

SIMULTANEOUS ANODIC AND CATHODIC ELECTRODEPOSITION OF Cu_2O FOR SOLAR ENERGY CONVERSION

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Received 28.03.2024

Accepted 06.06.2024

Abstract: Copper oxide, Cu_2O is a highly versatile product that can be 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 $\text{Cu}(0)$ plate is oxidized to $\text{Cu}(I)$ in the anodic compartment, while a $\text{Cu}(II)$ -lactate complex is formed in the cathodic compartment of the cell and then $\text{Cu}(II)$ is reduced to $\text{Cu}(I)$, all in aqueous media.

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

1. Introduction

$\text{Cu}(I)$ 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 $a = b = c = 4.27 \text{ \AA}$ [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 Γ^- [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 $\text{Ti}_3\text{C}_2/\text{Cu}_2\text{O}$ 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, $E_g = 2.17 \text{ eV}$ [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 Cu₂O'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 Cu₂O, 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 Cu₂O 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, Cu₂O 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. Cu₂O Production

Cu₂O 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 Cu₂O 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, Cu₂O 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 Cu₂O. 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 Cu₂O on both sides of an electrolytic cell now follow.

1.2. Electrochemical Synthesis of Cu₂O

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 Cu₂O 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*-Cu₂O [39], Cu₂O 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 Cu₂O 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 Cu₂O cathodic films [43].

The electrolytic baths most commonly used involve CuSO₄ at molarities ranging from 0.01 M to 0.4 M [7, 40]. The use of CuNO₃ [44], and Cu(CH₃COO)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 Cu₂O 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 CuNO₃ in acidic media, the reaction mechanism involves a local pH increase prior to the formation of Cu₂O due to the OH⁻ ions produced after the reduction of NO₃⁻ to NO₂⁻ [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 Cu₂O can be incremented by forming a heterojunction between CuO and Cu₂O through the initial deposition of Cu₂O on a Pt electrode and the subsequent application of heat treatment up to approximately 500 °C to convert part of the Cu₂O to CuO [44].

1.3. Convergent Electrochemical Synthesis

The simultaneous convergent electrosynthesis of materials is very rarely attained [48, 49], and that of Cu₂O 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 Cu₂O is enabled at the same time as the direct anodic conversion of Cu(0) to Cu₂O. 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 Cu₂O 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, C₃H₆O₃ (as complexing agent), and b) 0.3 M CuSO₄. 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].

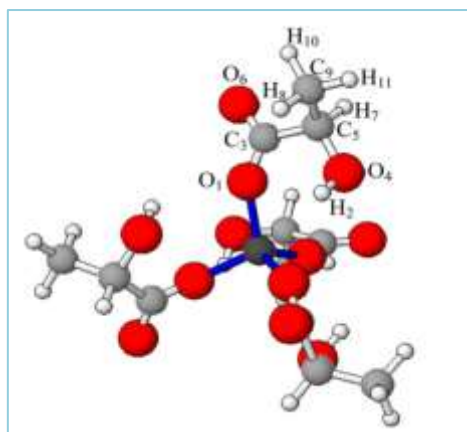


Fig. 1. Structure of the Cu(II) lactate complex. Adapted with permission from Ref. [45].

For the anodic deposition, a 0.5 M Na₂SO₄ 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; Na₂SO₄, Sigma Aldrich; CuO, J.T. Baker; Cu₂O, J.T. Baker; NaOH, Meyer), except lactic acid (80% pure, J.T. Baker), without further treatment and the solutions were prepared using deionized water.

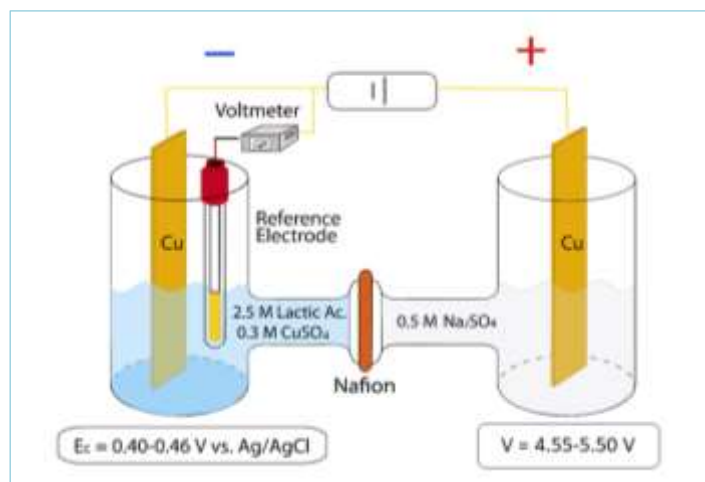


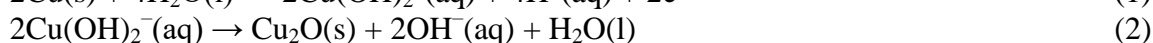
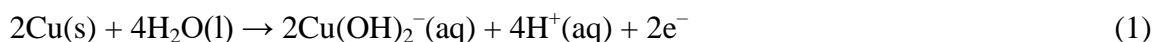
Fig. 2. Schematic representation of the H-type glass cell used in this work for the convergent electrosynthesis of Cu₂O.

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% HNO₃ and then washed with distilled water. Current density stayed essentially constant at approx. 20 mA/cm². 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]



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]

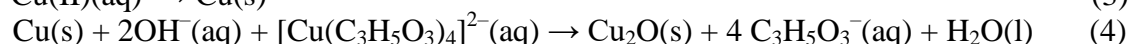


Fig. 3 shows optical images of the oxide layers deposited on the anode and cathode of the cell. The reddish hue is characteristic of Cu₂O. The darker hue observed in the anodic deposit may be due to disturbances in the crystal lattice.



Fig. 3. Images of Cu plates with Cu₂O deposited: (a) at the anode, and (b) at the cathode of the H-cell.

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 Cu₂O deposits from the anodic and cathodic convergent syntheses, and those obtained with a pure Cu₂O sample. Fig. 5 shows the summary comparison. The peaks at $2\theta = 29.8, 36.6, 42.7, 52.6, 61.7, 66.1, 69.9,$ 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 Cu₂O (JCPDS card No. 05-0667). Concerning the possible presence of CuO, the lack of peaks at $2\theta = 37.1^\circ, 61.8^\circ,$ and 74.3° that correspond to the (200), (220), and (311) CuO planes indicates their absence, although the peak at $2\theta = 36.6^\circ$ may indicate that some CuO is present in the (111) phase.

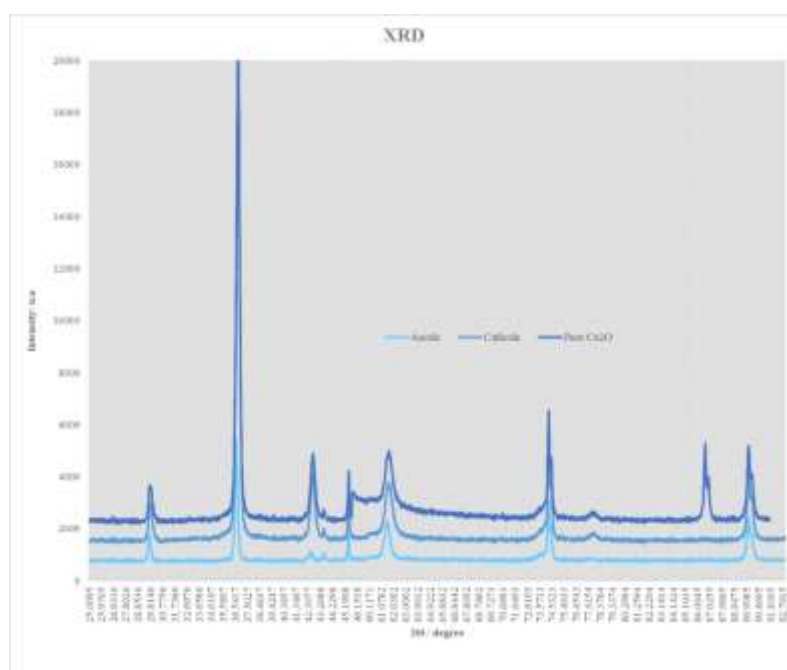


Fig. 4. XRD of the Cu₂O deposits from the anodic and cathodic convergent synthesis, and those obtained with a pure Cu₂O sample. The conditions for the anodic deposits were: $pH_i = 11.38$, $pH_f = 5.2$, $V_{cell,i} = 4.55$ V, $V_{cell,f} = 5.50$ V, and for the cathodic deposits they were: $pH_i = 10.4$, $pH_f = 9.18$; $V_{cell,i} = 0.40$ V, $V_{cell,f} = 0.46$ V. $t = 15$ min, and $T = 65^\circ\text{C}$.

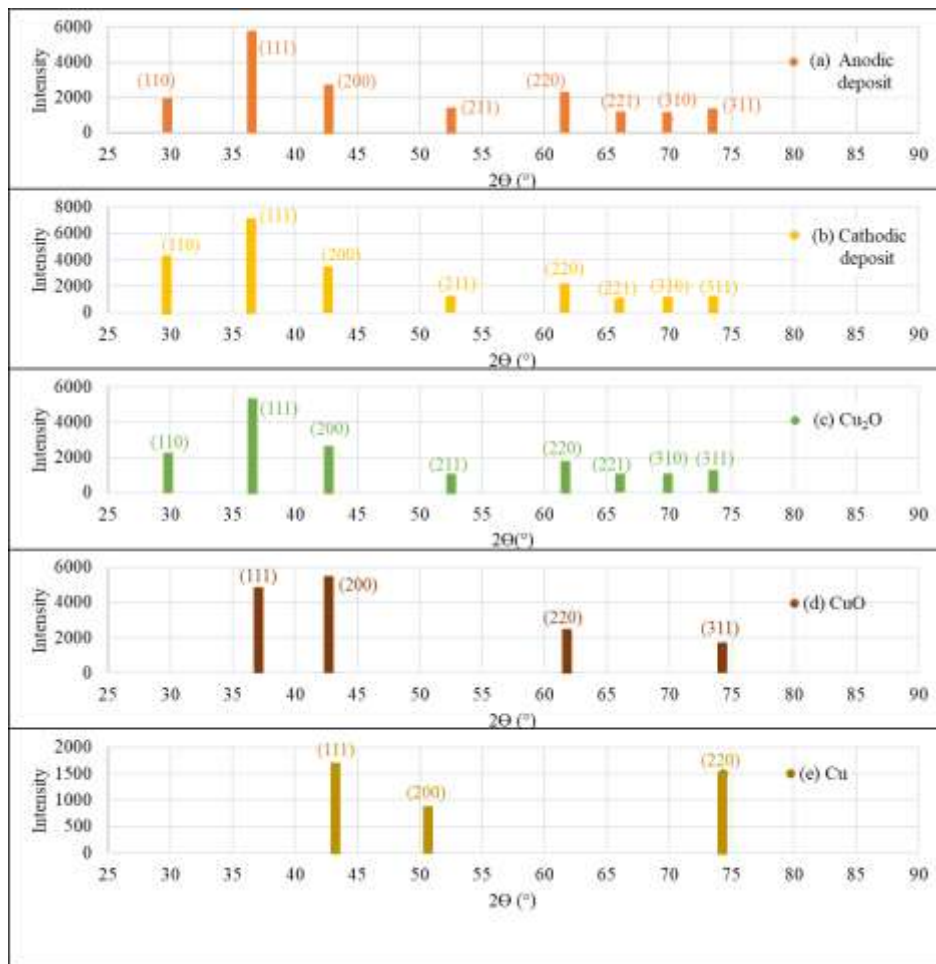


Fig. 5. XRD summary of the Cu_2O deposits from the anodic and cathodic convergent synthesis. The conditions for the anodic deposits were: $pH_i = 11.38$, $pH_f = 5.2$, $V_{cell,i} = 4.55$ V, $V_{cell,f} = 5.50$ V, and for the cathodic deposits they were: $pH_i = 10.4$, $pH_f = 9.18$; $V_{cell,i} = 0.40$ 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.

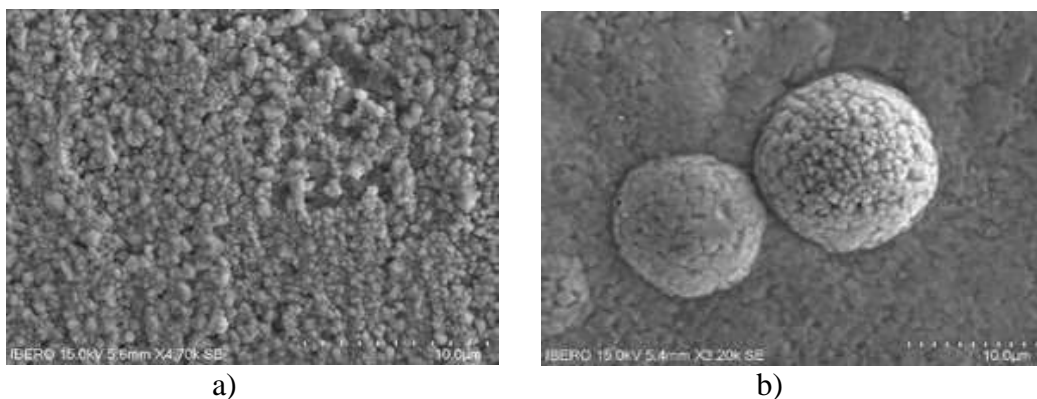


Fig. 6. SEM images of Cu_2O prepared by convergent electrosynthesis. (a) Anodic deposit ($pH_i = 11.38$, $pH_f = 5.20$, $V_{cell,i} = 4.55$ V, $V_{cell,f} = 5.50$ V), and (b) cathodic deposit ($pH_i = 10.40$, $pH_f = 9.18$; $V_{cell,i} = 0.40$ V, $V_{cell,f} = 0.46$ V). $t = 15$ min, and $T = 65$ °C.

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.

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

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Xülasə: Mis oksid Cu_2O yüksək/aşağı temperaturu 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 dövrdə həyata keçirilən eyni vaxtda konvergent oksidləşmə-reduksiya reaksiyalarına əsaslanan yeni metod işləyib hazırlamışıq. $\text{Cu}(0)$ lövhəsi anodda $\text{Cu}(I)$ -ə qədər oksidləşir, dövrənin katod hissində isə $\text{Cu}(II)$ -laktat kompleksi əmələ gəlir. Sonra $\text{Cu}(II)$ ionu $\text{Cu}(I)$ -ə qədər reduksiya olunur (bütün proseslər sulu mühitdə aparılır).

ОДНОВРЕМЕННОЕ АНОДНОЕ И КАТОДНОЕ ЭЛЕКТРООСАЖДЕНИЕ Cu_2O ДЛЯ ПРЕОБРАЗОВАТЕЛЕЙ СОЛНЕЧНОЙ ЭНЕРГИИ

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Абстракт: 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 $\text{Cu}(0)$ окисляется до $\text{Cu}(I)$ в аноде, а в катоде ячейки образуется комплекс $\text{Cu}(II)$ -лактат, а затем $\text{Cu}(II)$ восстанавливается до $\text{Cu}(I)$ (все реакции протекают в водных средах).