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Oxidation of Methanol aqueous solution by Nanocomposite ZnO:CuO

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Abstract

In this study, zinc oxide was loaded onto cuprous oxide. The substrate used was cupric oxide, which was deposited and loaded onto the semiconductor using hydrogen peroxide. The reactants and the prepared inorganic complex were characterized using X-ray diffraction and scanning electron microscopy, in addition to elemental analysis of the binary complex before and after heat treatment. The experimental activity of the prepared binary complex was determined through the oxidation reaction of methanol solution to formaldehyde by irradiation with a lamp emitting light in the ultraviolet region. The results showed the successful photocatalytic transformation of the prepared complex in the methanol oxidation process, with higher efficiency than zinc oxide.

Keywords

ZnO:Cu₂O,
Formaldehyde,
EDX,
Oxidation,
CH₃OH/H₂O



Introduction:

semiconductors commonly used in huge application with conventional technologies currently used to degrade contaminated water includes firstly by adsorption, which did not represent final solution, then secondary process such chemical with photocatalytic reaction. The same reaction was depending for hydrogen production in addition to many catalytic reactions for many chemicals [1]. Binary semiconductors commonly modified by metal and non-metal doping, which coupling together and that also considered an important approach to improve photocatalytic preparation formaldehyde and hydrogen production. The semiconductors in Nano scale beehive specific properties such more surface charge, and reactivity, surface area, with sensitivity, and stability, therefore, are significant for commercial purposes [2]. Zinc oxide ZnO as a semiconductor and in nanoscale has many advantages, but still the disadvantages are represented by the problem of band gap, which limited the use and reduced the activity [3].

There are many attempts to enhance the effectiveness of zinc oxidase or at least reduce the negative impact of the energy required for stimulation. Many procedures have been developed by researchers in this field, including preparation or loading methods with selectively stimulating substances, especially [4]. The $\text{Cu}_2\text{O}/\text{ZnO}$ was synthesized [5] as a heterojunction photocatalyst by the in situ precipitation method and applied as a photocatalytic dye degradation by visible light irradiation, which succeeded in removing 73.3% of methylene blue within 60 min and showed higher activities than individual Cu_2O and ZnO.

The Cu_2O -ZnO matrix was synthesized [6] by using a hydrothermal process, X-ray diffraction, SEM, TEM, and energy-dispersive X-ray techniques to study structural, morphological, and crystallite properties. A novel heterojunction ZnO- Cu_2O was synthesized [7] by a hydrothermal process from nanorods of ZnO and Cu_2O nanoparticles with different ratios and applied for paraoxon insecticide degradation with visible light

irradiation. The results show that an inorganic oxide matrix with 40% of Cu_2O has the best photocatalytic activity of 0.0201 min^{-1} , and that is due to the harvesting ability of light, which increased, and the reduced e^-/h^+ of the recombination. In this work ZnO was also modified with CuO by a modifying method, which caused the creation of a new motivational boost capable of producing new effectiveness by using hydrogen peroxide as an oxidation and precipitation agent.

Experimental:

Synthesis of $\text{ZnO}:\text{Cu}_2\text{O}$

All chemicals (ZnO, CuO, acetylacetone, acetic acid, and ammonium acetate) were supplied from Aldrich, which were used without any purification process, while 40% hydrogen peroxide was supplied by Brenntag, Evonik, a Spanish producer. The methodology of synthesis of inorganic binary composites is represented by preparing two solutions, which are mentioned as A and B. The first solution was dissolved with 2 g of ZnO in 50 mL of distilled water using a magnetic stirrer to help disperse all particles. The second solution was B, and that required dissolving 2 g of CuO in 50 mL of distilled water before dropping 15 mL of 40% H_2O_2 (the addition was kept slow at a rate of addition of 4 mL/min.) with continuous stirring. After completing the prepared B solution, the first solution, A, was added dropwise, and the stirring was still at a rate of 250 rpm for 30 min. The solution after addition changed from black to green and then to light green/orange in solutions, which converted to green after filtration and black after thermal treatment at 200°C .

Oxidation reaction of CH_3OH

The Nash reagent, as an indicator for formaldehyde, was prepared by dissolving 1 m acetic acid and acetyl acetone with 50 g of ammonium acetate in 300 mL of distilled water. The activities of synthesized $\text{ZnO}:\text{Cu}_2\text{O}$ were tested in the photocatalytic oxidation reaction when making the oxidation of methanol to formaldehyde. Figure 1 includes the reaction requiring jacketed glass vessels (250 mL) as a reactor and 10 mL of ethanol with 90 mL of distilled water and 250 mg of

synthesized catalyst, which is stirred by a magnetic stirrer at 300 rpm. and kept the temperature by a recycled water bath system with UV light intensity of 1.4 mW m^{-2} . The mixture of reaction was purged for 15 min. with a flow rate of $2 \text{ cm}^3/\text{min}$ with N_2 gas to remove dissolved O_2 before starting irradiation. The

UV light is on, and then the reaction mixture is withdrawn 3 mL during specified (30 min.) intervals, to which 2 drops of Nash reagent are added. After filtration, the absorbance is measured at 550 nm by UV-visible spectroscopy.

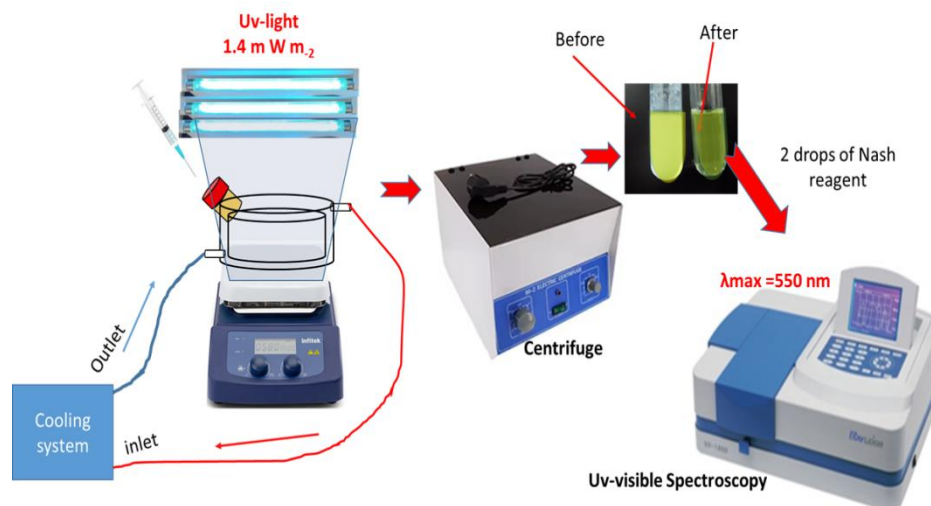


Figure 1: Skim of photocatalytic reaction by Uv-light steps and absorbance analysis at 550 nm at different temperatures.

Characterization:

The samples ZnO, CuO, and ZnO:Cu₂O before and after calcination were characterized by Philips X'Pert MPD X-ray diffractometer as X-ray diffraction XRD which provided radiation of Cu Kα at $\lambda = 1.54056 \text{ \AA}$.

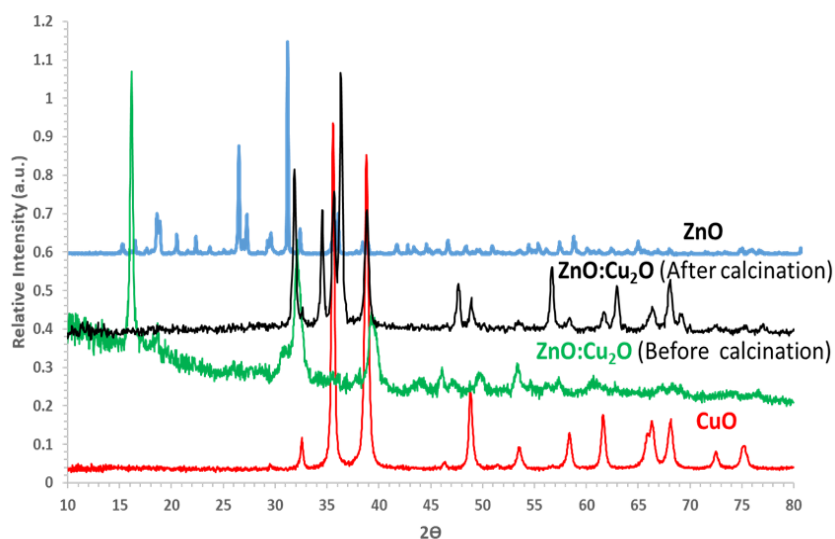


Figure 2: Skim of XRD patterns for ZnO, CuO, and ZnO:Cu₂O before and after calcination.

As shown in figure 2, the 32.6° (110), 35.7° (002), 38.9° (111), 49.0° (202), 53.6° (020), 61.7° (113), 66.2° (311), and 68.4° (220) all referred to CuO, which was determined to be pure copper oxide, and the diffraction peaks of the samples were sharp, which indicates that the CuO is monoclinic. Figure 2 reported ZnO nanoparticles with a characterized peaks spectrum of materials when the peaks at 30.3° (100), 32.4° (002), 36.4° (002), 56.9° (100), and 65.1° (200) referred to [8] the hexagonal phase of ZnO. The skim of Cu₂O nanoparticles, all the peaks [9] starting from $2\theta = 32.7^\circ$ and ending with 68.5° , which corresponds to the cubic Cu₂O structure, can be assigned to the (110) until (220) planes, respectively. The skim [10] previously refers to pure copper oxide (CuO), and the skim of diffraction peaks was sharp, and that indicates the monoclinic form of CuO.

The XRD peaks were strong and sharp, which showed at 30.5° , 32.7° , 38.3° , 45.8° , 50.3° , 53.2° , 57.8° , 67.1° , and 68.2° and were identified as (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3), (2 0 0), (1 1 2), and (2 0 1) reflections, respectively, in addition to the product before thermal treatment being a green fine crystalline structure. After thermal treatment of ZnO:Cu₂O, sharper peaks were shown, which mostly refer to CuO and Cu₂O with more intensity at 32.5° CuO (110), 35.2° Cu₂O (002), 38.2° CuO (111), 47.8° CuO (-202), 53.9° Cu₂O (020), 62.1° Cu₂O (-113), and 63.2° Cu₂O (-311). The primary peaks of ZnO in binary composites were shown to interfere with the peaks of

CuO and Cu₂O at 32.5° CuO 110, 35.2° Cu₂O 002, 38.2° and 47.8° CuO -202, and 53.9° Cu₂O 020, while the pristine peaks for ZnO were shown at 16.1° ZnO-100, 18.2° ZnO-202, and 31.5° ZnO-110 [11].

The Debye-Scherrer equation ($D = k\lambda/\beta \cos\theta$) was depended on to estimate the crystalline size [12-13] of the nanomaterial by the most intense peak at 32.4° (200), 35.8° (002), and 16.1° with 35.2° , which was 14 nm, 9 nm, 16 nm, and 21 nm for ZnO, CuO, and ZnO:CuO before and after calcination, respectively.

Scanning electron microscopy:

The SEM images were taken by scanning electron microscopy (SEM-VP 1450) and transmission electron microscopy to study the morphology of the resulting powders. Figure 3 reported the prepared ZnO:Cu₂O before thermal treatments, which included mostly regular shapes with tightly packed rectangular structures with diameters arranged between 48.5 nm X 40 nm and about 70 nm X 200 nm. The stacking of particles was seen, and that could not be distinguishing between Zn groups or Cu groups, and that could be related to obvious agglomeration. Figure 3 includes the EDX spectrum for elemental analysis with the mapping spectra offering information about the composite, which indicates the presence of Cu, Zn, and O. The element analysis has shown the percent of O with Zn and Cu. It is likely forming Cu₂O more than CuO [14-15].

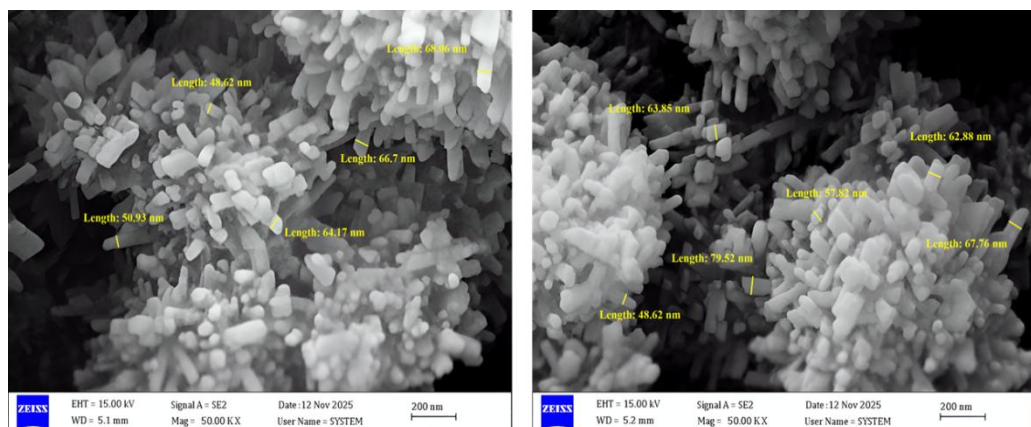


Figure 3: SEM micrographs of ZnO:Cu₂O powders before thermal treatment.

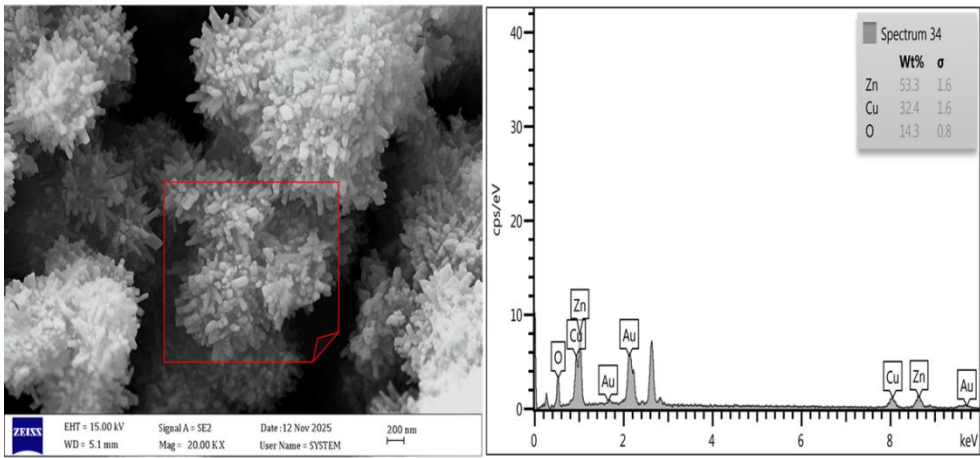


Figure 4: SEM, and EDAX spectrum showing the composition of ZnO: Cu₂O before thermal treatment.

The XRD patterns information and SEM with EDX are confirmatory of the synthesis of the ZnO:Cu₂O to form a heterojunction hybrid, and that was improved when taking the same analysis after thermal treatment as shown in figures 4 and 5. The main difference after thermal treatment could be seen in

reduced agglomerations, which formed after heating and reached a particle size of less than 50 nm x 50 nm, with a change in the shape of particles when they took on a spherical shape with more systematic orientations and diameters [16-17].

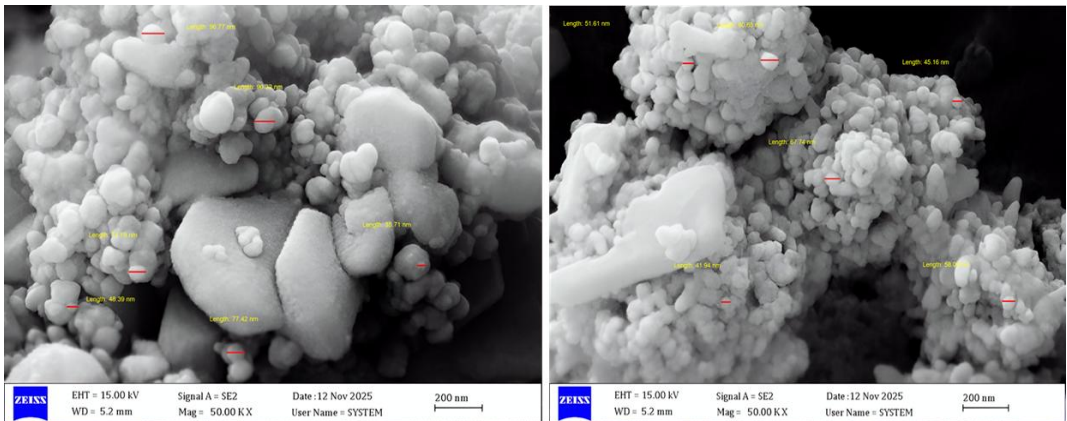


Figure 5: SEM micrographs of ZnO:Cu₂O powders after thermal treatment

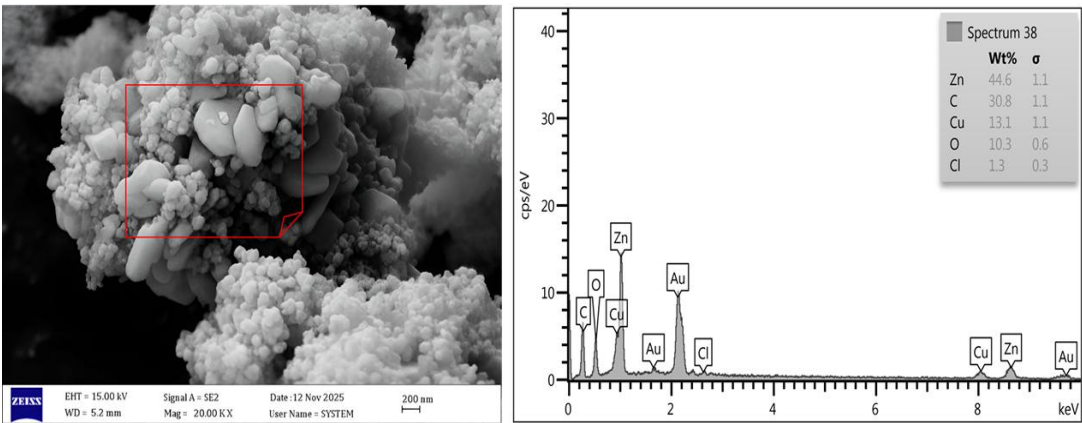
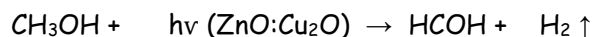


Figure 6: SEM, and EDAX spectrum for the composition of ZnO: Cu₂O after thermal treatments.

It can be seen from figure 6, which includes EDX analysis for ZnO:Cu₂O after thermal treatments, that the Cu, Zn, and O elements are uniformly dispersed in orientation on the ZnO:Cu₂O composite. The contents of Zn, Cu, and O are 44.6, 13.1, and 10.3 wt%, respectively. Therefore, that refers to the spherical particles distributed on the ZnO surface, which are Cu₂O particles. These ratios confirmed the reduced ratios of Cu₂O in binary composites of ZnO:Cu₂O after thermal treatments with the formation of C and Cl as byproducts for the remaining materials after the synthesis process [18-19].

Activity of ZnO:Cu₂O

The oxidation reaction of Methanol in aqueous solution was depended to identified the oxidation photocatalytic activity for synthesized ZnO-Cu₂O which forming formaldehyde as product materials and that was [20-21] measured at calculated periods as the chemical reaction:



To ensure the tracing of the transformation from methanol to formaldehyde, the last material's determined concentration during the reaction was colorimetrically measured by the absorbance at 550 nm after adding Nash reagent [22]. The activity of synthesized ZnO:Cu₂O was tested firstly to identify the effect of mass for the catalyst, which is reported in figure 7, and it was shown that 250 mg represented the best amount for the catalyst to achieve the largest [23] conversion $\{\%C = ((A_0 - A_t)/A_0)100\}$.

The best value is at 250 mg, as compared with more than this value, which may be related to the shielding effect of the catalyst, which prevents penetration of the UV light to the inner reactor [24], while the lower value of mass under 250 mg may be related to the existence of enough area to load more of the catalyst.

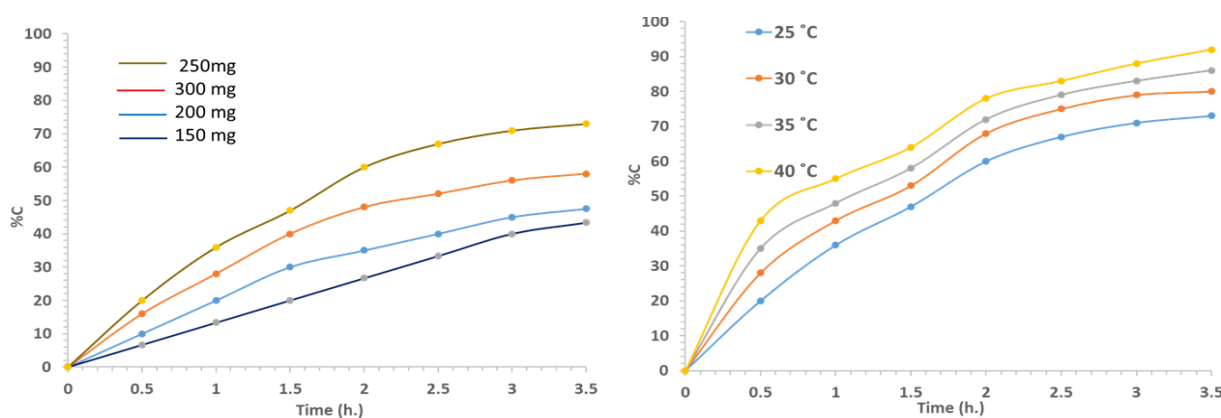


Figure 7: The skim of effect of different mass ZnO:Cu₂O (in the left) , (in the right) effect of temperature for binary composite (250 mg) in the photocatalytic degradation (10 % CH₃OH) at 25 °C and light intensity 1.4 m Wm⁻²

The enhancement was shown to increase with the change in temperature to more value as reported in figure 8, when it changed from 73.7%, 80.3%, 86.4%, and 92.3% for 25°C, 30°C, 35°C, and 40°C, respectively. The effect of mass for catalysts also can be related to creating more active sites capable of exporting species capable of carrying out the

oxidation process, as well as groups capable of sustaining the activity of the active groups. The two enhancement parameters were related to maintaining the condition of ideal exposure to the energy source necessary for stimulation, which is ultraviolet radiation [25].

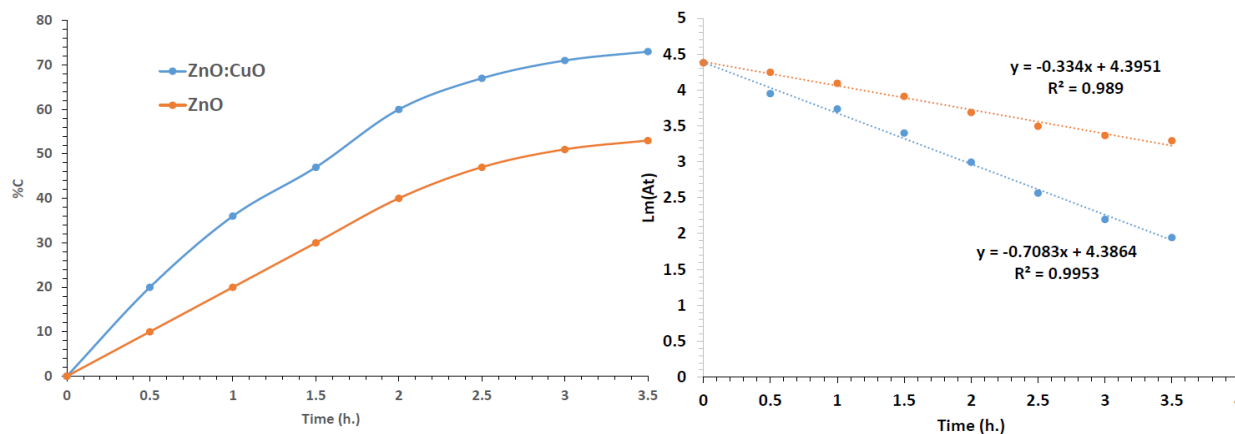


Figure 8: Skim for %C vs Time for oxidation CH₃OH/H₂O with ZnO:Cu₂O and ZnO by Uv-light lamb at the left and (LnAt) vs Time for calculation rat constant.

The best masses were compared with ZnO, which showed the highest activity, as reported in figure 8 on the right. The value of %C methanol to formaldehyde was 53.2% and 73.7% for ZnO and ZnO:Cu₂O, respectively, after 3.5 h under the irradiation of UV light. As shown in figure 8, the enhancement of the UV-light harvesting capability due to the existence of Cu₂O caused the reduction of the electron-hole pairs

recombination on the ZnO particles, and that considerably enhanced photocatalytic activity by more than 25%. The superior performance of the composite ZnO:Cu₂O compared to ZnO was also demonstrated by its significantly faster transformation rate, which was approximately double that of the transformation process, as documented in Figure 8 on the right.

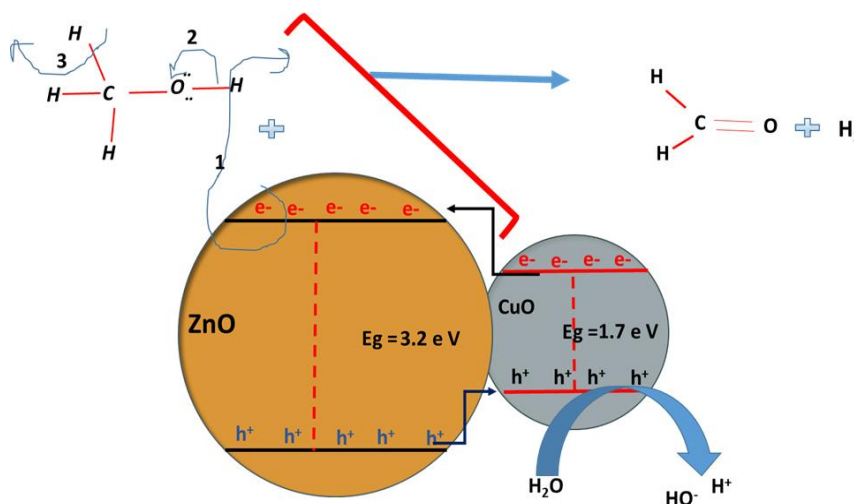


Figure 9: skim of propose mechanism for activities of ZnO:Cu₂O in Methanol oxidation reaction to formaldehyde

The clear enhancement of the effectiveness of the binary complex after loading zinc oxide with cuprous oxide is represented by the mechanism documented in Figure 9. The novel activity involves the positioning of cuprous oxide (Cu₂O) with ZnO in a way that enhances the release of species capable of carrying out the oxidation process, such as superoxide and

hydroxide free radicals, and converting methanol to formaldehyde [26].

Furthermore, cuprous oxide also acts as a catalyst, preventing the return of the catalyzed electrons to their initial state (h⁺), or at least delaying their return. This, in turn, increases the likelihood of the formation of new oxidizing species to carry out and

continue the conversion process from alcohol to aldehyde [27]. The role of cuprous oxide was also ideal because the preparation method prevented the formation of agglomerates and clumps that cause a loss in the number of active groups, as observed through X-ray diffraction analysis and in the images by SEM, where a reduction in particle size of approximately 30% was noted.

Conclusion:

Zinc oxide, as a nanostructured semiconductor, had its efficiency enhanced in the oxidation reaction of methanol solution by loading it with cuprous oxide. Hydrogen peroxide successfully acted as both an oxidizing and precipitating agent, successfully precipitating cupric oxide onto zinc oxide in the form of cuprous oxide. X-ray diffraction analysis revealed the productive deposition of a hybrid bond capable of reducing the size of the particles and increasing the concentration of the active groups, which were shown in scanning electron microscopy to have few clusters. The increase and enhancement in effectiveness can also be attributed to the hybrid bonding that enabled zinc oxide in the new structure to provide high effectiveness and efficiency compared to pristine zinc oxide.

References:

- 1- V. Shanmugam, R. A. Mensah, K. Babu, S. Gawusu, A. Chanda, Y. Tu, R. E. Neisiany, M. Försth, G. Sas, and O. Das, "A Review of the Synthesis, Properties, and Applications of 2D Materials", Part. Part. Syst. Charact. 2022, 39, 2200031, doi.org/10.1002/ppsc.202200031.
- 2- Z. Jannatun and M. S. S. R. Tejaswini, "Advancements in binary and ternary transition metal-based composites for high-performance super capacitors: a comprehensive review", journal "RSC Adv.", 2025, 15(12), pp. 9055-9080. [doi = "10.1039/D5RA00528K](https://doi.org/10.1039/D5RA00528K).
- 3- O. A. Bankole, and O. T. Olasimbo, "Binary CuO/ZnO Nanocomposites: A Mini-Review on Synthesis, Properties, and Emerging Applications", Journal Envi., Clim., and Ecol., 2025, 2(2), 163-172. <https://doi.org/10.69739/jece.v2i2.1024>.
- 4- K. K. Supin, P. M. Parvathy, M. Vasundhara, "Enhanced photocatalytic activity in ZnO nanoparticles developed using novel Lepidagathis ananthapuramensis leaf extract", RSC Advances, 2023, 13 (3), pp. 1497 - 1515, [10.1039/D2RA06967A](https://doi.org/10.1039/D2RA06967A).
- 5- J. Avinash, S.P. Vijaya, "Synthesis and characterization of Cu₂O/ZnO heterojunction for photocatalytic removal of methylene blue", Vacuum, 240, 2025, 114482, <https://doi.org/10.1016/j.vacuum.2025.114482>.
- 6- M.A. Soto-Mendoza, C.X. Tirado-López, A. Manzo-Robledo, "Cu₂O-ZnO oxide matrix synthesized by the hydrothermal method", MRS Advances 10, 1351-1357 (2025). <https://doi.org/10.1557/s43580-025-01155-5>.
- 7- H. Ghader, "Synthesis of novel p-n heterojunction photocatalyst from ZnO nanorod and Cu₂O nanoparticles for degradation of Paraoxon insecticide under visible light irradiation", Journal of Wat. Envi. Nanot., 2023, 8, 1, pp. 13-22, [10.22090/jwent.2023.08.002](https://doi.org/10.22090/jwent.2023.08.002).
- 8- X. Chao, C. Lixin, S. Ge, L. Wei, L. Hui, Y. Yaqin, Q. Xiaofei, "Preparation of ZnO/Cu₂O compound photocatalyst and application in treating organic dyes", Journal of haz. Mate., 2009, 176, pp. 7-13, [DO - 10.1016/j.jhazmat.2009.11.106](https://doi.org/10.1016/j.jhazmat.2009.11.106).
- 9- S. Tiwari, S. Kumar, A.K. Ganguli, "Role of MoS₂/ rGO co-catalyst to enhance the activity and stability of Cu₂O as photocatalyst towards photo electrochemical water splitting", Journal of Photoch. and Photob. A: Chemistry, 424 (2022) 113622. <https://doi.org/10.1016/j.jphotochem.2021.113622>.
- 10- V. N. Lam Uyen, N. T. Thuy Van, N. Van Minh, N. Tri, H. K. Phuong Ha, "Fabrication of Cu₂O-

- ZnO Nanocomposite by the Sol-gel Technique and its Antibacterial Activity", *J Biochem Tech* (2020) 11(1): 18-24.
- 11- P. Mathumba, M. P Bilibana, O. C Olatunde and D. C Onwudiwe, "X-ray diffraction profile analysis of green synthesized ZnO and TiO₂ nanoparticles", *Materials Research Express*, 2024, 11, (7) , *Mater. Res. Express* 11 075011 DOI 10.1088/2053-1591/ad63ff.
 - 12- Mohammed, Raghad S.; Aadim, Kadhim A.; and Ahmed, Khalid A. "Synthesis of CuO/ZnO and MgO/ZnO Core/Shell Nanoparticles with Plasma Jets and Study of their Structural and Optical Properties," *Karbala International Journal of Modern Science*, 2022, 8 (2) , <https://doi.org/10.33640/2405-609X.3225>.
 - 13- M. M. Khaled, M. Umair, C. M. Pecoraro, A. Kheniche, M. Bellardita, S. Soltani, "Green synthesis of ZnO and CuO nanoparticles and ZnO-CuO nanocomposites: Characterization and photocatalytic dyes removal efficiency's determination", *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 2026, 728(1) , <https://doi.org/10.1016/j.colsurfa.2025.138544>.
 - 14- P. F. Jony; S. Zuriah, T. Kerista; and S. Nurdin "Enhanced Photocatalytic Activity of Cu₂O/ZnO/GO Nanocomposites on the Methylene Blue Degradation," *Baghdad Science Journal*, 2024, 21(1), DOI: <https://doi.org/10.21123/bsj.2023.8087>.
 - 15- I. H. Bhuiyan, S. . Moulick, Md. R. Islam, Md. S. Hossain, S. S. Dey, S. A. Chhanda, F. Ahmed, Md. F. Ahmed, T. Muslim, " Green Synthesis and Characterization of Copper Oxide (CuO) Nanoparticles Using Mesua ferrea Leaf Extract and Evaluation of Biological Activities", *Angewandte Chemie Novit* , 2025, [10 \(43\)](https://doi.org/10.1002/slct.202503202). <https://doi.org/10.1002/slct.202503202> Digital Object Identifier (DOI).
 - 16- Y. Li , M. Yan, X. Li , J. Ma, " Construction of Cu₂O-ZnO/Cellulose Composites for Enhancing the Photocatalytic Performance", . *Catalysts*. 2024; 14(8):476. <https://doi.org/10.3390/catal14080476>.
 - 17- M. Ibn Mahrsi, B. Chouchene, T. Gries, V. Carré, G. Medjahdi, F. Ayari, L. Balan, R. Schneider, " OD/1D CuO-Cu₂O/ZnO p-n heterojunction with high photocatalytic activity for the degradation of dyes and Naproxen", *Journal of Envi. Chem. Eng.*, 12 (3), 2024, 113072, <https://doi.org/10.1016/j.jecce.2024.113072>.
 - 18- G. Si-Tong, T. Zi-Yuan, D. Yu-Wei, L. Ting, O. Ting, L. Zhao-Qing, "Chlorine anion stabilized Cu₂O/ZnO photocathode for selective CO₂ reduction to CH₄", *Appl. Catal. B: Environmental*. 2022, 321, sp.122035, 10.1016/j.apcatb.2022.122035.
 - 19- Al-Saeedi, Sameerah I., Ghadah M. Al-Senani, Omar H. Abd-Elkader, and Nasrallah M. Deraz. 2021. "One Pot Synthesis, Surface and Magnetic Properties of Cu₂O/Cu and Cu₂O/CuO Nanocomposites" *Crystals* 11(7), 751. <https://doi.org/10.3390/cryst11070751>.
 - 20- H. Inokawa, S. F. Zaman, H. Driss, M. Daous, A. Al-Zahrani, H. Miyaoka, T. Ichikawa, Y. Kojima, L. A. Petrov, "Formaldehyde production via partial oxidation of methanol over oxides of Cr, Mo and W supported on ceria-zirconia", *IOP Conference Series: Materials Science and Engineering*, 2018, 458, pp. - 1757-899X- 1757-8981, 10.1088/1757-899X/458/1/012018.
 - 21- Q. Shi, Z. Qin, C. Yu, "Experimental and mechanistic understanding of photo-oxidation of methanol catalyzed by CuO/TiO₂-spindle nanocomposite", *Oxygen vacancy engineering. Nano Res.* 2020, 13, 939-946, <https://doi.org/10.1007/s12274-020-2719-7>.
 - 22- D. Sabahattin and A. Adnan, " A New Spectrophotometric Method for Determination of Formaldehyde in Aqueous Medium", <https://ssrn.com/abstract=>

5859752 or <http://dx.doi.org/10.2139/ssrn.5859752>.

- 23-Z. Li, A. Ivanenko, X. Meng, Z. Zhang, "Photocatalytic oxidation of methanol to formaldehyde on bismuth-based semiconductors", *Journal of Haz. Mate.*, 380,2019,120822,<https://doi.org/10.1016/j.jhazmat.2019.120822>.
- 24-X. Li, Y. Chen, Y. Tao, L. Shen, Z. Xu, Z. Bian, H. Li, "Challenges of photocatalysis and their coping strategies", *Chem Catalysis*,2,(6),2022,pp. 1315-1345, <https://doi.org/10.1016/j.checat.2022.04.007>.
- 25-X. Yanghui, O. Qin, V. Hoek Jan Peter, L. Gang, L. Kim Maren, "Photo-oxidation of Micro- and Nanoplastics: Physical, Chemical, and Biological Effects in Environments", 2024, *Envir. Science & Techn.*,58, (2), pp.991-1009. doi: 10.1021/acs.est.3c07035.
- 26-K. Yin, Y. Yang, M. Xu, L. Li, Y. Li, J. Dai, W. Cao, T. Wu, J. Gu, D. Wang, " simultaneously inhibiting thermodynamic and kinetic photocorrosion of p-type Cu₂O via amorphous hole transfer conformal interfaces", *Journal of Colloid and Interface Science*,2026, 703, (139175), 10.1016/j.jcis.2025.139175, .
- 27-M. M. Bhat, S. A. Bhat, A. Hamid, A. Bhat, C. M. Suresh, P. P. Ingole, M. A. Bhat, " TiO₂ - Supported Cu-MOF Nanocomposites for Photoboosted Electrochemical CO₂ Reduction to Methane", *ACS Applied Nano Materials*, 2026, 10.1021/acsanm.5c04197.