MECHANICAL ENGINEERING | RESEARCH ARTICLE

Electrodeposition of Cu2O nanostructures with improved semiconductor properties

Andrés Boulett¹, Guadalupe Del C. Pizarro¹, Rudy Martín-Trasanco¹, Julio Sánchez²*, Federico Tasca³, Omar E. Linarez Pérez⁴,⁵, Alejandra Tello⁶ and Diego P. Oyarzún*⁷

Abstract: In the present research, nanocomposites based on copper (I) oxide poly(1-vinyl-2—pyrrolidone-co-itaconic acid) nanostructures (Cu2O/p(NVP-co-AI)) were synthesized by the electrodeposition method using the copolymer p(NVP-co-AI) as a stabilizing agent in the reduction of Cu²⁺ to Cu⁺. The chemical and physical properties of the nanostructures were characterized by techniques such as scanning electron microscopy, infrared (IR) spectroscopy, Raman and ultraviolet-visible spectrophotometry. The obtained nanostructures are mainly a mixture of agglomerated nanospheres with a diameter of approximately 78 to 91 nm, with an alternation of nanolaminar structures, composed of copper (I) oxide species. In the case of the Cu2O/p(NVP-co-AI) nanocomposite, it was observed a decrease in the carbon-oxygen vibration links of the carbonyl groups in IR intensity for the polymer when it was dissolved in the electrolytic solution, which indicates that interactions are produced by the carbonyl groups with the Cu₂O species. In addition, bandgap values of 1.80 and 1.63 eV were estimated by the Kubelka–Munk method for Cu₂O and Cu₂O/p(NVP-co-AI) samples, respectively.

Subjects: Materials Science; Nanoscience & Nanotechnology; Chemical Engineering

ABOUT THE AUTHOR
Diego P. Oyarzún Jerez obtained his PhD in Chemistry (2014) from Pontifical Catholic University of Valparaíso (Valparaíso, Chile). He did a postdoctoral training at the Center of Applied Nanosciences of Faculty of Exact Sciences of Andrés Bello University (Santiago, Chile) and in the Department of Physical Chemistry, Faculty of Chemical Sciences Córdoba National University (Córdoba, Argentina) focusing his research on the synthesis and characterization of polymers materials and anodic metal oxide films. Currently, he is professor and researcher at the Laboratory of Applied Nanosciences at Atacama University (Copiapó, Chile). Dr. Oyarzún Jerez research interests are focused on the preparation, characterization and different applications of nanocomposite materials based on anodic metal oxide and polymeric matrix. This research provides new synthesis conditions of a fundamental component to generate these new nanocomposites with potential applications in areas such as photoelectrochemistry, photovoltaics, solar cells, LEDs, water photolysis and photocatalysis.

PUBLIC INTEREST STATEMENT
This work shows the approaches to prepare of copper oxide/polymer (Cu₂O/p(NVP-co-AI)) nanocomposite films by the method of electrodeposition in aqueous solution of Cu²⁺ using p(NVP-co-AI) as stabilizer. In addition, the chemical and physical properties of the nanostructures were characterized by scanning electron microscopy (SEM), UV-Vis spectrometry, Fourier transformed infrared (FTIR) and Raman spectroscopy. In particular, we analyze the optical properties and how they vary with the different morphologies obtained via stabilization with the polymer.
Keywords: Cu$_2$O nanocomposite; electrodeposition; semiconductor properties; spectroscopic analysis

1. Introduction
Nanostructured oxides have attracted the attention of scientific researchers due to their ease of obtaining and their morphological order at the nanoscale, generating a control in their chemical and physical properties, which gives rise to numerous potential applications (Mutalib et al., 2013), such as in areas of medicine, optoelectronics, acoustics, photonics, sensors and catalysis (Alvarado, 2017; Lara-Judrez et al., 2018; Verdaguer, 2016). Among the nanostructured oxides, Cu$_2$O is classified as a "p" type semiconductor material due to the copper electron vacancies in the crystalline system, which results in low bandgap values, between 1.9 and 2.17 eV (Osherov et al., 2013; Oyarzúñ et al., 2018). These characteristics classify it as a highly photoactive material in the visible region and, therefore, a good candidate for phot электрохимical and photovoltaic applications (Stepniowski & Misiolk, 2018). In addition, it can be used for the design of solar cells, LEDs, and water photolysis due to the fact that the energies of conduction bands and valence are close to the reduction and oxidation potentials of water (Gattinoni & Michaelides, 2015; Musselman et al., 2017; Stepniowski & Misiolk, 2018). It can represent an extremely promising material to be used as a catalyst in the photodegradation of dyes or organic pollutant molecules, being a low-cost catalyst, easy to obtain, non-toxic nature and coming from the metal copper, which is obtained from the minerals that are exhaustively extracted in mining (Osherov et al., 2013).

Currently, there are several methods reported in the literature for obtaining Cu$_2$O nanostructures, such as thermal oxidation of metallic copper at high temperatures (Rai, 1988), template-assisted growth (Prieto et al., 2003), colloidal methods (Wang et al., 2010) and by electrochemical techniques of anodization or electrodeposition (Kar et al., 2017; Oyarzún et al., 2018). However, high temperature processes generally limit the control of the interfacial characteristics of Cu$_2$O thin films, which significantly affects the optical and photoelectrochemical properties of the resulting oxide (Read et al., 2009). As an alternative, electrodeposition is a simple, versatile and low-cost method to obtain ordered nanostructures, allowing a better control of their growth (Oyarzún et al., 2018). In this context, the appropriate selection of the chelating or stabilizing agent can promote the growth of diverse morphologies, such as wires, bars, points, pores and tubes, among other nanostructures (Allam and Grimes, 2011; Kar et al., 2017; Read et al., 2009). In particular, the use of lactic acid, tartaric acid, ammonium nitrate, amino acids or polymers as chelating agents or stabilizers, have attracted great attention for different technological applications (Oyarzún et al., 2018; Zolfakar et al., 2014), due to the improvement that nanostructures present in their physical and optical properties, caused by the incorporation of the chelating agent in the synthesis process (Oyarzún, Pizarro et al., 2017; Oyarzún, Tello et al., 2017). In this sense, it has been previously reported the synthesis of zinc oxide nanoparticles with poly(N-PhMI-co-HEMA) as stabilizing agent. The function that this polymer fulfills is that zinc is coordinated by poly(N-PhMI-co-HEMA), which allows the speed at which the metal oxidation occurs to be slower, obtaining zinc oxide surfaces with more uniform nanostructured morphologies (Oyarzún, Tello et al., 2017). Therefore, it is expected that in similar way the polymer p(NVP-co-Al) coordinates the metal Cu$^{2+}$ in solution during the electrodeposition process, being the stabilizing agent of this reaction (Oyarzún, Tello et al., 2017). Precisely the use of a water-soluble polymeric material as chelating agent during the electrodeposition of Cu$_2$O nanostructures has not been previously reported in scientific literature (Ait et al., 2020; Anastasiadou et al., 2019; Anower et al., 2017; Bao et al., 2012; Das et al., 2018; Gu et al., 2010; Kim et al., 2014; Lee et al., 2004; Y. Liu et al., 2016; R. Liu et al., 2003; Messaoudi et al., 2016; Nian et al., 2009; Paracchino et al., 2012; Rahal et al., 2018; Ravichandiran et al., 2019; Shahbazi & Kiani, 2016; Xua et al., 2012; Yang et al., 2016; Zhao et al., 2011; Zhu et al., 2013), therefore, the develop this simple, low-cost synthesis method under novel chemical conditions is novel.
In the present work, it is reported the synthesis of Cu₂O/p(NVP-co-AI) based nanocomposite films by the method of electrodeposition in aqueous solution of Cu²⁺ using p(NVP-co-AI) as stabilizer. In addition, the chemical and physical properties of the nanostructures were characterized by scanning electron microscopy (SEM), UV-Vis spectrometry, Fourier transformed infrared (FTIR) and Raman spectroscopy.

2. Materials and methods
The synthesis of p(NVP-co-AI) was carried out by radical radical polymerization at 70°C during 120 min, using benzoyl peroxide as initiator, in addition to the monomers 1-vinyl-2-pyrrolidone (NVP) and itaconic acid (AI) in ratios 1:1, 1:3, 3:1, dissolved in distilled water (Pizarro et al., 2009).

The electrochemical synthesis was performed in a conventional electrochemical cell containing an Ag/AgCl/KCl(sat) reference electrode, as a counter electrode a spiral shaped platinum wire and as a working electrode a glass plate coated with indium tin-doped oxide (ITO). The working electrode was rinsed with MILLI-Q water and then cleaned with an ultrasound bath. The electrode was immersed in an acetone/ethanol solution in a ratio of 1:1 for 15 min at room temperature to improve film adhesion.

The deposition of Cu₂O in the absence of the copolymer was carried out by cyclic voltammetry in the potential range (−0.8; 0) V in an electrolyte composed of 5 mL of aqueous solutions of 0.005 M CuSO₄ + 5 mL of 0.05 M NaNO₃ (this solution will be called “C”). This electrodeposition range was selected by performing electrodeposition in a range of (−1; 1) V depending on the chemical composition of the electrolyte solution (see Figures 1, Figures 2 and Figures 3 of the supplemental material).

Figure 1. (A) Photographs of the ITO surface and (B) Cyclic voltammograms obtained in the electrodeposition of the Cu₂O/p(NVP-co-AI) nanocomposite, using electrolytic solutions composed by 0.05 M NaNO₃ + 0.005 M CuSO₄ + the p(NVP-co-AI) copolymer in proportion 1:1, concentration 0%; 0.1% (A and B) and 1.0% (B) at a scanning speed of 0.1 V s⁻¹.
For the preparation of the nanocomposite, the same procedure was followed but in the presence of x % w/v of copolymer (1:1), 0.1 < x < 2, using copolymer ratios of 1:1, 3:1, 1:3.

Potential and current were monitored on an Autolab 100 potentiostat/galvanostat. The surface morphology of the nanocomposite electrodes was characterized with scanning electron microscopy (SEM), using a Zeiss EVO MA10 model microscope, and the analysis of the micrographs obtained was performed with Gwyddion imaging software 2.53, the characteristic band vibrations were characterized by attenuated total infrared spectroscopy (ATR-FTIR), using an FT-IR spectrometer, Spectrum Two, (UATR Two), PerkinElmer. Raman spectroscopy was carried out using a Horiba LabRAM HR spectrometer and employing a He/Ne laser (wavelength 632.8 nm). While in Uv-Vis spectroscopy a LAMBDA 35, PerkinElmer, spectrometer was used.

Figure 2. A) Raman spectra of Cu$_2$O nanostructures obtained by electrodeposition in ITO using a concentration “x” of copolymer (1:1), x % w/v: 0.1 (Red) and 0 (Black). B-C) FT-IR spectra for Cu$_2$O/polymer compounds obtained in proportion (1:3) and z %w/v + 0.005 M CuSO$_4$ + 0.05 M NaNO$_3$, z: 0.1 (black); 0.5 (red); 1.0 (blue); 2.0 (green) and without (black) (B), or 0.1 %w/v + 0.005 M CuSO$_4$ + 0.05 M NaNO$_3$ (blue) (C).

Figure 3. SEM micrographs of the ITO surface with Cu$_2$O/poly (NVP-co-AI) nanocomposite, synthesized with the copolymer in proportion (1:1) and in concentration I: 0.1 % w/v, II: 0.5% w/v, III: 2.0%w/v (IA: Mag 10KX, IB: Mag 20KX, IC: Mag 50KX, ID: Mag 50KX).
3. Results and discussion

Figure 1A shows pictures of the ITO surface after electrodeposition. It can be seen that the surfaces of the ITO are covered with a brown film, which decreases in opacity as the concentration of the copolymer increases. Also, due to the higher concentration of the copolymer, the electrodeposited oxide film is expected to be thinner than that obtained in a synthesis without the copolymer (Niveditha et al., 2016; Oyarzún, Pizarro et al., 2017; Oyarzún, Tello et al., 2017; Pizarro et al., 2009; Riveros et al., 2012; Talib et al., 2016). If we look at the curve representing the synthesis of nanostructures without copolymer (black line, Figure 1B), in the first electrodeposition cycle, the signal at ~0.3 V corresponds to the reduction of Cu^{2+} to Cu^{+}, this is much more intense than those obtained in the synthesis with copolymer (red line). This indicates that the polymer material decreases its electrodeposition speed at the ITO surface. Furthermore, in the absence of polymer, a higher current is obtained for the second cycle, which indicates that the ITO surface is more conductive than the film deposited in the presence of the copolymer in the first cycle. While when the polymer is present, a decrease in current intensity is caused during the second cycle, indicating that the ITO surface is partially covered by oxide (Niveditha et al., 2016; Riveros et al., 2012).

The chemical composition of the nanostructure was analyzed by Raman and ATR-FTIR spectroscopies. Figure 2A shows the Raman spectra for the films obtained by electrodeposition in the presence and absence of p(NVP-co-AI) copolymer. The appearance of the signals at 149 cm\(^{-1}\), 542 cm\(^{-1}\) and 623 cm\(^{-1}\), and the absence of the bands at 289 cm\(^{-1}\), 296 cm\(^{-1}\) and 345 cm\(^{-1}\), show the presence mainly of copper (I) oxide species on the ITO surfaces (Oyarzún, López et al., 2017).

When analyzing the ATR-FTIR spectra (see Figure 2B), a weak band at approximately 3000 cm\(^{-1}\) is observed in each spectrum, which is characteristic of C-H bending—type vibrations for alkanes. In addition, a very wide band between 2400 cm\(^{-1}\) and 3600 cm\(^{-1}\) is observed, which is characteristic of stress type vibrations of O-H bonds for the carboxylic acid functional group from the AI monomer. A very wide band between 1725 and 1705 cm\(^{-1}\) is also observed which corresponds to a stress type vibration of the C = O bonds of the ketone functional groups and carboxylic acid of the NVP and AI monomers. Between 1680 and 1620 cm\(^{-1}\) another strong band is observed, corresponding to a C = C stretching type vibration of the alkene functional group. Finally, two medium bands are observed at 1450 and 1375 cm\(^{-1}\), which are characteristic for bending vibrations of—CH\(_3\)—and—CH\(_2\)—respectively. When analyzing the difference in intensity of each band obtained, only differences are obtained between the bands at 1725–1705 cm\(^{-1}\) and 1680–1620 cm\(^{-1}\) corresponding to ketones (C = O), carboxylic acid and alkenes (C = C), respectively. As the concentration of copolymers increases, the intensity of these two bands is greater, although for the C = O band the intensity increases significantly more, due to the greater presence of this functional group, since a greater amount of asymmetric vibrations of the carbon-oxygen bond is produced, which is represented in the spectrum with a more intense band (Oyarzún, Pizarro et al., 2017; Oyarzún, Tello et al., 2017; Pizarro et al., 2009).

On the other hand, when only the synthesis with solution “C” is carried out (see Figure 2C), the bands corresponding to ketones, carboxylic acid and alkenes are absent at 1725–1705 cm\(^{-1}\) and 1680–1620 cm\(^{-1}\), respectively, since there is no presence in the electrolytic solution of the copolymer, which is what provides this type of vibration. If we compare the corresponding band of ketones or carboxylic acid at 1705 cm\(^{-1}\) we observe that in the copolymer without copper sulfate solution the band is very intense, while in the copolymer + “C” solution the intensity of the band decreases. This is because the oxygen atoms are coordinated with the Cu^{2+} ions in solution, causing a decrease in the amount of C = O vibrations that were initially present (Oyarzún, Pizarro et al., 2017; Oyarzún, Tello et al., 2017; Pizarro et al., 2009).

By performing the electrodeposition in the presence of p(NVP-co-AI) copolymer at 0.1 %w/v (1:1), nanostructures were obtained along the surface of the ITO in the form of nanospheres, accompanied by nanosheets (Figure 3 “IA” and “IB”). In addition, a uniform morphology is
observed with a higher concentration of nanospheres above the nanosheets, which are deposited at random on the surface of the substrate (see Figure 3 “ID”). By observing the SEM micrographs with the highest magnification, it was determined that the nanoshells tend to agglomerate with each other, while the nanoshells are deposited on the surface individually (Figure 3 “IC” and “ID”). Finally, it was determined that the average diameter of the nanoshells ranges from 78 nm to 91 nm (Figure 3 “IE” and “IF”).

SEM microographies of the nanocomposite obtained in the syntheses with 0.5% w/v and 2% w/v copolymer (1:1), nanoscales were obtained. The sample synthesized with 2% w/v copolymer presents a more uniform morphology, but the copolymer tends to agglomerate on the surface of the ITO more than the one obtained with 0.5% w/v copolymer (Figure 3 II and III) (Niveditha et al., 2016; Oyarzún et al., 2018; Oyarzún, Tello et al., 2017).

The influence of p(NVP-co-AI) on the semiconductor properties was studied by UV-Vis spectrometry (see Figure 4A). The absorbance spectrum of Cu$_2$O nanostructures shows a weak absorption below 300 nm (black curve) compared to Cu$_2$O/p(NVP-co-AI) nanosheets, which also shows an absorption only below 300 nm but significantly more intense. In addition, it can be determined by observing the UV-Vis spectrum that both samples were completely transparent films in the visible region. In the direct transition semiconductors as Cu$_2$O it is possible to make an estimation of the band gap by the Kubelka–Munk method. It is plotting (-Ln(\(T\)) * h\(\nu\))^2 against the photon energy (\(h\nu\)), being \(T\) the % of transmittance of the sample, \(h\) the Planck constant, \(v\) the frequency of the energy and then extrapolating the linear adjustment of the highest energy to (Ln(\(T\)) = 0) (Figure 4B) (Meyer et al., 2012). With this method, bandgap values of 1.63 eV for Cu$_2$O (black line) and 1.80 eV for Cu$_2$O/p(NVP-co-AI) (red line) were estimated. The values obtained for this material are much lower than those previously reported for various types of Cu$_2$O nanostructures obtained by electrodeposition (1.92–2.47 eV), using various substrates, chelating agents and chemical composition of the electrolytic solution (see Table 1). This corroborates that the use of soluble polymeric materials have not been previously studied to stabilize the electrodeposition reaction of Cu$_2$O nanostructures, besides that in these conditions the semiconductor properties of Cu$_2$O nanostructures are considerably benefited, generating a material with potential applications (Ait et al., 2020; Anastasiadou et al., 2019; Anower et al., 2017; Bao et al., 2012; Das et al., 2018; Gu
Table 1. Chelating agent type, electrolyte, substrate and bandgap values of films with Cu₂O nanostructures obtained by electrodeposition

| Chelating agent | Electrolyte (aqueous solution) | Substrate (working electrode) | bandgap (eV) | Ref. |
|----------------|--------------------------------|--------------------------------|--------------|------|
| -              | Copper sulphate + Sodium nitrate | ITO                            | 1.63         | Present study |
| p(NVP-co-Al)   | Copper sulphate + Sodium nitrate | ITO                            | 1.80         | Present study |
| Lactic Acid    | Copper sulphate                  | ITO                            | [2.10–2.47]  | (Y. Liu et al., 2016, Xua et al., 2012, Messaoudi et al., 2016) |
| Lactic Acid    | Copper sulphate                  | FTO                            | [1.92–2.2]   | (Ravichandiran et al., 2019, Kim et al., 2014, Nian et al., 2009, Paracchino et al., 2012, Ait et al., 2020, Das et al., 2018) |
| Lactic Acid    | Copper sulphate                  | n-InP wafers (001)              | –            | (R. Liu et al., 2003) |
| Lactic Acid    | Copper sulphate                  | Stainless steel                 | –            | (Bao et al., 2012) |
| Lactic Acid    | Copper sulphate                  | Pt/Ti/SiO₂/Si                   | –            | (Lee et al., 2004) |
| Lactic Acid    | Copper sulphate                  | Gas diffusion layer (GDL)       | –            | (Anastasiadou et al., 2019) |
| Sodium Citrate | Copper sulphate                  | vitreous carbon                 | 2.18         | (Gu et al., 2010) |
| Sodium Citrate | Copper sulphate                  | FTO                            | 2.2–2.4      | (Anower et al., 2017) |
| Copper Lactate | Copper Acetate                  | ITO                            | 2.08–2.17    | (Zhao et al., 2011) |
| -              | Copper Acetate + Sodium Acetate  | ITO                            | 2.1          | (Rahal et al., 2018) |
| Sodium Lactate | Copper sulphate                  | ITO                            | –            | (Zhu et al., 2013) |
| -              | Sodium sulfate                   | Cu sheet                        | 2.0–2.3      | (Shohbazi & Kiani, 2016) |

et al., 2010; Kim et al., 2014; Lee et al., 2004; Y. Liu et al., 2016; R. Liu et al., 2003; Messaoudi et al., 2016; Nian et al., 2009; Paracchino et al., 2012; Rahal et al., 2018; Ravichandiran et al., 2019; Shahbazi & Kiani, 2016; Xua et al., 2012; Yang et al., 2016; Zhao et al., 2011; Zhu et al., 2013. The band separation value obtained in the presence of the copolymer is higher than without it, probably due to the presence of the polymeric material adhered to the Cu₂O nanostructures, which increases the energy between the conduction and valence bands of the semiconductor, generating a higher quantum confinement of the nanostructures (Tello et al., 2012).

4. Conclusions

The results of this research show that it is possible to obtain Cu₂O nanostructures in ITO by electrodeposition in the potential range of 0 V to −0.8 V from an aqueous solution of Cu²⁺ in the presence of p(NVP-co-Al). The morphology obtained shows a uniform film, composed of a mixture of agglomerated nano-grains with a diameter of approximately 78 nm to 91 nm and an alternation of nanoscales for a polymer concentration of 0.1% w/v. In addition, similar nanostructures are obtained by increasing the polymer concentration, where the surface uniformity increases, but in turn the polymer material is agglomerated on the surface of the ITO.
From the ATR-FTIR spectra obtained, it is confirmed that Cu²⁺ is effectively coordinated with the oxygen atoms of the carboxylic and carbonyl groups of the polymer. Besides, the decrease of the bandgap of Cu₂O nanostructures obtained in comparison to those previously reported using the same synthesis technique indicates that the growth of Cu₂O nanostructures takes place inside the polymer, which causes an important improvement in the semiconductor properties of Cu₂O.

Acknowledgements
The authors thank to Master Program in Chemistry mention of Materials Technology of the Metropolitan Technological University, Internal Project (L217-15) and Fondecyt project n° 1191336. OEL thanks the financial support from SECYT-UNC. RAMAN equipment at LANN, INFIOC-UNC/CONICET, Sistema Nacional de Microscopía-MINCyT, Argentina, are gratefully acknowledged.

Funding
The authors received no direct funding for this research.

Author details
Andrés Boulett
Guadalupe Del C. Pizarro
Rudy Martin-Trasanco
Julio Sánchez
E-mail: julio.sanchez@usach.cl
Fedimiro Tasca
Omar E. Linárez Pérez
Alejandra Tello
Diego P. Oyarzún
E-mail: diequm@gmail.com
1 Departamento De Química, Universidad Tecnológica Metropolitana, Santiago, Chile.
2 Departamento De Ciencias Del Ambiente, Facultad De Química Y Biología, Universidad De Santiago De Chile, Chacabuco 675, Santiago, Chile.
3 Departamento De Ciencias De Los Materiales, Facultad De Química Y Biología, Universidad De Santiago De Chile.
4 Universidad Nacional De Córdoba. Facultad De Ciencias Químicas, Departamento De Fisicoquímica. Haya De La Torre Esq. Medina Allende, X5000HUA. Córdoba, Argentina.
5 Conicet, INFIOQ. Haya De La Torre Esq. Medina Allende, X5000HUA. Córdoba, Argentina.
6 Facultad De Ciencias Naturales, Departamento De Química Y Biología, Universidad De Atacama, Copayapu 485, Copiapó, Chile.

Citation information
Cite this article as: Electrodeposition of Cu₂O nanostructures with improved semiconductor properties. Andrés Boulett, Guadalupe Del C. Pizarro, Rudy Martin-Trasanco, Julio Sánchez, Fedimiro Tasca, Omar E. Linárez Pérez, Alejandra Tello & Diego P. Oyarzún, Cogent Engineering (2021), 8: 1875534.

References
Alt, A., Atourki, L., Labchir, N., Abouabassi, K., Ouafi, M., Mouhib, H., Ihlal, A., Elfanaoui, A., Benmokhtar, S., & Bouabd, K. (2020). Structural and optical properties of electrodeposited Cu₂O thin films. Mater. Today, 22 (1), 89–92. https://doi.org/10.1016/j.mattod.2019.08.100
Allam, N., & Grimes, C. (2011). Electrochemical fabrication of complex copper oxide nanoarchitectures via copper anodization in aqueous and non-aqueous electrolytes. Mater. Lett., 65(12), 1949–1955. https://doi.org/10.1016/j.matlet.2011.03.105
Alvarado, J. (2017). Analysis of the perovskite structure La₃SrₓCrₓMn₄₋ₓO₉₋₄ₓ with potential application as an anode for solid oxide fuel cells. Bol. Soc. Esp. Ceram. 56 (2), 73–82. https://doi.org/10.1016/j.bsecv.2016.09.003
Anastasiadou, D., Schellekens, M., de Heer, M., Verma, S., & Negro, E. (2019). Electrodeposited Cu₂O films on gas diffusion layers for selective CO₂ electroreduction to ethylene in an alkaline flow electrolyzer. ChemElectroChem, 6(15), 3928–3932. https://doi.org/10.1002/celc.201900971
Anower, M., Al-Ghoshani, R., Hamoudi, H., Al Marri, M., Hussein, I., Belaidi, A., Merzougui, B., Alhori, F., & Tabet, N. (2017). Controlled growth of Cu₂O thin films by electrodeposition approach. Mat Sci. Semicon. Proc, 63(1), 203–211. https://doi.org/10.1016/j.mssp.2017.02.012
Bao, M., Wang, D., Liu, S., Kuang, L., Sun, J., Wang, F., & Wen, Y. (2012). Electrodeposition and electrocatalytic activity of Cu₂O film on stainless steel substrate. Appl. Surf. Sci., 258(20), 8008–8014. https://doi.org/10.1016/j.apsusc.2010.03.065
Das, C., Singh, A., Heo, Y., Aggarwal, G., Majuya, S., Seidel, J., & Kavaipatti, B. (2018). Effect of grain boundary cross-section on the performance of electrodeposited Cu₂O photocathodes. The Journal of Physical Chemistry C, 122(3), 1466–1476. https://doi.org/10.1021/acs.jpcc.7b10103
Gattinoni, C., Michaelides, A. (2015). Atomistic details of oxide surfaces and surface oxidation: The example of copper and its oxides. Surf. Sci. Rep., 70(3), 426–447. https://doi.org/10.1016/j.surfrep.2015.07.001
Gu, Y., Su, X., Du, Y., & Wang, C. (2010). Preparation of flower-like Cu₂O nanoparticles by pulse electrodeposition and their electrocatalytic application. Appl. Surf. Sci., 256(20), 5862–5866. https://doi.org/10.1016/j.apsusc.2010.03.065
Kar, P., El-tahawy, M., & Zhang, Y. (2017). Anodic copper oxide nanowire and nanopore arrays with mixed phase content: Synthesis, characterization and optical limiting response. J. Phys. Commun., 1(4), 1–9. https://doi.org/10.1088/2399-6528/ao9304
Kim, T., Oh, H., Ryu, H., & Lee, W. (2014). The study of post annealing effect on Cu₂O thin-films by electrochemical deposition for photoelectrochemical applications. J. Alloys Compd, 612(1), 74–79. https://doi.org/10.1016/j.jallcom.2014.05.158
Lara-jurado, D., Garcia-contreras, R., & Concepción, M. (2011). Sutures functionalised with nanomaterials for oral surgery. A systematic review. Rev. Esp. Cir. Oral Maxilofac, 40(1), 33–40. https://doi.org/10.1016/j.maxilo.2017.01.001
Lee, Y., Leu, I., Chang, S., Liao, C., & Fung, K. (2004). The electrochemical capacities and cycle retention of electrochemically deposited Cu₂O thin film toward lithium. Electrochimica Acta, 50(2-3), 4553–4559. https://doi.org/10.1016/j.electacta.2003.12.072
Liu, R., Oba, F., Bohannan, E., Ernst, F., & Switzer, J. (2003). Shape control in epitaxial electrodeposition: Cu₂O nanocubes on InP(001). Chem. Mater, 15(26), 4882–4885. https://doi.org/10.1021/cm034807c
Liu, Y., Liu, Y., Mu, R., Yang, H., Shao, C., Zhang, J., Lu, Y., Shen, D., & Fan, X. (2016). The structural and optical properties of Cu₂O films electrodeposited on different substrates. Semicond. Sci. Technol, 2011, 44–49. https://doi.org/10.1088/0268-9248/17/1/002
Messaoudi, O., Ben Assaker, I., Gannouni, M., Sassi, A., Makhlouf, H., Bardaoui, A., & Chtrourou, R. (2016). Structural, morphological and electrical
characteristics of electrodeposited Cu2O Effect of deposition time. Appl. Surf. Sci. 366(1) 383–388. https://doi.org/10.1016/j.apsusc.2016.01.035.

Meyer, B., Polity, A., Reppin, D., Becker, M., Hering, P., Kilar, P. J., Sander, T. H., Reinl, C., Benz, J., Eickhoff, M., Heiliger, C., Heinemann, M., Blasing, J., Krost, A., Shokovets, S., Muller, C., & Ronning, C. (2012). Binary copper oxide semiconductor: From materials towards devices. Phys. Status Solid B, 249(8), 1487–1509. https://doi.org/10.1002/pssb.201248128

Musselman, K., Wisnet, A., Iza, D., Hesse, H., Scheu, C., MacMonas-Driscoll, J., & Schmidt-Mende, L. (2017). Strong efficiency improvements in ultra-low-cost inorganic nanowire solar cells. Adv. Mater, 22(35), 254–258. https://doi.org/10.1002/adma.201001455

Mutalib, A., Losic, D., & Voelcker, N. H. (2013). Nanoporous anodic aluminium oxide: Advances in surface engineering and emerging applications. Prog. Mater. Sci, 58(5), 636–704. https://doi.org/10.1016/j.pmatsci.2013.01.002

Nian, J., Tsai, C., Lin, P., & Teng, H. (2009). Elucidating the conductivity-type transition mechanism of p-type Cu [sub J]O films from electrodeposition. J. Electrochem. Soc, 156(7), H567–H573. https://doi.org/10.1149/1.3125800

Niveditha, C., Fatima, M., & Sindhu, S. (2016). Comprehensive interfacial study of potentiodynamically synthesized copper oxide thin films for photoelectrochemical applications. J. Electrochem. Soc, 163(6), 426–433. https://doi.org/10.1149/2.0971606jes

Osherov, A., Zhu, C., & Panzer, M. (2013). Role of solution chemistry in determining the morphology and photocoercivity of electrodeposited cubic oxide films. Chem. Mater, 25(5), 692–698. https://doi.org/10.1021/cm303287g

Oyarzún, D., Berns, M., Linaro, O., López, M., Islas, R., & Arratia-Pérez, R. (2018). Simple and rapid one-step electrochemical synthesis of nanogranular Cu2O films. ChemSelect, 3(30), 8610–8614. https://doi.org/10.1002/slct.201703128

Oyarzún, D., López, M., Ramos, W., Pérez, O. L., Sánchez, J., Pizarro, G., Acosta, G., Flores, M., & Arratia-Pérez, R. (2017). Nanostructuring of anodic copper oxides in fluoride-containing ethylene glycol media. J. Electroanal. Chem, 807(1), 181–186. https://doi.org/10.1016/j.jelechem.2017.11.047

Oyarzún, D., Pizarro, G., Asenja, A., Tello, A., Martín-Trasanco, R., Zúñiga, C., Sanchez, J., & Arratia-Pérez, R. (2021). Synthesis and morphological characterization of nanocomposite based on anodic tio2 nanotubes and poly (n-maleyl glycine-co-acrylic acid). J. Chil. Chem. Soc, 62(3), 3634–3636. https://doi.org/10.4067/S0717-9707201700303634

Oyarzún, D., Tello, A., Pizarro, G., Martín-Trasanco, R., Zúñiga, C., Perez-Domingo, J., & Arratia-Pérez, R. (2017). Electrochemical synthesis, optical properties and morphological characterization of ZnO/Poly (N-PhMI-co-HEMA) nanocomposite. J. Electroanal. Chem, 799(1), 358–362. https://doi.org/10.1016/j.jelechem.2017.06.039

Porcaroano, A., Brauer, J., Moser, J., Thimsen, E., & Grotezel, M. (2012). Synthesis and characterization of high-photocactivity electrodeposited Cu2O solar absorber by Photoelectrochemistry and Ultrafast Spectroscopy. The Journal of Physical Chemistry C, 116(3), 7341–7350. https://doi.org/10.1021/jp201176y

Pizarro, G., Marambio, O., Jerías-Orell, M., Oyarzún, D., Rivas, B., & Habicher, W. (2009). Synthesis and characterization of hydrophilic copolymer of maleimide derivatives with 2-hydroxyethyl methacrylate: Electrochemical and thermal behavior. Polym. Int, 58(10), 1160–1166. https://doi.org/10.1002/pi.2644

Prieto, A., Martín-González, M., Keyani, J., Gronsky, R., Sands, T., & Stacy, A. (2003). The electrodeposition of high-nanopurity, ordered arrays of Bi1xSbxNano-wires. J. Am. Chem. Soc, 125(9), 2388–2389. https://doi.org/10.1021/ja029394f

Rahal, H., Kihal, R., Affoune, A., & Rahal, S. (2018). Electrodeposition and characterization of Cu2O thin films using sodium thiosulfite as an additive for photovoltaic solar cells. J. Chem. Eng, 26(2), 421–427. https://doi.org/10.1016/j.jche.2017.06.023

Rai, B. (1988). Cu2O solar cells: A review. Sol. Cells, 25(3), 265–272. https://doi.org/10.1007/BF01379688-90065-8

Ravichandiran, C., Sakhthivelu, A., Davidprabu, R., Valanarasu, S., Kathalingam, A., Ganesh, V., Shik, M., Alapahi, G., & Alliyuf, S. (2011). In-depth study on structural, optical, photoluminescence and electrical properties of electrodeposited Cu2O thin films for optoelectronics: An effect of solution pH. Microelectr. Eng, 210(1), 27–34. https://doi.org/10.1016/j.mee.2019.03.013

Read, C., Steinmiller, E., & Choi, K. (2009). Atomic plane-selective deposition of gold nanoparticles on metal oxide crystals exploiting preferential adsorption of additives. J. Am. Chem. Soc, 131(34), 12040–12041. https://doi.org/10.1021/la9036884

Riveros, G., Gamezandia, A., Ramirez, D., Tejos, M., Grez, P., Gomez, H., & Dalchielec, E. A. (2012). Study of the electrodeposition of Cu2O thin films from DMSO solution. J. Electrochem. Soc, 160(1), 28–33. https://doi.org/10.1149/2.029302jes

Shahbazi, P., & Kiani, A. (2016). Fabricated Cu2O porous foam using electrodeposition and thermal oxidation as a photocatalyst under visible light toward hydrogen evolution from water. Int. J. Hydrog. Energy, 41(39), 17247–17256. https://doi.org/10.1016/j.ijhydene.2016.07.080

Stępniowa, W., & Misiolik, W. (2018). Review of fabrication methods, physical properties, and applications of nanostructured copper oxides formed via electrochemical oxidation. Nanomaterials, 8(6), 379–398. https://doi.org/10.3390/nano8060379

Telib, R., Abdullah, M., Al-salman, H., Mohammad, S., & Allam, N. (2016). ZnO nanorods/polyaniline-based inorganic/organic heterojunctions for enhanced light sensing applications. J. Solid State Sci. Tech, 4(2), 142–147. https://doi.org/10.1109/JSSST.2015.7430167j

Tello, A., Gómez, H., Muñoz, E., Riveros, G., Pereyra, C., Dalchiele, E., & Moratti, R. E. (2012). Electrodeposition of nanostructured ZnO thin films from dimethylsulfoxide solution: Effect of temperatures on the morphological and optical properties. J. Electrochem. Soc, 159(12), 750–755. https://doi.org/10.1149/2.017301jes

Verdugue, J. (2016). The specific immunotherapy of autoimmune diseases through the nanomedicine. Endocrinol Y Nutr, 63(9), 437–439. https://doi.org/10.1016/j.endonu.2016.05.003

Wang, D., Peng, Q., & Li, Y. (2010). Nanocrystalline intermetallics and alloys. Nano Res, 3(8), 574–580. https://doi.org/10.1007/s12274-010-0018-4

Xia, L., Xua, H., Wua, S., & Zhang, X. (2012). Synergy effect over electrodeposited submicron Cu2O films in photocatalytic degradation of methylene blue. Appl. Surf. Sci, 258(11), 4934–4938. https://doi.org/10.1016/j.apsusc.2011.06.031

Yang, Y., Li, Y., & Pritzker, M. (2016). Control of Cu2O film morphology using potentiostatic pulsed electrodeposition. Electrochim. Acta, 213(1), 225–235. https://doi.org/10.1016/j.electacta.2016.07.116
Zhao, W., Fu, W., Yang, H., Tian, C., Li, M., Li, Y., Zhang, L., Sui, Y., Zhou, X., Chen, H., Zou, G. (2011). Electrodeposition of Cu$_2$O film and their photoelectrochemical properties. CrystEngComm, 13(8), 2871–2877. https://doi.org/10.1039/C0CE00829J

Zhu, C., Osherov, A., & Panzer, M. (2013). Surface chemistry of electrodeposited Cu$_2$O films studied by XPS. Electrochimica Acta, 111(1), 771–778. https://doi.org/10.1016/j.electacta.2013.08.038

Zoolfakar, A., Rani, R., Morfa, A., O'Mullane, A., & Kalantar-zadeh, K. (2014). Nanostructured copper oxide semiconductors: A perspective on materials, synthesis methods and applications. J. Mater. Chem, 27(2), 5247–5270. https://doi.org/10.1039/C4TC00345D