169** (2022) 112502. https://doi.org/10.1149/1945-7111/ac9e21.

[19] S. Kim, Y. Kim, J. Jung, W.S. Chae, Photoassisted electrodeposition of a copper(I) oxide film, *Mater Trans*. **56** (2015) 377–380. https://doi.org/10.2320/matertrans.M2014391.

[20] Y.J. Lin, M.S. Wang, C.J. Liu, H.J. Huang, Defects, stress and abnormal shift of the (0 0 2) diffraction peak for Li-doped ZnO films, *Appl Surf Sci*. **256** (2010) 7623–7627. https://doi.org/10.1016/j.apsusc.2010.06.016.

[21] O.M. Abdulmunem, A.M. Jabbar, S.K. Muhammad, M.O. Dawood, S.S. Chiad, N.F. Habubi, Investigation of Co-doped Cu_2O thin films on the structural, optical and morphology by SPT, in: J Phys Conf Ser, IOP Publishing Ltd, 2020. https://doi.org/10.1088/1742-6596/1660/1/012055.

[22] S. Nasiri, M. Rabiei, A. Palevicius, G. Janusas, A. Vilkauskas, V. Nutalapati, A. Monshi, Modified Scherrer equation to calculate crystal size by XRD with high accuracy, examples Fe_2O_3, TiO_2 and V_2O_5, *Nano Trends*. **3** (2023) 100015. https://doi.org/10.1016/j.nwnano.2023.100015.

[23] A.M. El Sayed, M. Shaban, Structural, Optical and Photocatalytic Properties of Fe and (Co, Fe) Co-doped Copper Oxide Spin Coated Films, *Spectrochim Acta A Mol Biomol Spectrosc*. **149** (2015) 638–646. https://doi.org/10.1016/j.saa.2015.05.010.

[24] A. Muhammad, M. Sajid, M.N. Khan, M. Sheraz, A. Khalid, P. Ahmad, S. Alotibi, H.M. Alsaidi, N. Sobahi, M.M. Alam, S. Althahban, A.M. Saeedi, H.B. Albargi, Optimization of Physical and Dielectric Properties of Co-doped ZnO Nanoparticles for Low-frequency Devices, *PLoS One*. **18** (2023) 1–15. https://doi.org/10.1371/journal.pone.0287322.

[25] X. Jiang, Q. Lin, M. Zhang, X. Song, Z. Sun, Effect of temperature and additive on the structural, morphological and optical properties of Cu_2O thin films, *Optik (Stuttg)*. **126** (2015) 5544–5547. https://doi.org/10.1016/j.ijleo.2015.09.073.

[26] K.P. Ganesan, A. Amaliroselin, I. Joseph Panneer Doss, N. Anandhan, R. Ramesh, S. Prabhu, G. Sivakumar, R. Panneerselvam, High-performance energy storage of highly saturated ferromagnetic cobalt-doped cuprous oxide thin films, *Journal of Materials Science: Materials in Electronics*. **32** (2021) 7509–7527. https://doi.org/10.1007/s10854-021-05463-y.

[27] I. Djabri, T. Rezkallah, F. Chemam, Structural, electronic, optical, and magnetic properties of Co-doped Cu_2O, *Chinese Physics B*. **26** (2017). https://doi.org/10.1088/1674-1056/26/2/027102.

[28] M. Mikolasek, P. Ondrejka, F. Chymo, P. Novak, M. Pavuk, I. Novotny, V. Rehacek, J. Breza, A. Vincze, I. Hotovy, Potentiostatic electrodeposition under light irradiation for preparation of highly photoactive Cu_2O for water splitting applications, *Appl Surf Sci*. **461** (2018) 196–201. https://doi.org/10.1016/j.apsusc.2018.05.225.