

# INFLUENCE OF THE DIP AND SPIN COATING METHODS ON THE SEEDING FOR THE GROWING OF CuO NANORODS BY A HYDROTHERMAL TECHNIQUE

## INFLUENCIA DE LOS MÉTODOS DE INMERSIÓN Y CENTRIFUGADO EN LA DEPOSICIÓN DE SEMILLAS PARA EL CRECIMIENTO DE NANOBARRAS DE CuO POR UNA TÉCNICA HIDROTHERMAL

S. FORTUNÉ-FÁBREGAS<sup>a</sup>, J. BENAVIDES<sup>a</sup>, A. M. DÍAZ-GARCÍA<sup>b</sup>, Y. GONZÁLEZ<sup>c</sup>, A. RUEDIGER<sup>c</sup> AND L. VAILLANT-ROCA<sup>a†</sup>

a) Photovoltaic Research Laboratory, Institute of Materials Science and Technology-Physics Faculty, University of Havana, Cuba; †

b) Inorganic and General Chemistry Department, Bioinorganic Laboratory (LBI), University of Havana, Cuba.

c) Institut National de la Recherche Scientifique- Énergie, Matériaux, Télécommunications, 1650 Boulevard Lionel-Boulet, J3X 1S2, Varennes, Québec, Canada.

† corresponding author

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Copper(II) oxide (CuO) nanostructures based solar cells have a great potential due to the optimal absorber characteristic of this material. Furthermore, CuO is stable, composed by abundant elements in the Earth's crust and can be obtained by inexpensive and simple synthesis methods. The substrates seeding is an important technological step with great influence in the morphology of CuO nanorods obtained by the hydrothermal technique. We have studied the influence of dip coating and spin coating as seeding techniques on the CuO nanorods properties. The materials are also evaluated after a sequential annealing until 500°C. The samples were characterized by means of scanning electron microscopy (SEM) and Raman spectroscopy.

El óxido de cobre(II) (CuO) es un material inorgánico estable con óptimas propiedades para su aplicación como material absorbente en celdas solares. Además, está compuesto por elementos abundantes en la corteza terrestre y puede ser obtenido por métodos simples y de bajo costo. El semillado de los sustratos tiene una gran influencia en la morfología y alineación vertical de nanobarras de CuO obtenidas mediante la técnica hidrotermal. En este trabajo se estudia la influencia de la inmersión y el centrifugado como técnicas de semillado en las características de las nanobarras de CuO. También se evalúa el efecto del tratamiento térmico secuencial hasta 500°C. Los materiales obtenidos fueron caracterizados mediante microscopía electrónica de barrido (SEM) y espectroscopía Raman.

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### I. INTRODUCTION

Nanostructured transition metal oxides (TMO) have attracted a great attention because of their versatility, abundance, low toxicity, and simple and low-cost obtention techniques [1–3]. TMO are used in photodetectors, gas sensors, superhydrophobic surfaces and solar cells [1]. A few p-type metal oxides exist in nature that can be used as absorbent materials in photovoltaic devices [1, 3, 4]. Among these, copper(II) oxide (CuO) has an suitable band gap of 1.21–1.55 eV [1]. CuO is also stable, non-toxic and composed by abundant elements in the Earth's crust [5,6]. These advantages make this material very promising for solar cells.

Indeed, there are several reports of CuO nanostructures obtained by solution-based methods due to their low cost and effectiveness to produce nanostructures at large scale and low temperatures [2, 7]. In general, the preliminary substrate preparation is critical for the achievement of a homogeneous surface coverage with these techniques. In particular the hydrothermal method requires a pre-deposition of the seed layer which provides specific nucleation points, facilitating the growth of elongated nanoparticles with

excellent alignment, columnar aspect and space between them for further infiltration process, on almost any substrate like TCO (transparent conductive oxide), glass and even polymers [8, 9]. Dip coating and spin coating are widely used as low cost seeding processes. They are both simple experimental techniques with different advantages. Spin coating is faster and allows the preparation of thinner seed layers in comparison with dip coating. On the other hand, dip coating can be manually performed with great reproducibility. Taking into consideration the great impact of the seeds layer in the nanorods morphology, the main goal of this work is to evaluate both; spin coating and dip coating, as seeding methods for the preparation of CuO nanorods with potential applications as absorber materials in nanostructured solar cells. The CuO nanorods are obtained on top of spin coated and dip coated seeded substrates and are analyzed and compared by SEM and Raman spectroscopy. Additionally, a selected sample are thermally treated in air, in a sequential process looking to further improve the properties of the absorber material.

## II. EXPERIMENTAL DETAILS

**Substrate cleaning process:** The substrates were cleaned using two different processes to improve the CuO seed layer adherence. First, they were washed with a soap solution and rinsed with distilled water. Then, the substrates were immersed in a nitric acid and water solution (1:2), again rinsed with water and later ultrasonicated in distilled water during 15 minutes. In the other method the slides were soaked in ethanol and ultrasonicated after the previous cleaning process during 10 minutes followed by soaking in 1 M solution of KOH and ultrasonicated during the same amount of time. The glass substrates were finally rinsed in the ultrasonic bath in distilled water during 20 minutes [10].

**Deposition of CuO seed layer and CuO nanorods synthesis:** Dip coated seeds samples were prepared by wetting the substrate during one minute with a 5 mM copper acetate solution in ethanol on the substrate, and later tilting it to drain the excess solution. Once the remaining solution dries out, the wetting, draining and drying process were repeated for 5 times. In the spin coating technique, the same copper(II) acetate solution was spin-coated on the substrates at 2000 rpm during 20 seconds for four times. Then the samples obtained by the two techniques were treated in air at 250 °C for 30 minutes to form the CuO seeds layer from the copper(II) acetate thermal decomposition. The CuO nanorods were grown by chemical bath deposition (CBD) by placing the CuO seeded substrate upside down in an equimolar 0.025 M aqueous solution of copper(II) nitrate trihydrate ( $Cu(NO_3)_2 \cdot 3H_2O$ , Merck GR for analysis) and hexamethylenetetramine (HMT, Sigma-Aldrich ACS reagent  $\geq 99.0\%$ ) at 90 °C for 4 hours. After reaction, the resulting nanorods were thoroughly rinsed with distilled water and ethanol, and dried under a nitrogen gas stream [5]. The seeding layer and nanorods growing processes are depicted in Fig. 1.

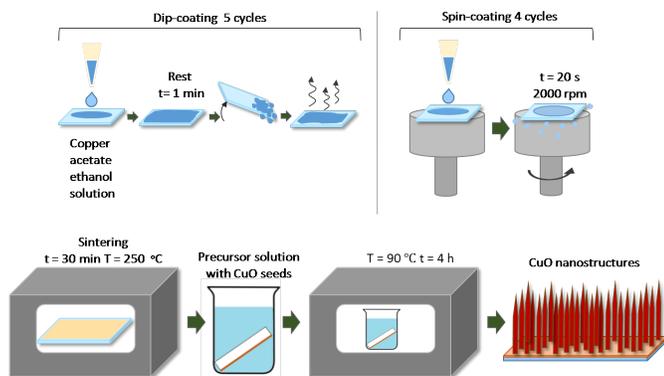


Figure 1. CuO NRs synthesis process.

**CuO nanorods heat treatments:** The spin coating samples were treated using a cumulative thermal treatment from 200 to 500 °C in air during 1 hour in each cycle. To perform this, the as grown samples is introduced in the oven and taken at 200 °C during 1 hour after which one sample was retired. This sample is labeled 200 °C. The rest were kept in the oven and taken into 300 °C for another hour after which a second sample labeled

200 + 300 °C was extracted. The process is repeated until the last sample had received the 4 sequential treatments 200, 300, 400 and 500 °C. This cumulative process would increase the crystalline quality of the samples in a continuous process.

**Characterization and instruments:** The samples were characterized by means of Scanning Electron Microscopy (SEM) using a Hitachi S530 G microscope. Raman spectroscopy was carried out with a confocal optical microscope coupled with a modular Raman spectrometer from Horiba (iHR320). The light source was a continuous wave diode-pumped solid-state laser with a wavelength of 473 nm (Cobolt Inc.), linearly polarized operating in single mode TEM 00.

## III. RESULTS AND DISCUSSION

Copper(II) oxide nanorods were successfully obtained, as Fig. 2 displays, on top of substrates seeded by dip and spin coating methods. The substrates were homogeneously covered by tapered CuO nanorods with leaves morphology leading to comparably similar materials thicknesses of 427 and 405 nm for spin and dip coating seeded samples respectively (inserts in Fig. 2a and 2c). These values are around the optimal thickness for achieving good light absorption in CuO thin films [11]. The multiple optical reflection as a result of the interaction between the light and the tapered nanorods would increase the optical pathway giving space for a further minimization of this thickness value in the nanostructured samples. The spin coating seeded sample shows an apparent higher porosity than the dip coating seeded one.

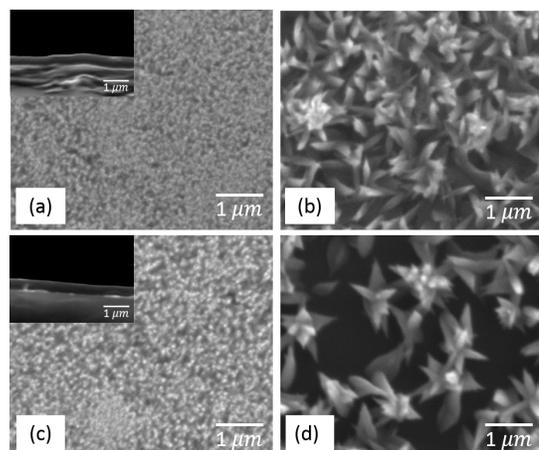


Figure 2. SEM images of CuO NRs samples. Surface and cross sectional view of dip coating (a and b) and spin coating (c and d) samples.

In the samples borders for both type of procedures (Fig. 2b and 2d), the surface coverage is not complete and the nanorods are larger, with a tendency to create nanoflowers in the spin coating seeded sample. This would be produced by a difference in the seeds density and sizes from the center to the borders, which is a possible feature in both types of deposition techniques to be taken into account. Larger seeds increase the tapered nanorods size with a detrimental effect in the vertical alignment [12]. This effect is stronger in the spin coating

sample, suggesting a larger impact of this problem by using this technique.

Fig. 3 shows the Raman spectra of CuO bulk [13] and the tapered nanorods samples, confirming that the grown CuO belongs to space group  $C_{2h}^6$  with monoclinic structure. The standard sample data was provided by the RRUFF Project, and belongs to a massive sample of the mineral tenorite (RRUFF ID:R060978). CuO present 3 Raman active modes ( $A_g + 2B_g$ ) [14]. The peaks at  $281$  and  $287\text{ cm}^{-1}$  were assigned to  $A_g$ , while  $327$  and  $338\text{ cm}^{-1}$  to  $B_{g1}$ , and  $617$  and  $616\text{ cm}^{-1}$  to  $B_{g2}$  modes. The shift to lower wavenumbers are generally explained due to size effects in comparison with the bulk material [13].  $A_g$  and  $B_{g1}$  tend to be sharper in spin coated seeded samples suggesting that CuO layers obtained by this method have a better crystalline quality. This sample was selected for the following thermal treatment.

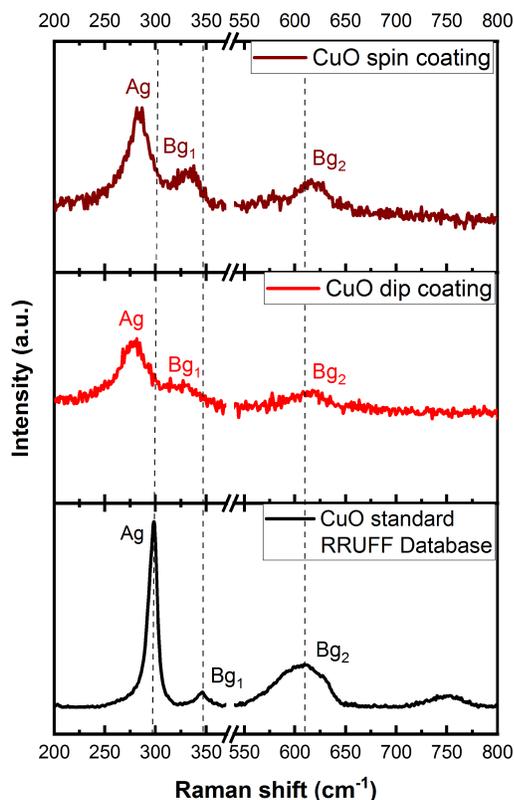


Figure 3. Raman spectra of CuO NRs samples obtained by different seed deposition methods. (RRUFF Project, <https://rruff.info/>)

Thermal treatments, among other advantages, improve the crystalline quality, especially in materials obtained by low cost methods. After CuO NRs synthesis the spin-coated samples were thermally treated using the sequential method previously described in the experimental section. Fig. 4 presents the surface SEM pictures, showing the increase in nanorods diameter size with thermal treatment. In particular for the sample annealed until  $500\text{ }^\circ\text{C}$ , the rods tend also to be more compact, with an apparent decrement of the porosity of the sample, which would later introduce a barrier for the infiltration of the electron transporter material. This result suggests the need for keeping thermal treatment temperatures below  $500\text{ }^\circ\text{C}$  for sequential treatment in such a way to improve the crystallinity without a detrimental effect in the

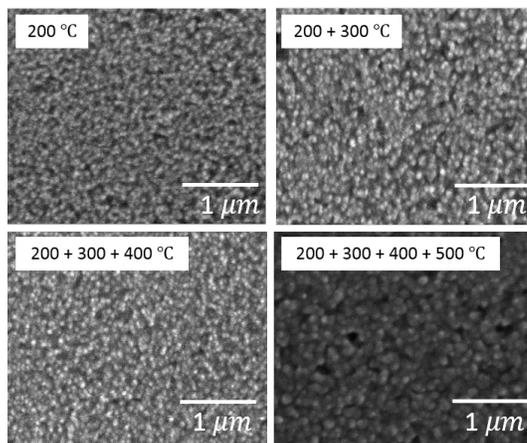


Figure 4. SEM images of CuO NRs thermally treated.

Fig. 5 shows the Raman spectra for the as grown and annealed samples. The peaks position and FWHM can be seen in Table 1, where is possible to observe that  $A_g$  and  $B_{g1}$  peaks become sharper with the increase of thermal treatments temperature, evidencing the improvement in crystallinity with the annealing process. The peaks show displacements to higher wavenumbers which has been previously reported as a result of larger grains [15]. The increments in grain sizes is a common consequence of thermal treatment as well.

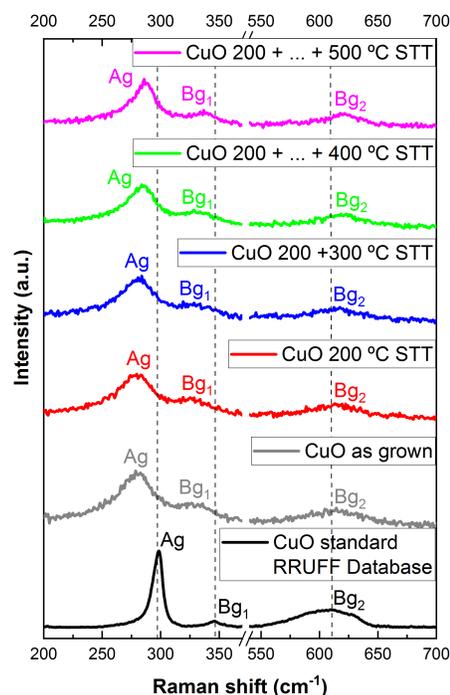


Figure 5. Raman spectra of sequential thermally treated CuO NRs.

#### IV. CONCLUSIONS

CuO NRs were obtained by an hydrothermal low cost method on top of dip- and spin-coated seeded substrates. The spin coating seeding method produce a CuO nanorod layer with a

slight better crystalline quality than dip coating, according to the Raman spectra, but worse surface coverage homogeneity. Taking this into account, spin coating can be selected as a better option for the seeding process. The sequential thermal treatment (STT) increases the crystalline quality as reaches the 500 °C, and a decrease in the porosity of the sample, probably due to grain size increment. This suggests limiting the thermal treatment below this value, achieving a compromise between crystalline quality and porosity.

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## REFERENCES

- [1] Q. Zhang et al, *Prog. Nater. Sci.* **60**, 208 (2014).
- [2] T. H. Tran and V. T. Nguyen, *Int. Scholarly Res. Not.* **2014**, 14 (2014).
- [3] A. S. Zoolfakar et al, *J. Mater. Chem. C* **2**, 5247 (2014).
- [4] H. Kidowako et al, *J. Mater. Sci. Res.* **1**, 138 (2012).
- [5] F. Wu et al, *Nanotechnology* **29**, 215403 (2018).
- [6] D. L. Anderson, *Theory of the Earth* (Blackwell Scientific Publications, Cambridge, UK; New York, US, 1989).
- [7] F. Zhang et al, *Phys. Chem. C* **114**, 19214 (2010).
- [8] N. Basinova et al, *Crystals* **9**, 566 (2019).
- [9] M. Kokotov and G. Hodes, *J. Mater. Chem.* **19**, 3847 (2009).
- [10] K. D. Malviya et al, *J. Mater. Res.* **31**, 1565 (2016).
- [11] T. Dimopoulos et al, *J. Renewable Sustainable Energy* **5**, 11205 (2013).
- [12] A. Peukert et al, *Sol. RRL* **1**, 1700132 (2017).
- [13] B. Lafuente, R. T. Downs, H. Yang and H. Stone, *Highlights Mineral. Crystallogr.*, 1-29 (Walter de Gruyter GmbH, 2016).
- [14] J. C. Irwin, T. Wei and J. Franck, *J. Phys. Condens. Matter* **3**, 299 (1991).
- [15] J. F. Xu et al, *J. Raman Spectrosc.* **30**, 413 (1999).

Table 1. Position and FWHM of Raman peaks for the as grown and thermally treated CuO NRs.

Sample	Ag		Bg <sub>1</sub>		Bg <sub>2</sub>	
	Peak Position (cm <sup>-1</sup> )	FWHM (cm <sup>-1</sup> )	Peak Position (cm <sup>-1</sup> )	FWHM (cm <sup>-1</sup> )	Peak Position (cm <sup>-1</sup> )	FWHM (cm <sup>-1</sup> )
as grown	279	45	326	31	614	45
200°C	280	51	329	21	613	43
200°C + 300°C	284	54	329	12	617	40
200°C+...+400°C	284	39	329	21	618	33
200°C+...+500°C	286	32	337	16	621	28

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