UDC 544.654.2

SIMULTANEOUS ANODIC AND CATHODIC ELECTRODEPOSITION OF Cu_2O FOR SOLAR ENERGY CONVERSION

Kevin F. Genaro-Saldivar[1], Geovanni R. Negrete-Reyes[1], Esther Ramirez-Meneses[1], Carlos Juarez-Balderas[2], Flor Avendano-Sanjuan[1], Diana A. Garcia-Najera[1], Jorge G. Ibanez[1,*]

[1] *Department of Chemical, Industrial, and Food Engineering, Iberoamerican University, Mexico City, Mexico*
[2] *Department of Engineering Studies for Innovation, Iberoamerican University, Mexico City, Mexico*
**Corresponding author: jorge.g.ibanez@gmail.com*

Received 28.03.2024
Accepted 06.06.2024

Abstract: *Copper oxide, Cu_2O is a highly versatile product that can obtained by different techniques including high/low temperature thermal oxidation, sputtering, chemical oxidation, anodic oxidation, electrodeposition, among others. Until now, the most efficient synthetic processes to obtain Cu_2O require relatively expensive equipment; therefore, we have developed a novel method based on simultaneous convergent oxidation-reduction reactions in an electrolytic cell at ambient pressure and relatively low temperature. In this work, a Cu(0) plate is oxidized to Cu(I) in the anodic compartment, while a Cu(II)-lactate complex is formed in the cathodic compartment of the cell and then Cu(II) is reduced to Cu(I), all in aqueous media.*

Keywords: *Cu_2O synthesis, convergent synthesis, copper (I) oxide, electrodeposition, simultaneous processes.*

DOI: 10.32737/2221-8688-2024-4-447-457

1. Introduction

Cu(I) oxide (Cu_2O, copper oxide) is found in nature as the reddish mineral *cuprite* that crystallizes in a face-centered cubic crystal lattice (FCC), similar to the NaCl structure, with lattice parameters a = b = c = 4.27 Å [1]. Cu_2O represents a highly versatile material. Many antifouling paints contain Cu_2O as the main active compound [2]. It is also used in agricultural products [3], fungicides [4], glucose sensors [5,6], photovoltaic devices [7,8], photocatalytic decomposition of water [9,10], dye-sensitized solar cells [11], piezoelectric and thermoelectric sensors [12], electrodes in Li^+ batteries [13,14], fuel cell catalysis [15], pigments for ceramics [3], and for the removal of pollutants like I^- [16], O_3 [17], and dyes [18, 19]. For this last application, Cu_2O recyclability may become an invaluable asset [20]. On the other hand, its use in glucose sensors represents one of the most important niches regarding health, especially for those with diabetes; for example, a Ti_3C_2/Cu_2O composite is used for the non-enzymatic photoelectrochemical glucose detection [6]. Alternatively, Cu_2O is electrodeposited to provide a sensitive response to glucose and offers the advantage of low-cost production as compared to other alternatives [5].

Some of Cu_2O′s most promising applications rely on its properties as a semiconductor that allows the flow of electrons with an electrical conductivity smaller than a metallic conductor, and higher than an insulating material; excess electrons or holes yield the *n*-type or *p*-type semiconductor, respectively. In addition to its intrinsic characteristic as an ionic, non-stoichiometric *p*-type semiconductor, Cu_2O can be artificially doped by a trivalent atom (*acceptor impurity*),

where each of the "holes" contributed by this trivalent species can accept a free electron [21, 22]. Its direct band gap energy, E_g = 2.17 eV [23] with an acceptor level at 0.4 eV above its valence band and an electron donor level at 1.1 eV below its conduction band —together with its low cost and toxicity, high optical absorption coefficient, and short minority carrier diffusion length make Cu_2O a good candidate for solar conversion [7, 21].

Another potentially important use that takes advantage of Cu_2O´s semiconductivity is its application as a photocatalyst for the decomposition of water due to its favorable energetics and high chemical stability [24]. Photocatalysis in a *p*-type semiconductor implies that the majority charge carriers (i.e., holes) oxidize water to molecular oxygen, whereas the photogenerated minority charge carriers (i.e., electrons) reduce water to molecular hydrogen [9, 25]. In the case of Cu_2O, its conduction band-edge is favorably located at 0.7 V more negative than the reduction potential of H^+(aq) [26].

One of the current topics of greatest interest is sustainable energy, where the use of Cu_2O in Li^+ battery electrodes is gaining importance [14]. The benefits of these cells include high interconversions and a low degree of electrolyte decomposition. Due to its semiconducting nature, Cu_2O is useful in these electrodes as it offers easy charging and discharging during electronic exchange with Li^+ ions. Furthermore, due to its vacancies, it has viable sites for the Li^+-promoted redox reactions to occur [14].

1.1. Cu_2O Production

Cu_2O production is achieved by different physical, chemical, and electrochemical methods such as pyrolysis [27], spraying or sputtering [28], vapor phase chemical deposition [29], thermal, hydrothermal, and chemical oxidation [16, 30], Cu(II) reduction [31], microgrowth within the pores of ion exchange resins [32], ultrasound and microwave assisted precipitation [24], and electrodeposition [13, 33]. The sputtering method, in addition to its high cost, has difficulties in the control of stoichiometry and the need for long deposition times to obtain coatings [34]. Pyrolytic spraying is an important alternative for industrial use and does not require a large investment, since the use of vacuum is avoided; however, the surface deposits obtained are not entirely clean, which significantly influences the purity of the synthesized material [35]. Even at a considerable economic cost, composites of Cu_2O thin films on carbon networks (CNW) have been designed with flexible structures [20].

A promising alternative for several of the above applications is the electrochemical pathway due to its low cost and eases of control. Here, Cu_2O is produced by passing an electric current through a circuit consisting of two electrodes separated by an ionic aqueous medium (i.e., electrolyte), promoting oxidation-reduction reactions at the electrodes that cause the formation of insoluble deposits of Cu_2O. This is possible due to the transfer of electrons between the electrode-substrate interface and the adjacent electrolyte [36]. Further discussion of these principles and the results of our preliminary tests to achieve the simultaneous production of Cu_2O on both sides of an electrolytic cell now follow.

1.2. Electrochemical Synthesis of Cu_2O

Electrodeposition has several practical advantages as it is performed in aqueous solutions at ambient pressure and relatively low temperatures [37], normally limited only by the boiling point of the electrolyte. The electrochemical production of Cu_2O has been reported both cathodically and anodically [7, 22, 38-40]. Both the galvanostatic and the potentiostatic modes have been used [7, 21, 37, 40]. When working in the galvanostatic mode, there is a linear relationship between the deposition rate and time, and the deposits are essentially not affected by temperature, whereas in the potentiostatic mode the growth rate changes exponentially with deposition time and it is temperature dependent [38]. The temperature range is typically between 30 °C [38], and 86 °C [7]. The deposition requires a substrate that can vary among different metals such as Au [40], Cu [5, 7], Pt [38, 40], Ti [38], and stainless steel [21, 38].

While anodic electrosynthesis typically produces *p*-Cu_2O [39], Cu_2O can also acquire an *n*-type character by varying the pH of the electrodeposition bath since oxygen and copper vacancies are thereby generated. Excess copper in the lattice is believed to be responsible for the *n*-type behavior [39]. The pH and temperature can impact the final morphology of the deposit,

where the exposed atomic planes of the polycrystals can experience preferential orientation [41] probably due to alternate kinetic pathways [21, 42]. Electrodeposition has been reported at various pH values from 3.6 [38], to 12 [21]. For example, sheets deposited at pH = 9 show a uniform deposit with a preferential (100) crystal orientation of Cu_2O grains, whereas at higher pH the grains show a (111) crystal orientation [38]. Current cycling is an alternative strategy to obtain single-phase, uniform and compact Cu_2O cathodic films [43].

The electrolytic baths most commonly used involve $CuSO_4$ at molarities ranging from 0.01 M to 0.4 M [7, 40]. The use of $CuNO_3$ [44], and $Cu(CH_3COO)_2$ [38,39], as electrolytes has also been reported. For deposition at basic pH it is necessary to avoid $Cu(OH)_2$ precipitation by using complexing agents such as lactate [21, 26, 41], citrate [14, 40], 1,3,5–benzentricarboxylate [5], among others. An essential factor in an electrochemical synthesis is the imposed potential (*E*) because, according to the corresponding Pourbaix diagram, this and the pH of the electrolyte determine the existence of the predominant species. The stability region for the formation of Cu_2O under standard conditions in the Cu-Pourbaix diagram is rather small [46], which call for the need of complexing agents to amplify it and favor the formation of the semiconductor.

For $CuNO_3$ in acidic media, the reaction mechanism involves a local pH increase prior to the formation of Cu_2O due to the OH^- ions produced after the reduction of NO_3^- to NO_2^- [47]. On the other hand, the anodic deposition is simpler; it consists of performing the oxidation of a Cu(0) electrode at temperatures ranging from room temperature to 85 °C, where the required electrolyte is simply an ionic solution at different possible pH values [5]. The photovoltaic ability of Cu_2O can be incremented by forming a heterojunction between CuO and Cu_2O through the initial deposition of Cu_2O on a Pt electrode and the subsequent application of heat treatment up to approximately 500 °C to convert part of the Cu_2O to CuO [44].

1.3. Convergent Electrochemical Synthesis

The simultaneous convergent electrosynthesis of materials is very rarely attained [48, 49], and that of Cu_2O has not been reported yet. By using an electrochemical cell divided by a cation exchange membrane, and adjusting the solution variables on both sides (i.e., pH, concentration, and temperature) as well as the applied potential, it is possible to form a Cu(II) lactate complex from which the cathodic deposition of Cu_2O is enabled at the same time as the direct anodic conversion of Cu(0) to Cu_2O. Using this rationale, we were able to obtain this oxide in both - the anodic and cathodic compartments - which opens a new frontier of possibilities for its production in a simple and economical way as described below.

2. Experimental part

The convergent synthesis of Cu_2O was enabled in an H-type glass reactor divided by a Nafion membrane (Nafion 417, Aldrich). For the cathodic deposition, two solutions were prepared: a) 2.5 M lactic acid, $C_3H_6O_3$ (as complexing agent), and b) 0.3 M $CuSO_4$. The latter solutions were placed in the catholyte in equal volumes, and the pH of the resulting mixture was adjusted to 9 by adding 3.0 M NaOH, as necessary. The reported structure for the Cu(II) lactate complex is given in Fig. 1 [45].

For the anodic deposition, a 0.5 M Na_2SO_4 solution was prepared and its final pH adjusted to 9 - 11.3 with 0.1 M NaOH (see Fig. 2). All substances used were reagent grade (NaCl, J.T. Baker; Na_2SO_4, Sigma Aldrich; CuO, J.T. Baker; Cu_2O, J.T. Baker; NaOH, Meyer), except lactic acid (80% pure, J.T. Baker), without further treatment and the solutions were prepared using deionized water.

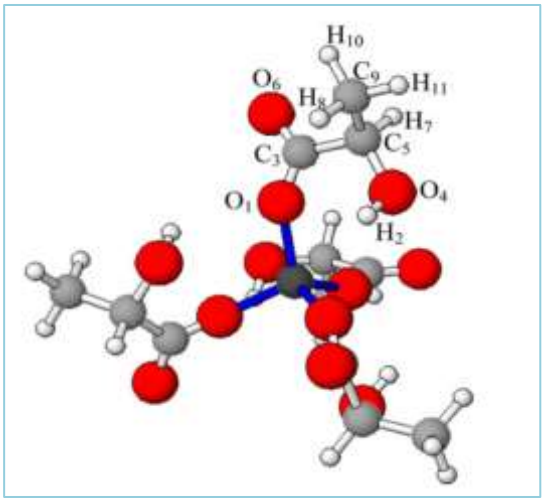


Fig. 1. Structure of the Cu(II) lactate complex. Adapted with permission from Ref. [45].

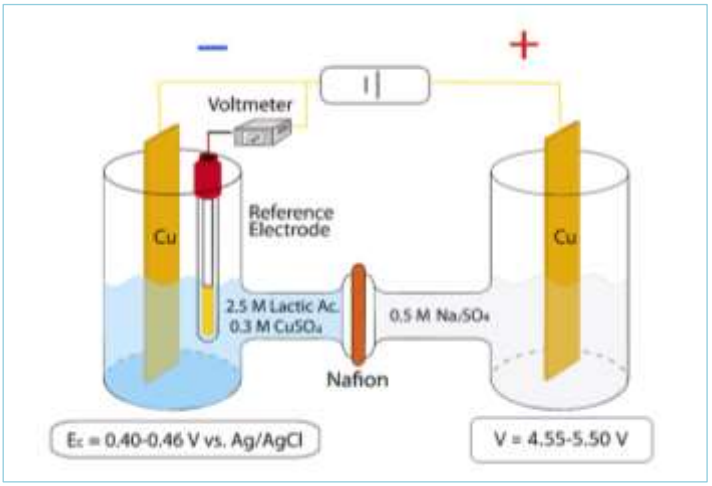


Fig. 2. Schematic representation of the H-type glass cell used in this work for the convergent electrosynthesis of Cu_2O.

All experiments were performed at 65 °C for both the catholyte and the anolyte. The potentials were imposed with a TES-6100 power source and measured with a high-precision Steren model Mul-630 multimeter (Steren, Mexico). The electrodes used were 5 cm × 1 cm Cu plates, electrolytic grade (minimum purity: 99.99%), gauge 26, pretreated with 50% HNO_3 and then washed with distilled water. Current density stayed essentially constant at approx. 20 mA/cm^2. An Ag/AgCl reference electrode (Bioanalytical Systems, USA) was used throughout the procedure.

3. Results and discussion

Plausible reactions occurring at each electrode are as follows:

a) Anode [50, 51]

$$2Cu(s) + 4H_2O(l) \rightarrow 2Cu(OH)_2^-(aq) + 4H^+(aq) + 2e^- \quad (1)$$

$$2Cu(OH)_2^-(aq) \rightarrow Cu_2O(s) + 2OH^-(aq) + H_2O(l) \quad (2)$$

The excess Cu(II) present in the anolyte can migrate together with H^+ ions through the Nafion membrane towards the cathode where they become reduced as follows.

b) Cathode [45]

$$Cu(II)(aq) \xrightarrow{2e^-} Cu(s) \quad (3)$$

$$Cu(s) + 2OH^-(aq) + [Cu(C_3H_5O_3)_4]^{2-}(aq) \rightarrow Cu_2O(s) + 4\ C_3H_5O_3^-(aq) + H_2O(l) \quad (4)$$

Fig. 3 shows optical images of the oxide layers deposited on the anode and cathode of the cell. The reddish hue is characteristic of Cu_2O. The darker hue observed in the anodic deposit may be due to disturbances in the crystal lattice.

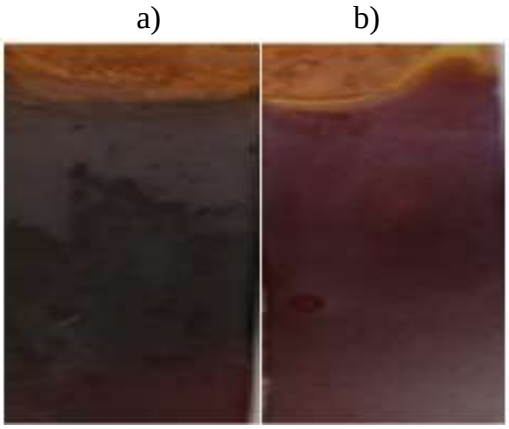


Fig. 3. Images of Cu plates with Cu_2O deposited: (a) at the anode, and (b) at the cathode of the H-cell.

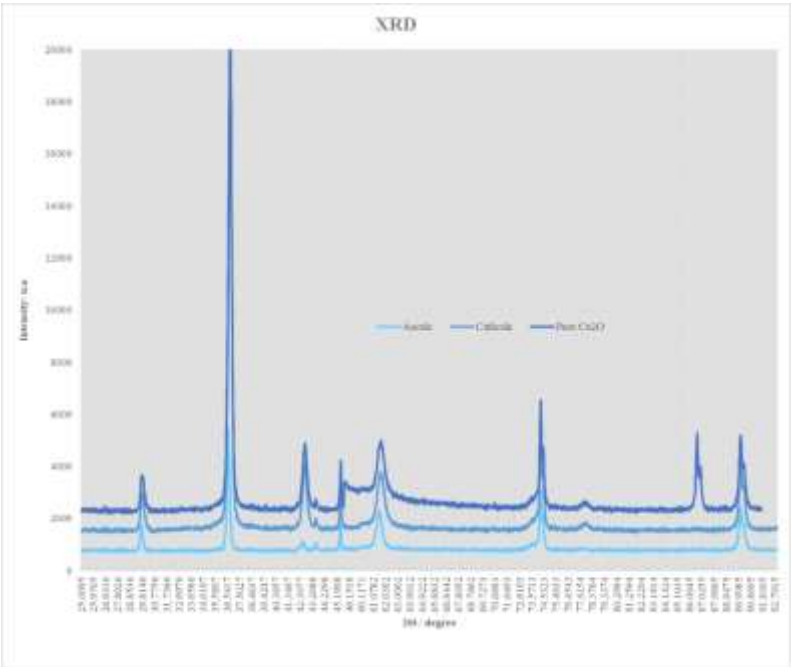


Fig. 4. XRD of the Cu_2O deposits from the anodic and cathodic convergent synthesis, and those obtained with a pure Cu_2O sample. The conditions for the anodic deposits were: pH_i = 11.38, pH_f = 5.2, $V_{cell,i}$ = 4.55 V, $V_{cell,f}$ = 5.50 V, and for the cathodic deposits they were: pH_i = 10.4, pH_f = 9.18; $V_{cell,i}$ = 0.40 V, $V_{cell,f}$ = 0.46 V. t = 15 min, and T = 65 °C.

To ascertain the nature and characteristics of the as-obtained deposits, structural and morphological characterizations were performed with a Hitachi model SU3500 Scanning Electron Microscope (SEM) and a Bruker model D8 Advance ECO X-Ray Diffractometer (XRD).

The initial and final pH values (pH_i, pH_f), and the initial and final cell voltages ($V_{cell,i}$, $V_{cell,f}$) are given below.

Fig. 4 shows the obtained XRD results of the Cu_2O deposits from the anodic and cathodic convergent syntheses, and those obtained with a pure Cu_2O sample. Fig. 5 shows the summary comparison. The peaks at 2θ = 29.8, 36.6, 42.7, 52.6, 61.7, 66.1, 69.9, and 73.6 ° correspond to the (110), (111), (200), (211), (220) (221), (310), and (311) planes, respectively, in good agreement with the corresponding JCPDS data for polycrystalline Cu_2O (JCPDS card No. 05–0667). Concerning the possible presence of CuO, the lack of peaks at 2θ = 37.1 °, 61.8 °, and 74.3 ° that correspond to the (200), (220), and (311) CuO planes indicates their absence, although the peak at 2θ = 36.6 ° may indicate that some CuO is present in the (111) phase.

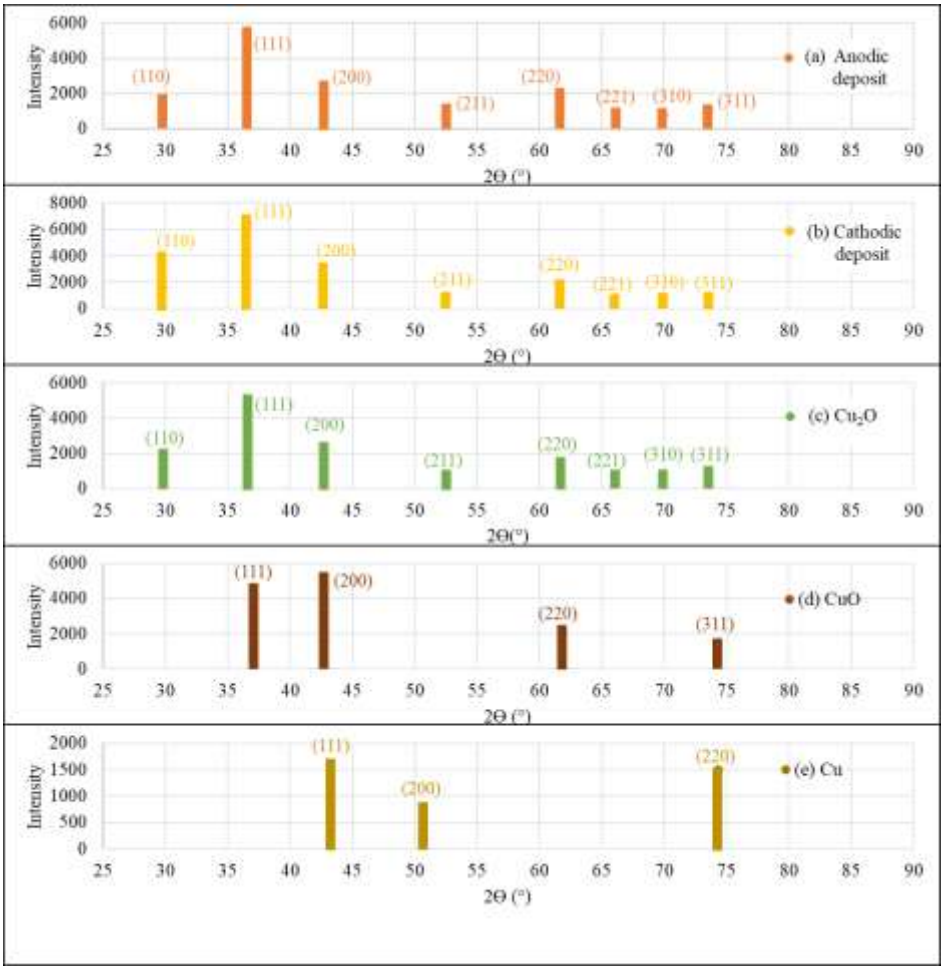
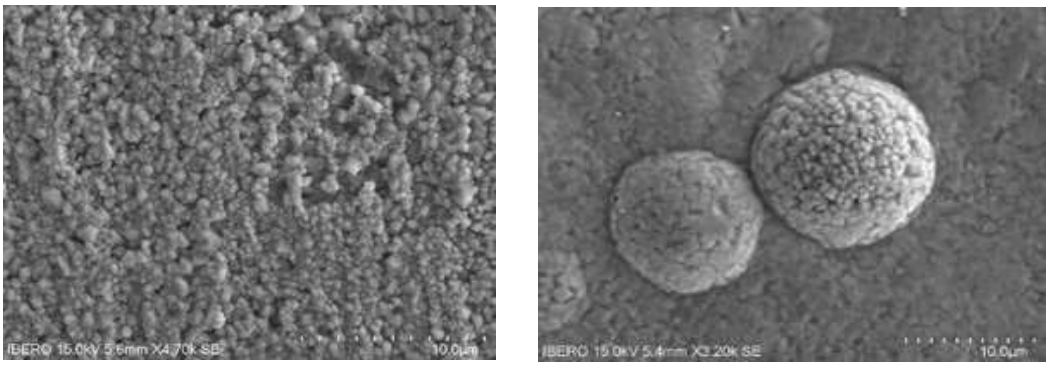


Fig. 5. XRD summary of the Cu_2O deposits from the anodic and cathodic convergent synthesis. The conditions for the anodic deposits were: pH_i = 11.38, pH_f = 5.2, $V_{cell,i}$ = 4.55 V, $V_{cell,f}$ = 5.50 V, and for the cathodic deposits they were: pH_i = 10.4, pH_f = 9.18; $V_{cell,i}$ = 0.40 V, $V_{cell,f}$ = 0.46 V. t = 15 min, and T = 65 °C. XRD line patterns of pure Cu_2O, CuO and Cu are also shown for comparison.



a) b)

Fig. 6. SEM images of Cu_2O prepared by convergent electrosynthesis. (a) Anodic deposit (pH_i = 11.38, pH_f = 5.20, $V_{cell,i}$ = 4.55 V, $V_{cell,f}$ = 5.50 V), and (b) cathodic deposit (pH_i = 10.40, pH_f = 9.18; $V_{cell,i}$ = 0.40 V, $V_{cell,f}$ = 0.46 V). t = 15 min, and T = 65 °C.

4. Conclusions

Adequate conditions were found for the simultaneous convergent deposition of Cu_2O at the anode and cathode of an electrochemical cell. Using SEM and XRD, the presence of Cu_2O was verified in both compartments, with some possible CuO contamination. The use of an electrochemical process as an alternative synthetic route is very attractive and has several advantages, including the low cost of the equipment and reagents, and its ease of application.

Acknowledgments

K. G., G. N. and F. A. acknowledge student assistantships provided by the National Council for Science and Technology (CONACYT, Mexico) numbers 893221, 843910, and 843508 respectively.

References

1. Korzhavyi P.A., Soroka I.L., Isaev E.I., Lilja C., Johansson B. Exploring monovalent copper compounds with oxygen and hydrogen // Proceedings of the National Academy of Sciences, USA. 2012, V. 109, pp. 686-689. DOI: 10.1073/pnas.1115834109.
2. Rejeki S., Susilowati T., Wisnu-Aryati R. Application of copper oxide paints as prevention for macrofouling attachment on a marine floating net cage // Journal of Coastal Development, 2010, V. 13, no. 3, pp. 166-178.
3. González O., Bisang J.M. Electrochemical synthesis of cuprous oxide with a cylindrical bipolar reactor // Journal of Chemical Technology and Bioechnology, 2012, V. 88, no. 7, pp. 1314-1320. DOI.org/10.1002/jctb.3977.
4. Pesticide Properties DataBase, PPDB. University of Hertfordshire, UK. https://sitem.herts.ac.uk/aeru/ppdb/en/Reports/176.htm, accessed on Jun. 5, 2024.
5. Wang L., Fu Y., Hou H., Song Y. A facile strategy to prepare Cu_2O/Cu electrode as a sensitive enzyme-free glucose sensor // International Journal of Electrochemical Science, 2012, V. 7, no. 12, pp. 12587-12600. DOI.org/10.1016/S1452-3981(23)16568-0.
6. Li M., Wang H., Wang X., Lu Q., Li H., Zhang Y., Yao S. Ti_3C_2/Cu_2O heterostructure based signal-off photoelectrochemical sensor for high sensitivity detection of glucose // Biosensors and Bioelectronics. 2019, V. 142, p. 111535. DOI.org/10.1016/j.bios.2019.111535.

7. Fortin E., Mason D. Photovoltaic effects in Cu_2O-Cu solar cells grown by anodic oxidation // Solid-State Electronics. 1982, V. 25, no. 4, pp. 281-283. DOI.org/10.1016/0038-1101(82)90136-8.
8. Sears W.M., Fortin E. Preparation and properties of Cu_2O/Cu photovoltaic cells // Solar Energy Materials. 1984, V. 10, no. 1, pp. 93-103. DOI.org/10.1016/0165-1633(84)90011-X.
9. de Jongh P., Vanmaekelbergh D., Kelly J. Cu_2O: A catalyst for the photochemical decomposition of water? // Journal of Chemistry Communications. 1984, V. 12, pp. 1069-1070. DOI.org/10.1039/A901232J.
10. Wang P., Xi M., Qin L., Kang S-Z, Fang Y., Li X. Cubic cuprous oxide-based nanocomposites for photocatalytic hydrogen generation // ACS Applied Nano Materials. 2019, vol. 2, no. 11, pp. 7409-7420. DOI.org/10.1021/acsanm.9b01930.
11. Ursu D., Vajda M., Miclau M. Investigation of the p- type dye- sensitized solar cell based on full Cu_2O electrodes // Journal of Alloy Compounds. 2019, V. 802, pp. 86-92. DOI:10.1016/j.jallcom.2019.06.180.
12. Chang V., Rojas H., Jorge J. Piezoelectric and thermoelectric response of cuprous oxide Cu_2O // Sensors and Actuators A: Physics. 1993, V. 37, pp. 375-378. DOI.org/10.1016/0924-4247(93)80064-N.
13. Lee Y.H., Leu I.C., Liao C.L., Chang S.T., Wu M.T., Yen J.H., Fung K.Z. Fabrication and characterization of Cu_2O nanorod arrays and their electrochemical performance in Li-ion batteries // Electrochemical Solid-State Letters. 2006, V. 9, no. 4, p. A207-A210. DOI 10.1149/1.2171815.
14. Bijani S. Electrodeposition and characterization of Cu_2O sheets; their application as Li-ion battery electrodes // D. Sc. Thesis (in Spanish), University of Málaga, Málaga, Spain, 2007. https://riuma.uma.es/xmlui/bitstream/handle/10630/2597/17116697.pdf?sequence=1, accessed on Jun. 5, 2024.
15. Pat. CN 111200134 (publ. May 26, 2020). Cuprous oxide film with levorotatory chiral structure and its application in reduction catalyst of fuel cell.
16. Mao P., Qi L., Liu X., Liu Y., Jiao Y., Chen S., Yang Y. Synthesis of Cu/Cu_2O hybrids for enhanced removal of iodide from water // Journal of Hazardous Materials. 2017, V. 328, pp. 21-28. DOI.org/10.1016/j.jhazmat.2016.12.065.
17. Jiang Y., Chen J., Zhao X., Ma G. Synthesis of highly porous Cu_2O catalysts for efficient ozone decomposition // Catalysts. 2021, V. 11, no. 5, p. 600. DOI.org/10.3390/catal11050600.
18. Nguyen D.C.T., Cho K.Y., Oh W-C. Synthesis of mesoporous SiO_2/Cu_2O-graphene nanocomposites and their highly efficient photocatalytic performance for dye pollutants // RSC Advances. 2017, V. 7, no. 47, p. 29284-29294. DOI.org/10.1039/C7RA03526H.
19. Wu Y., Xu L., Hu Y., Jiang Y. Synthesis and photocatalytic activity of superfine Cu_2O sphere with smooth surface on degradation of methyl orange // IOP Conference Series: Materials Science and Engineering. 2019, Int. Conf. Energy, Chemistry and Materials Science. V. 738, p. 012001. DOI 10.1088/1757-899X/738/1/012001.
20. Wang B., Xie Y., Yang T., Wang L., Wang L., Jin D. Synthesis and photocatalytic properties of flexible Cu_2O thin film // Surface Engineering. 2020, V. 36, no. 2, pp. 199-205. DOI.org/10.1080/02670844.2019.1647939.
21. Joseph S., Kamathz P.V. Electrodeposition of Cu_2O coatings on stainless steel substrates. Control over orientation and morphology // Journal of The Electrochemical Society. 2007, V. 154, no. 7, p. E102. DOI 10.1149/1.2737661.
22. Fiore J.M. Semiconductor fundamentals, Chapter 1 in: Semiconductor devices: Theory and application. CC BY-NC-SA, Open Textbook Library. 2018. https://open.umn.edu/opentextbooks/textbooks/semiconductor-devices-theory-and-application, accessed on Jun. 5, 2024.
23. Rakhshani A.E. Preparation, characteristics and photovoltaic properties of cuprous oxide—a review // Solid-State Electronics. 1986, V. 29, no. 1, p. 7-17. DOI.org/10.1016/0038-1101(86)90191-7.

24. Luevano-Hipolito E., Torres-Martinez L.M., Sanchez-Martinez D. Alfaro-Cruz M.R. Cu_2O precipitation-assisted with ultrasound and microwave radiation for photocatalytic hydrogen production // International Journal of Hydrogen Energy. 2017, V. 42, no. 18, pp. 12997-13010. DOI.org/10.1016/j.ijhydene.2017.03.192
25. Li J., Wu N. Semiconductor-based photocatalysts and photoelectrochemical cells for solar fuel generation: A review // Catalysis Science and Technology. 2015, V. 5, no. 3, pp. 1360-1384. DOI.org/10.1039/C4CY00974F.
26. Fortna C.H., Fillinger A. Electrodeposition of Cu_2O from O_2 saturated deposition solution as an attempt for enhancement of Cu_2O electrical conductivity // Orlando, FL, USA. 257th. ACS National Meeting & Exposition, Mar. 31-Apr. 4, 2019. p. CHED-0373.
27. Kosugi K., Kaneko S. Novel spray-pyrolysis deposition of cuprous oxide thin films // Journal of the American Ceramics Society. 2015, V. 81, no. 12, p. 3117. DOI: 10.1111/j.1151-2916.1998.tb02746.x.
28. Richardson T. J., Slack J. L., Rubin M.D. Electrochromism in copper oxide thin films // 4th. International Meeting on Electrochromism. Uppsala, Sweden. 2000. pp. 1-6.
29. Ogura K., Nakaoka K., Nakayama M., Tanaka S. A new type of electrochemical formation of copper oxide during redox processes of the copper (II)–glycine complex at high pH // Journal of Electroanalytical Chemistry. 2001. V. 511, pp. 122-127. DOI:10.1016/S0022-0728(01)00568-X.
30. Bohannan E.W., Shumsky M.G., Switzer J.A. Epitaxial electrodeposition of copper (I) oxide on single-crystal gold(100) // Chemistry of Materials. 1999, V. 11, no. 9, pp. 2289-2291. DOI:org/10.1021/cm990304o.
31. Sawant S.S., Bhagwat A.D., Mahajan C.M. Novel facile technique for synthesis of stable cuprous oxide (Cu_2O) nanoparticles - an ageing effect // Journal of Nano-and electronic Physics. 2016, V. 8, pp. 01036-010364. DOI:10.21272/JNEP.8(1).01036.
32. Cai C., Guo J., Dong H., Zhao N., Xu J. Cu_2O-IER (ion-exchange resin) composites: A novel strategy for Cu_2O synthesis // Chemical Letters. 2016, V. 45, no. 2, pp. 238-240. DOI:10.1246/cl.150974.
33. Gong Y.S., Lee C., Yang C.K. Atomic force microscopy and Raman spectroscopy studies on the oxidation of Cu thin films // Journal of Applied Physics. 1995, V. 77, pp. 5422-5425. DOI: 10.1063/1.359234.
34. Cheng F.X., Jiang C.H., Wu J.S. Effect of sputtering input powers on $CoSi_2$ thin films prepared by magnetron sputtering // Materials and Design. 2005, V. 26, no. 4, pp. 369-372. DOI:10.1016/j.matdes.2004.06.004.
35. Morales J., Sánchez L., Martín F., Ramos-Barrado J.R., Sánchez M. Nanostructured CuO thin film electrodes prepared by spray pyrolysis: A simple method for enhancing the electrochemical performance of CuO in lithium cells // Electrochimica Acta. 2004, V. 49, no. 26, pp. 4589-4597. DOI:10.1016/j.electacta.2004.05.012.
36. Annal G.H., Kamath P.V. Electrochemical synthesis of metal oxides and hydroxides // Chemistry of Materials. 2000, V. 12, no. 5, p. 1195. DOI:10.1021/cm990447a.
37. Santra K., Chatterjee P., SenGupta S.P. Powder profile studies in electrodeposited cuprous oxide films // Solar Energy Materials and Solar Cells. 1999, V. 57, pp. 345-358. DOI: 10.5772/21307.
38. Rakhshani A.E., Varghese J. Galvanostatic deposition of thin films of cuprous oxide // Solar Energy Materials. 1987, V. 15, pp. 237-248. DOI:10.1016/0165-1633(87)90039-6.
39. Siripala W., Premasiri K. A photo-electrochemical investigation of the n- and p- type behaviour of copper(I) oxide films // Semiconductor Science and Technology. 1989, V. 4, p. 465. DOI:10.1016/j.jelechem.2006.05.019.
40. Eskhult J., Herranen M., Nyholm L. On the origin of the spontaneous potential oscillations observed during galvanostatic deposition of layers of Cu and Cu_2O in alkaline citrate solutions // Journal of Electroanalytical Chemistry. 2006, V. 594,

no. 1, pp. 34-49. DOI:10.1016/j.jelechem.2006.05.019.
41. Izaki M., Mizuno K., Shinagawa T., Inaba M., Tasaka A. Photochemical construction of photovoltaic device composed of p-copper(I) oxide and n-zinc oxide // Journal of The Electrochemical Society. 2006, V. 153, no. 9, pp. pp. C668-C672. DOI:10.1149/1.2218791.
42. de Jongh P., Vanmaekelbergh D., Kelly J. Cu_2O: Electrodeposition and characterization // Chemistry of Materials. 1999, V. 1, pp. 3512-3517. DOI:10.1021/CM991054E.
43. Lee J., Tak Y. Electrochemical deposition of a single phase of pure Cu_2O films by current modulation method // Electrochemical Solid-State Letters. 2000, V. 3, no. 2, pp. 69. DOI 10.1149/1.1390961.
44. Wijesundera R.P. Electrodeposited Cu_2O thin films for fabrication of CuO/Cu_2O heterojunction. Chapter 5 in: Solar Cells - Thin-Film Technologies, Edited by Leonid A. Kosyachenko. IntechOpen. 2011, pp. 89-110. DOI: 10.5772/19789.
45. Achilli E., Vertova A., Visibile A., Locatelli C., Minguzzi A., Rondinini S., Ghigna P. Structure and stability of a copper(II) lactate complex in alkaline solution: a case study by energy-dispersive X-ray absorption spectroscopy // Inorganic Chemistry. 2017, V. 56, no. 12, pp. 6982-6989. DOI: 10.1021/acs.inorgchem.7b00553.
46. Pourbaix M. Atlas of electrochemical equilibria in aqueous solutions. Houston: National Association of Corrosion Engineers. 1974.
47. Lee J., Tak Y. Epitaxial growth of Cu_2O (111) by electrodeposition // Electrochemical Solid-State Letters. 1999, V. 2, no. 11, p. 559. DOI 10.1149/1.1390903.
48. Gomez-Gonzalez A., Ibanez J. G., Vasquez-Medrano R., Zavala-Araiza D., Paramo-Garcia, U. Electrochemical paired convergent production of ClO_2 from $NaClO_2$ and $NaClO_3$ // Electrochemical Applications to Biology, Nanotechnology, and Environmental Engineering and Materials. ECS Transactions. 2009, V. 20, no. 1, p. 91. DOI 10.1149/1.3268376.
49. Ibanez J.G., Frontana-Uribe B.A., Vasquez-Medrano R. Paired electrochemical processes: Overview, systematization, selection criteria, design strategies, and projection // Journal of the Mexican Chemical Society. 2016, V. 60, no. 4, pp. 247-260.
50. Siripala W., Kumara K.P. A photoelectrochemical investigation of the n- and p-type semiconducting behaviour of copper (I) oxide films // Semiconductor Science and Technology. 1989, V. 4, no. 6, p. 465. DOI 10.1088/0268-1242/4/6/007.
51. Ibanez J.G., Finck-Pastrana A., Mugica-Barrera A., Balderas-Hernandez P., Ibarguengoitia-Cervantes M., Garcia-Pintor E., Hartasanchez-Frenk J.M., Bonilla-Jaurez C.E., Maldonado-Cordero C., Struck-Garza A., Suberbie-Rocha F. Semiconducting materials in the laboratory, Part 3: The one-penny photovoltaic cell // Journal of Chemical Education. 2011, V. 88, no. 9, pp. 1287-1289. DOI: 10.1021/ed100116h.

GÜNƏŞ ENERJİSİ ÇEVİRİCİLƏRİ ÜÇÜN Cu_2O-İN EYNİ ZAMANDA ANOD VƏ KATOD ELEKTROÇÖKDÜRÜLMƏSİ

Kevin F. Genaro-Saldivar[1], Geovanni R. Neqret-Reyes[1], Ester Ramirez-Meneses[1], Karlos Xuarez-Balderas[2], Flor Avendano-Sanjuan[1], Diana A. Qarsiya-Najera[1], Xorxe Q. İbanez[1,*]

[1]Kimya, Sənaye və Qida Mühəndisliyi Departamenti, İberoamerikan Universiteti, Mexiko, Meksika
[2]İnnovasiya üzrə Mühəndislik Araşdırmaları Departamenti, İberoamerikan Universiteti, Mexiko, Meksika

*e-mail: jorge.g.ibanez@gmail.com

Xülasə: Mis oksid Cu_2O yüksək/aşağı temperaturlu termiki oksidləşmə, püskürtmə, kimyəvi oksidləşmə, anodda oksidləşmə, elektroçökmə və s. müxtəlif üsullarla alına bilən çox universal məhsuldur. İndiyə qədər Cu_2O almaq üçün ən səmərəli sintetik proseslər kifayət qədər bahalı avadanlıq tələb edir. Bunu nəzərə alaraq, biz bu işdə normal təzyiq və nisbətən aşağı temperaturlarda elektrolitik dövrədə həyata keçirilən eyni vaxtda konvergent oksidləşmə-reduksiya reaksiyalarına əsaslanan yeni metod işləyib hazırlamışıq. Cu(0) lövhəsi anodda Cu(I)-ə qədər oksidləşir, dövrənin katod hissində isə Cu(II)-laktat kompleksi əmələ gəlir. Sonra Cu(II) ionu Cu(I)-ə qədər reduksiya olunur (bütün proseslər sulu mühitdə aparılır).
Açar sözləri: Cu_2O sintezi, konvergen sintez, mis (I) oksid, elektroçökdürmə, eyni zamanda baş verən proseslər

ОДНОВРЕМЕННОЕ АНОДНОЕ И КАТОДНОЕ ЭЛЕКТРООСАЖДЕНИЕ Cu_2O ДЛЯ ПРЕОБРАЗОВАТЕЛЕЙ СОЛНЕЧНОЙ ЭНЕРГИИ

Кевин Ф. Хенаро-Сальдивар[1], Джованни Р. Негрете-Рейес[1], Эстер Рамирес-Менесес[1], Карлос Хуарес-Бальдерас[2], Флор Авендано-Санхуан[1], Диана А. Гарсиа-Нахера[1], Хорхе Г. Ибанез[1,*]

[1]*Факультет химической, промышленной и пищевой инженерии, Ибероамериканский университет, Мехико, Мексика*
[2]*Факультет инженерных исследований инноваций, Ибероамериканский университет, Мехико, Мексика*
*e-mail: jorge.g.ibanez@gmail.com

Резюме: Оксид меди Cu_2O представляет собой универсальный продукт, который можно получить различными методами, включая высоко/низкотемпературное термическое окисление, напыление, химическое окисление, анодное окисление, электроосаждение и другие. До сих пор наиболее эффективные синтетические процессы получения Cu_2O требуют относительно дорогого оборудования; поэтому мы разработали новый метод, основанный на одновременных конвергентных окислительно-восстановительных реакциях в электролитической ячейке при атмосферном давлении и относительно низкой температуре. В данной работе пластина Cu(0) окисляется до Cu(I) в аноде, а в катоде ячейки образуется комплекс Cu(II)-лактат, а затем Cu(II) восстанавливается до Cu (I) (все реакции протекают в водных средах).
Ключевые слова: синтез Cu_2O, конвергентный синтез, оксид меди (I), электроосаждение, одновременные процессы