

Article

Facile Preparation of SnO₂/CuO Nanocomposites as Electrocatalysts for Energy-Efficient Hybrid Water Electrolysis in the Presence of Ethanol

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Abstract: Currently, great importance has been assigned to designing cutting-edge materials for oxygen and hydrogen generation from hybrid water electrolysis as an ideal fuel alternative in energy-conversion devices. This work reports on the electrochemical organic molecule oxidation in alkaline media, intending to promote water electrolysis at early onset potential with more current densities using Sn-Cu oxidized heterostructures. The electrocatalysts were easily and rapidly synthesized by the microwave-heated synthesis process in the presence of a small quantity of ethylene glycol. The X-ray diffraction and Field Emission Scanning Electron Microscopy analyses confirm the presence of CuO and SnO₂ phases, which significantly improves the electrochemical activity of the composite toward the Oxygen Evolution Reaction (OER) in alkaline media in the presence of 1.0 mol L⁻¹ ethanol, yielding 8.0 mA cm⁻² at 1.6 V. The charge transfer resistance (R_{ct}) was determined using electrochemical impedance spectroscopy, and the result shows that the R_{ct} of SnO₂/CuO drastically decreased. The findings in this work highlight that the designed oxidized heterostructures with non-noble metals are promising candidates for energy conversion devices and sensors. Furthermore, this work confirms the advantages of using an assisted microwave heating process to develop an advanced SnO₂/CuO composite with the potential to be used in electro-oxidation processes.

Keywords: electrocatalysts; SnO₂/CuO; assisted water electrolysis; facile synthesis; polyol method



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1. Introduction

Currently, tremendous research efforts have been achieved in designing and developing functional metal oxide materials to enhance the performance of electrochemical sensors, energy storage, and conversion devices [1–4]. Electrochemical water splitting is a fundamental process that has been considered for its potential applications in the upcoming high-tech devices since it is visualized as a clean and green process [5–7]. Henceforth, the scientific community has begun working on forthcoming metal oxide materials to face the barriers of the widespread application of water electrolysis [8,9]. One limitation is the sluggish reaction kinetics of the oxygen evolution reaction (OER) at the anode side due to the high energy bond of molecular oxygen (O=O), which is 498 kJ mol⁻¹ [10,11]. As well established, OER is a four-step process, and the adsorption and dissociation of OH⁻ and OOH⁻ species are the rate-determining steps [12], which limit the overall efficiency of fuel cells and metal–air batteries [13]. To overcome these drawbacks, various electrocatalytic materials, such as noble metals, metal chalcogenides, ceramic composites, metal oxides, and hydroxides have been proposed to decrease the activation energy for the OER during water electrolysis [14–16].

Among them, SnO₂-based composites demonstrate good versatility because they are n-type wide bandgap semiconductors with good chemical stability and affinity for bridge functional groups [17]. Unfortunately, this single material presents a poor activity for

the most studied electrochemical process, which precludes its widespread application in cutting-edge technologies. To this end, many proposals have been made to overcome the limitations of this semiconductive material, such as incorporating other chemical elements by creating functional defects in its crystal structure or improving its electrical conductivity [18,19]. In this pursuit, Han et al. investigated the ratio effect of Sn in Cu_xSn_y nanomaterial [20]. They proposed a simple preparation method using high-energy ball milling and thermal treatment. Surprisingly, these anode materials show high discharge capacity with an initial Coulombic efficiency of 91.37%. Moreover, Ayesb et al. synthesized CuO/SnO_2 metal oxide nanoparticles to fabricate electrodes for gas-sensing applications [21]. It should be highlighted that the authors carry out two separate synthesis processes in this work: the solvothermal process for CuO nanoparticles and the sol-gel method to obtain SnO_2 . The sensor electrode was created by mixing CuO and SnO_2 powder in different percentages and casting them on a conductive transparent glass. Recently, Zhang et al. proposed the synthesis of SnO_2 - CuO heterostructures by a single-step hydrothermal method for ethanol gas sensor applications [17]. Sodium stannate and copper nitrate were used as chemical precursors for Sn and Cu, respectively. According to the reported method, this author uses sodium citrate and ammonia water to assist the ion dissociation and reduction processes. The mixed solution was hydrothermally treated for 8 h at a temperature of 160 °C, and after recovery, the powder was further thermal treated by annealing at 800 °C for 0.5 h. From the aforementioned literature, it can be pointed out that designing electroactive catalysts is a feasible strategy to improve the efficiency of energy-converter devices. Some of the proposed materials are based on expensive chemical elements, which motivate the search for other tactics to enhance the operability of the future device.

An alternative to overcome the sluggish OER is implementing hybrid water electrolysis based on the electro-oxidation of organic molecules [22–24]. This way, a less demanding oxidation reaction is obtained while producing high-value-added chemical by-products with high conversion efficiency [25–27]. Notably, ethanol is a rich oxygen and hydrogen source that can be produced from bio-sourcing. Its electrochemical oxidation is more thermodynamically favorable and exhibits fast kinetic at low onset potential compared with the OER [28]. Therefore, it has been proposed as a promising candidate for generating water electrolysis and obtaining high-value-added products (acetic acid and acetaldehyde). Early research suggests that alkaline ethanol electrolysis on Pd/Ti electrodes facilitates the hybrid water electrolysis that results in high performance [29]. However, OER from water electrolysis commonly requires noble metals, but organic molecules can be oxidized using low-cost transition metals [30,31]. It is well known that the electrochemical activity of transition-metal-based electrocatalysts in alkaline media is activated via the formation of oxyhydroxides' MO_xHO_y active sites. Furthermore, the oxidation of organic molecules occurs at low overpotentials in this material: between 1.2 and 1.4 V vs. RHE [32,33].

For instance, Li et al. developed $\text{Co}(\text{OH})_2@\text{Ni}(\text{OH})_2$ nanostructures using a metal-organic precursor in a hydrothermal synthesis. The material shows excellent ethanol oxidation reaction (EOR) activity and high stability. Moreover, the catalyst easily converted ethanol to acetate, which was attributed to the double hydroxide layer [34]. In addition, cobalt hydroxide@hydroxysulfide on carbon paper was used as an electrocatalyst for the OER [35]. It was found that the methanol concentration greatly improves the onset potential and the electrochemical activity of the OER. For example, a current density of 15 mA cm^{-2} at 1.4 V was obtained in the presence of 3 mol L^{-1} methanol, which is a much lower value than water splitting, which is close to 1.58 V. Another interesting research was published by Patil et al., where the SnS nanosheet was supported on Ni-foam via a solution process. The fabricated catalysts show activity toward the generation of green H_2 under the presence of urea waste [36]. In this context, copper sulfide nanowire, supported on NiCo-layered double hydroxide, was proposed as a bifunctional electrocatalyst for water splitting in the presence of 5-hydroxymethylfurfural as an organic molecule [37]. F-FeOOH has also been used as the electrode for water electrolysis in the presence of ethanol, showing current densities of 10 mA cm^{-2} at the potential of 1.43 V. At the same time, this material favors

the generation of acetic acid as a high-value product [38]. As can be deduced from the literature mentioned, the synthesis methods inevitably lead to using costly and specialized equipment for a long time.

The present document reported a facile synthesis approach for producing SnO_2/CuO heterostructures using the single-step assisted microwave polyol method. It should be highlighted that this work intends to develop noble metal-free electrocatalysts active for the water-splitting process. Moreover, it is focused on demonstrating that electroactive materials can be produced quickly using non-sophisticated equipment and an overall scalable synthesis process that can be extended in different fields of science. It is hypothesized that the SnO_2/CuO composite could have electrochemical activity for ethanol and OER, but no studies have yet been reported. Based on the observations of this work, using X-ray diffraction (XRD), Field Emission Scanning Electron microscopy (FESEM), Raman spectroscopy, and electrochemical measurements, the electrocatalytic activity of SnO_2/CuO is promising and comparable with those reported in the literature.

2. Materials and Methods

The synthesis approach is based on a microwave-assisted polyol process. The typical synthesis process to prepare SnO_2/CuO (SC) electrocatalysts is depicted in Figure 1. Firstly, the desired amount of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (199.5 mg) and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (222.5 mg) was dissolved separately in two vessels containing 4 mL of deionized water and 1 mL of ethylene glycol in an ultrasonic bath for 5 min. Secondly, 0.3 mL of NaOH solution was added to each sample, and then, they were sonicated for another 5 min. The two samples were mixed in a one-neck bottom flask, transferred in a microwave oven, and heated for 2 min. Here, it must be emphasized that the ratio between water and ethylene glycol plays a critical role. Actually, from previous laboratory experiments, no SnO_2 nanoparticles were obtained in the absence of water. So, several trial experiments were conducted to finally have the above-explained method to develop SnO_2 and CuO in one step. The composite was recovered by vacuum filtration using a PTFE membrane and washed through deionized water. Then, the catalytic powder was dried at 110°C in an oven for 30 min. Finally, the powder was grounded in an agate mortar and stored for further characterization.

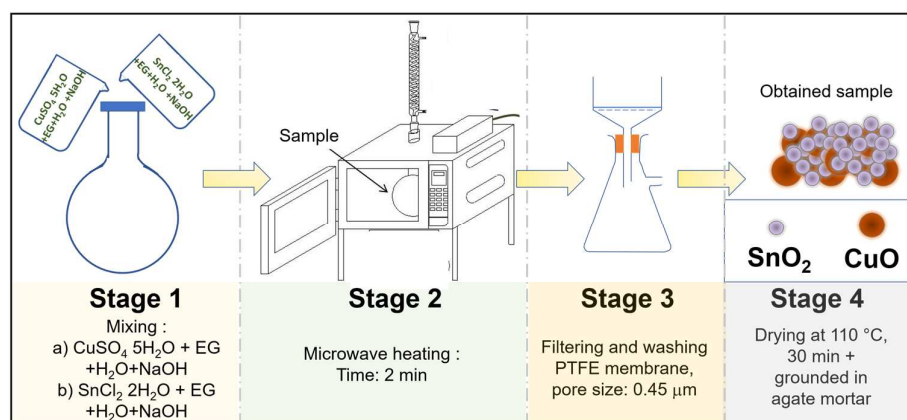


Figure 1. Schematic illustration of the proposed step for successfully synthesizing SnO_2/CuO electrocatalyst from the microwave-assisted polyol process.

The morphology and structure of the electrocatalyst were investigated by Field Emission Scanning Electron Microscopy (FESEM-EDS) on a Jeol Prime-7800F equipped with an energy spectrometer at 30 kV as working voltage. Meanwhile, the crystal structure and phases were studied by conducting X-ray diffraction (XRD) analyses on a Bruker D2 phaser where $\text{CuK}\alpha$ was used as a source with 30 kV and 30 mA. Fourier transform infrared spectroscopy (FTIR) was used to elucidate the functional groups and the bonds on the

surface of the materials (WQF-510A-Rayleigh instrument). Raman spectroscopy in Thermo Scientific DXR2 equipment analyzed purity and crystal defects.

The electrochemical characterization was conducted on a potentiostat/galvanostat (GillAC, ACM instruments). Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were taken in 0.5 mol L⁻¹ NaOH as a supporting electrolyte and in the presence or absence of ethanol as a sacrificial organic molecule. The measurements were achieved in a three-electrode configuration. The working electrode was a glassy carbon electrode (with a 0.125 cm² geometric area) modified by transferring an aliquot of the catalytic ink (5 mg of the material + 0.5 mL 2-propanol and 15 µL Nafion from Sigma-Aldrich). Meanwhile, silver–silver chloride (Ag/AgCl) filled with saturated KCl was used as the reference electrode, and a graphite bar was used as the counter electrode. All the reported potentials are converted to the reference hydrogen electrode (RHE) by using the Nernst equation. Before the electrochemical measurements, the supporting solution was bubbled with high-purity N₂ gas. Linear sweep voltammetry (LSV) was used to study the anodic and cathodic reactions at a low scan rate of 5 mV s⁻¹. In addition, chronoamperometry measurements are carried out at the constant potential of 1.5 V vs. RHE in N₂-deaerated 0.5 mol L⁻¹ ethanol. The Electrochemical Impedance Spectroscopy (EIS) measurements were recorded between the frequency windows of 100 kHz and 100 mHz with an AC signal of 10 mV amplitude and an applied potential of 1.5 V.

3. Results

3.1. Physical and Chemical Characterization

Figure 2 shows the XRD pattern of the commercial SnO₂, CuO and the synthesized SnO₂/CuO composite. The reflection peaks at the commercial material located at 2θ = 26.6°, 33.9°, 38°, 39°, 51.8°, 54.8°, 57.8°, 61.8°, 64.7°, 66°, 71.3°, and 78.7° are well indexed to (110), (101), (200), (111), (211), (220), (002), (310), (112), (301), (202), and (321) planes (JCPDS 41-1445) in the tetragonal structure of cassiterite (SnO₂), respectively [39].

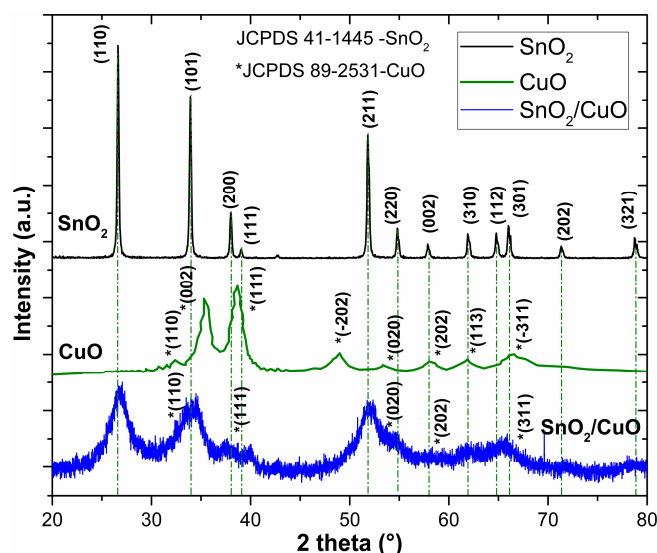


Figure 2. XRD patterns for commercial SnO₂, CuO and the SnO₂/CuO materials.

The CuO has reflections close to 32.2°, 35.1°, 38.5°, 48.8°, 53.4°, 58.2°, 67.1° and 66.7° 2θ, which are ascribed to the (110), (002), (111), (−202), (020), (202), (113), (−311) planes. In the case of the synthesized material, the XRD pattern displays an evident shape change and non-intense peaks compared to the commercial one. The main peaks located at 26.8°, 34.1°, 37.8°, 52°, 54°, 61.9°, and 65.7° could be also indexed with the SnO₂ structure. In addition, the broad peaks observed close to 2θ = 32.6°, 39.7°, and 53.6° are properly indexed to the (110), (111), and (020) planes of monoclinic CuO (JCPDS 89-2531), which is in good agreement with the literature [40].

This information suggests that the chemical precursors tend to form oxidized species under the synthesis conditions. From Figure 1, it can be observed that each chemical precursor is individually mixed with water and NaOH, and this favors the formation of oxides. No other relevant peaks were observed, confirming the high purity of the material synthesized by the microwave-assisted polyol process.

It should be mentioned that the synthesized electrocatalyst has broad and weak peaks that can be related to the small crystallite size, which was previously reported in the literature [41,42]. The crystallite size of the materials was determined by the Debye–Scherrer equation, concluding that commercial SnO_2 is 38 nm, while the synthesized composite is 3.5 nm. The pronounced narrow and broad peaks in SnO_2 have been previously studied by the research group of Osuntokun [41]. This group developed SnO_2 nanostructures by using biosynthesis based on cauliflower aqueous extract. The reported XRD pattern by this group is quite similar to the one obtained in this work, where the crystallite size was 3.6 nm compared with 3.5 nm determined for the composite.

Figure 3a,b depicts the FESEM images of the SnO_2/CuO composite at different magnifications. According to this micrograph, the morphological structure of the composite tends to form clusters with flakes shape covered with small nanoparticles. Figure 3a shows agglomerates with dimensions from 260 nm to 2.6 μm . It can be speculated that small nanoparticles stack to form large particles. Figure 3b shows a sample under large magnification, confirming that small nanoparticles form those large flakes. In addition, the former figure shows different regions: first, a small cluster ranging from 40 to 90 nm in diameter (in yellow), then a set of circles that contain tiny nanoparticles that make it almost impossible to assign a diameter value due to the small scale (in red). The FESEM result supports the XRD data where the calculated crystallite size was 3.5 nm, which was in good agreement with the red spot marked in Figure 3b. The aggregation of this type of composite was already reported by several researchers [21,43]. For example, Zhang et al. state that small nanoparticles tend to form large nanospheres [17].

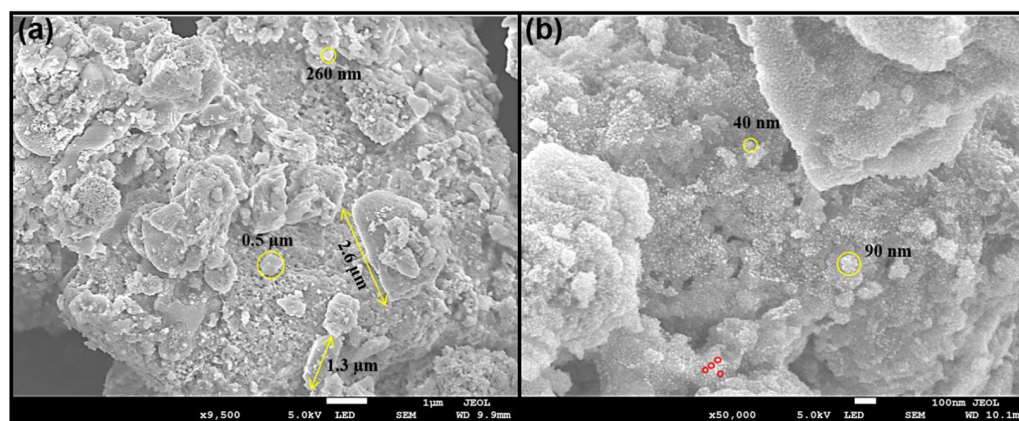


Figure 3. FESEM images for SnO_2/CuO composite at different magnifications. (a) FESEM micrograph taken at 9500 $\times$; (b) FESEM micrograph taken at 50,000 $\times$.

Figure 4a–d present the SnO_2/CuO selected region for elemental map analysis. Three of the total elements detected by the EDS measurement were chosen for this analysis: Cu, O, and Sn. As can be observed, all the chemical elements are well distributed, and in the case of Figure 4d, the saturated image is due to more Sn concentration in the SnO_2/CuO . The EDS measurements (Figure 4e) show that the Sn, Cu, and O experimental percentages in the SnO_2/CuO composite are 64.7%, 16.1%, and 19.1%, respectively. This result supports the formation of oxidized phases.

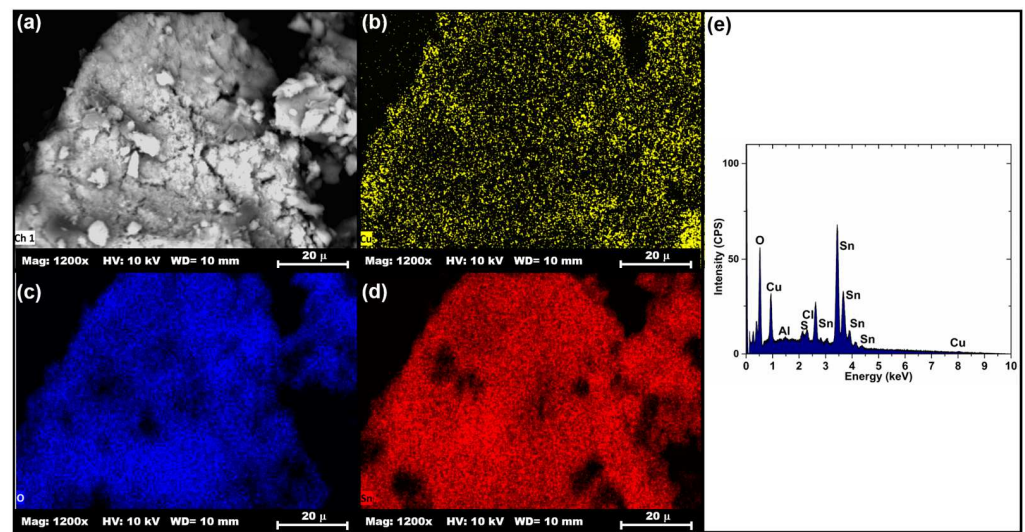


Figure 4. Elemental map image for the SnO₂/CuO. (a) Study area. (b) Dispersion of Cu element on the surface of the selected region. (c) Oxygen species along the surface. (d) Tin presence along the surface of the sample. (e) EDS spectra.

The FTIR spectra of SnO₂ and SnO₂/CuO are shown in Figure 5. Both materials exhibit a broad band around 3450 cm^{−1} and strong perturbation at 1630 cm^{−1}, which are attributed to the O-H stretching and bending vibrations of water molecules provoked by the adsorbed water and OH[−] groups.

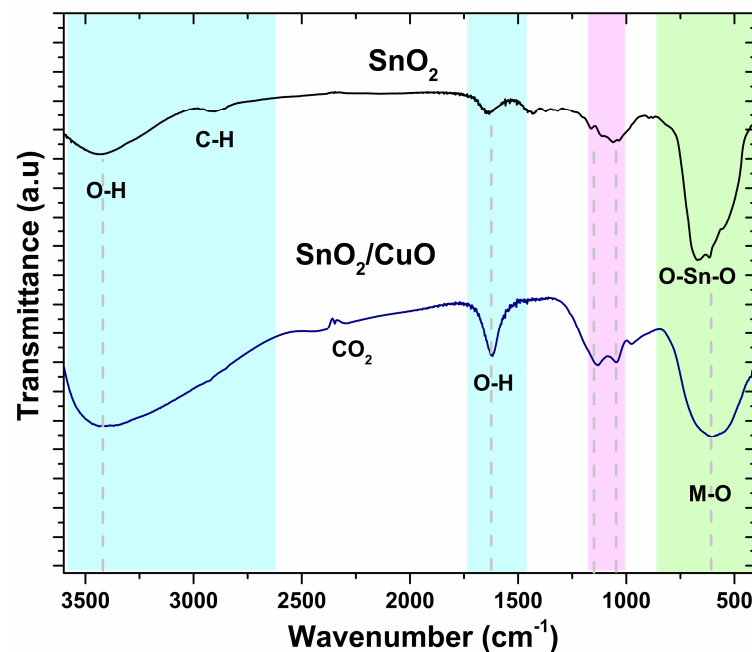


Figure 5. FTIR spectra for SnO₂ and SnO₂/CuO composites.

The large broadness of the perturbation at 2700–3580 cm^{−1} in the spectra of SnO₂/CuO suggests a rich hydrogen bonding. Moreover, two bands at 1133 cm^{−1} and 1037 cm^{−1} indicate C-O stretching vibration in the C-O-C bond [44].

The broad but intense peak around 500–800 cm^{−1} is ascribed to the M-O stretching vibration, where M represents the Sn and Cu metallic elements. It has been reported that CuO has vibrational modes close to 603 cm^{−1} and 666 cm^{−1}, respectively [43,45]. Thus, the difference in the shape of this peak, compared with the commercial SnO₂, is attributed

to the contribution of the vibration modes of each oxidized composite, confirming the successful formation of the SnO_2/CuO composite.

Raman measurements were conducted to gain insight into the vibrational modes of the structural phase and crystallographic defects. Figure 6 illustrates the Raman spectra for SnO_2 and SnO_2/CuO composites. As is reported elsewhere, the Raman signal for SnO_2 has 18 vibrational modes in the Brillouin zone. At 469 cm^{-1} , the double degenerate mode (E_g) is observed, while the Raman bands at 630 cm^{-1} and 770 cm^{-1} are assigned to the non-degenerate A_{1g} and B_{2g} modes in the rutile SnO_2 structure [46]. However, for the SnO_2/CuO composite, the Raman spectra have a different shape. The usually observed Raman active modes in SnO_2 were modified by the presence of CuO , which was mainly due to the overlapped Raman signal of the CuO compound, which usually occurs at 612 cm^{-1} (B_{2g} mode) [47]. Another peak is observed in SnO_2CuO occurring close to 1100 cm^{-1} attributed to the $2B_g$ vibrational mode. The presence of Cu species provokes the intensity reduction in the Raman signal due to increased structural defects [48].

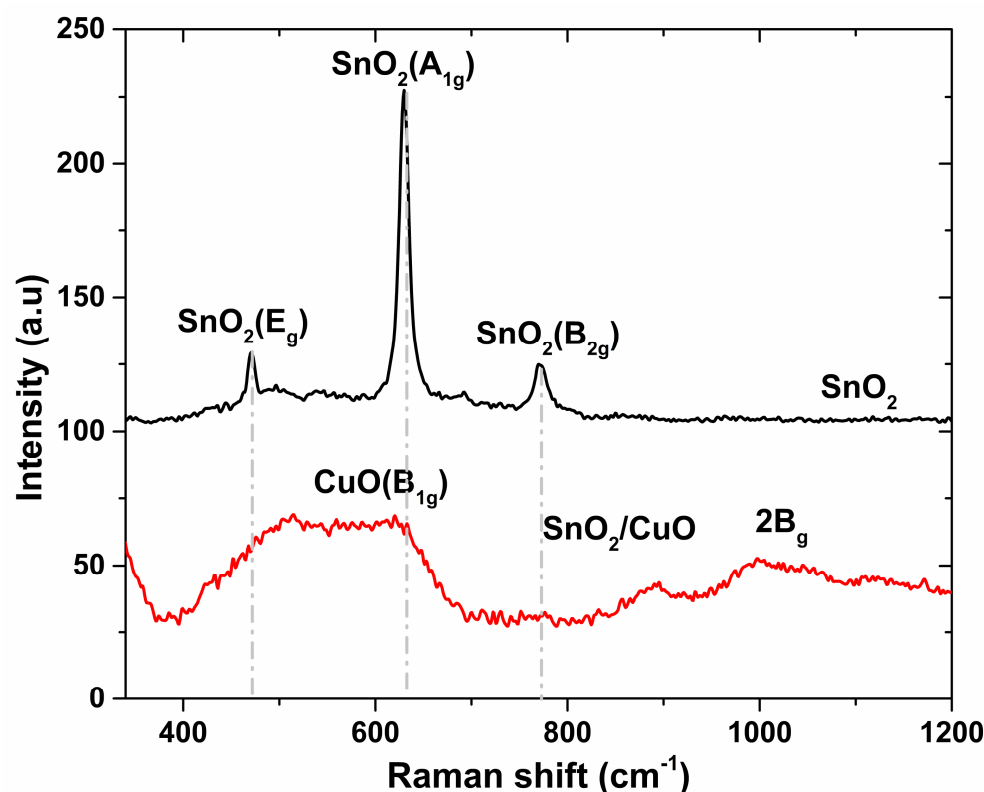


Figure 6. Raman spectra of SnO_2 and SnO_2/CuO materials.

3.2. Electrochemical Characterization

Figure 7a presents the cyclic voltammograms of the prepared electrocatalyst in N_2 purged 0.5 mol L^{-1} NaOH electrolyte. First, the electrode surface was conditioned by running 40 cycles with a scan rate of 50 mV s^{-1} in the potential windows of 0.9 to 1.6 V vs. RHE. There can be observed a surface change close to 1.48 V , which is assigned to the metal redox interconversion in alkaline media. The weak faradaic signal is due to the SC composite's high capacitive current that hinders the redox couple. This behavior has also been observed by Chuai et al. where SnO_2/CuO electrodes were studied by CV, and this electrode shows high capacitance [49]. In the case of SC, we observed an increase in current density at potential up to 1.5 V attributed to the oxygen evolution reaction on the surface of the catalyst. It should be mentioned that SC has a considerably low onset potential. Meanwhile, the SnO_2 exhibits a current density change after 1.6 V .

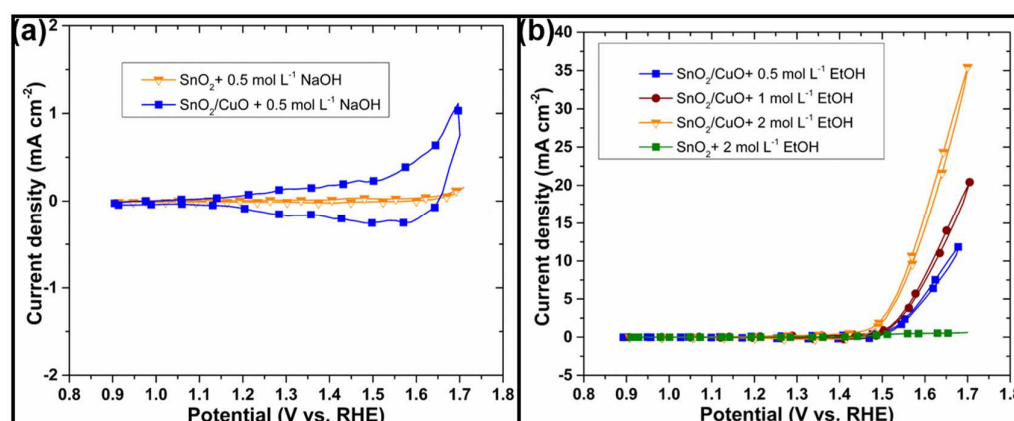


Figure 7. CV for SnO_2 and SnO_2/CuO heterostructure recorded at 20 mV s^{-1} in N_2 de-aerated $0.5 \text{ mol L}^{-1} \text{ NaOH}$. (a) In absence of ethanol; (b) in presence of ethanol.

The hybrid water splitting on SnO_2 and SC electrodes in $0.5 \text{ mol L}^{-1} \text{ NaOH}$ with different concentrations of ethanol is illustrated in Figure 7b. In the case of SnO_2 , no significant activity was observed when ethanol was added, whereas the SC heterostructure dramatically changes the current density and the overpotential in the presence of ethanol. Above 1.6 V, simultaneous EOR and OER reactions are achieved, as reported previously [50]. Actually, this composite increases its current density as the ethanol concentration increases. This confirms that the addition of organic molecules is an effective strategy to assist water splitting in an easy way. Miao observed a similar performance on RhNiFe-P/NF where the EOR and the HER were improved as the ethanol concentrations increased [51].

The SC delivers a significantly higher OER current while the commercial SnO_2 exhibits negligible current in the same window's potential. This suggests that incorporating CuO nanoparticles is responsible for the increase in EOR. The current value is similar to that reported on Ni_2MnO_8 (close to 10 mA cm^{-2} at 1.6 V) [52] but above the values recently reported on CM-ZnO , 6.0 mA cm^{-2} close to 1.6 V vs. RHE ($1.0 \text{ mol L}^{-1} \text{ EtOH} + 1 \text{ mol L}^{-1} \text{ KOH}$) [53].

It should be highlighted that no significant decrease in current density was observed under the test conditions when the ethanol concentration was increased. This is very important, because in the recently published work of López-Fernández, they observed a tendency of current decay when ethanol is increased [54]. This group claimed that this is associated with the decrease in ionic conductivity as ethanol concentration increases and because unreacted ethanol blocks the hydroxide species at the surface of the catalysts [55].

Figure 8a depicts the LSV for the OER in the presence and absence of ethanol recorded at 5 mV s^{-1} using $0.5 \text{ mol L}^{-1} \text{ NaOH}$ as a supporting electrolyte. The benefit of using ethanol to assist water electrolysis is observed even at small concentrations. In the absence of ethanol and at a potential higher than 1.6 V, the SnO_2/CuO composite shows an increase in current density ascribed to the oxygen evolution. When ethanol is added, the peak in the region of the OER dramatically changes. The current density was almost 9-fold compared with the test achieved only in the supporting electrolyte. Interestingly, the presence of ethanol does not deactivate hydrogen generation, as shown in Figure 8b. On the other hand, a chronoamperometry measurement is conducted to evaluate the stability and to mimic the practical operation of the SnO_2/CuO composite. Figure 8c displays the current versus time curve of the SnO_2/CuO composite at the potential of 1.5 V vs. RHE in the presence of 0.5 mol L^{-1} ethanol for 16 h. The initial current density reaches 0.9 mA cm^{-2} while decreasing slowly over the 5 h of measurement and then reaches a steady-state plateau of about 0.25 mA cm^{-2} by the following 11 h, thus showing that the electrocatalyst activity is stable. One can argue that the SnO_2/CuO material could undergo a rearrangement of the surface atoms, which may lead to the current decrease. It is also likely that some poisoning of the electrode surface by adsorbed hydroxyl species from electrolyte may cause

the decay in the current. Moreover, the fluctuations of the current density during the 11 h of electrolysis may be due to the difference in charge transfer kinetics. Nevertheless, the oxygen evolution reaction mechanism involves the electrochemical formation and desorption of oxygen species, which brings about the compensation between adsorbed species at the surface and reaction intermediates tending to form the final product [56]. Therefore, a surface rearrangement due to the electrochemical polarization or adsorption ability of the surface from water could provide a mutual balance to reach the required steady state. In conclusion, at the first 5 h, one can observe that when the electrode is polarized at 1.5 V vs. RHE, a decrease in the current density was observed in the course of 5 h and then attained by steady state by the following 11 h. This suggests that good stability toward the oxygen evolution reaction occurs at the SnO_2/CuO electrocatalyst.

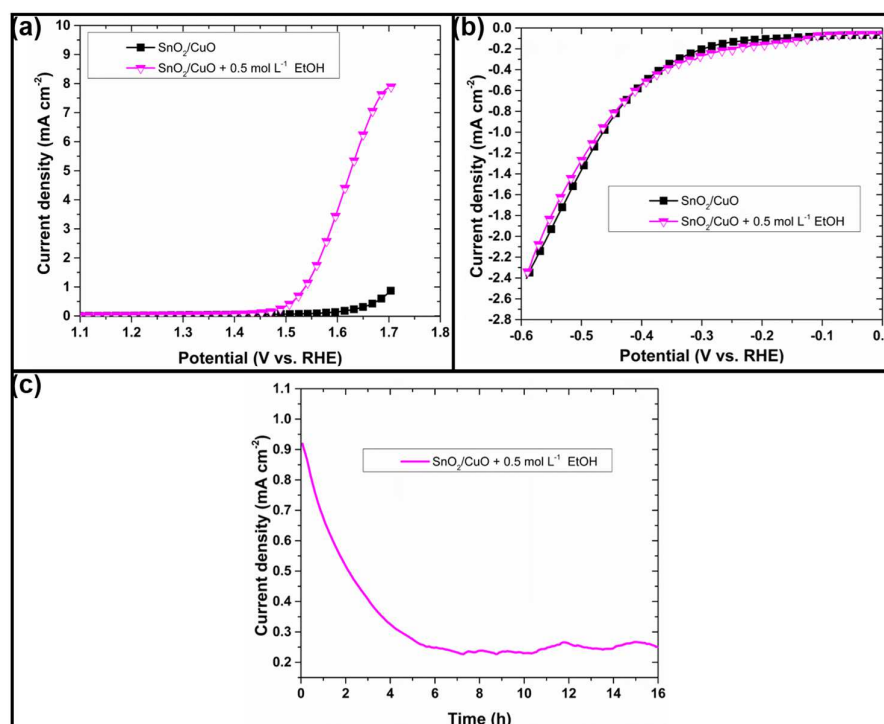


Figure 8. (a) LSV for the OER; (b) LSV for the HER, and (c) Chronoamperometry.

To examine the behavior of the SnO_2 and SnO_2/CuO nanocomposite, the EIS analyses were conducted at 1.5 V vs. RHE as complementary measurements shown in Figure 9. The EIS data were fitted with a characteristic EEC to an electron transfer reaction, which is presented (inset Figure 9a) by one capacitive loop, as indicated by R_s (cell resistance including the electrode connections and the electrolyte), R_1 (film resistance), and R_2 (charge transfer resistance for OER). In addition, C_{p1} and C_{p2} represent the constant phase elements (CPEs) for film resistance and charge transfer resistance, respectively, which take electrode roughness and heterogeneity into account. The electrochemical parameters were extracted by fitting the experimental EIS data with an equivalent circuit and listed in Table 1. Note that the CPE is assigned by pure capacitance when the α is equal to 1. As listed in Table 1, the α_2 values in our experiments decrease from 0.95 to 0.90 for SnO_2 and SnO_2/CuO , respectively, which is due to the difference of the heterogeneity and surface roughness of the electrode surfaces. In addition, the R_s values are noted between 2.0 and 2.1, suggesting that the catalyst contribution to the resistance is low and the electrical connections and electrolyte behavior are reproducible. Moreover, the charge transfer resistance values for SnO_2 and SnO_2/CuO were 891.9 and 203 $\Omega \text{ cm}^2$, respectively, revealing that charge transfer occurs more easily on the SnO_2/CuO electrode surface toward OER in the presence of ethanol. In parallel, the capacitance (C_{p2}) values increase from 0.23×10^{-3} to 6.88×10^{-3} .

for SnO₂ and SnO₂/CuO, respectively, indicating a superior efficiency for the charge storage at the SnO₂/CuO electrolyte interface. This suggests that incorporating CuO nanoparticles in the SnO₂-based material increases the activity of the electrocatalyst toward OER.

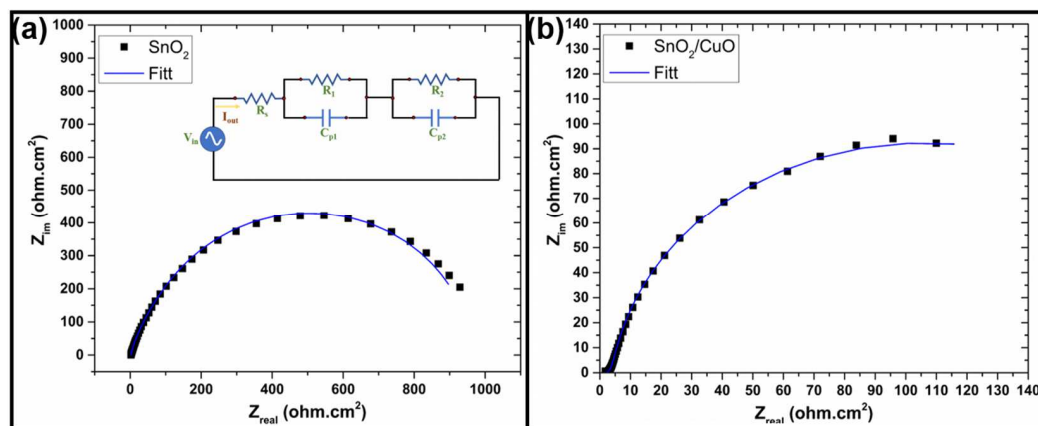


Figure 9. Nyquist plots for (a) SnO₂ and (b) SnO₂/CuO nanocomposites measured at 1.5 V vs. RHE from 100 kHz to 0.1 Hz in 0.5 mol L^{−1} NaOH + 1.0 mol L^{−1} EtOH during the OER. Solid curves indicate the fitting of experimental impedance data using the presented equivalent circuit inset.

Table 1. Parameters obtained by fitting EIS experimental spectra for SnO₂ and SnO₂/CuO nanocomposites in 0.5 mol L^{−1} NaOH + 1.0 mol L^{−1} EtOH during the OER.

Catalyst	Potential E (V vs. RHE)	R _s (Ω cm ²)	R ₁ (Ω cm ²)	Q _{CPE1, film} (F s ^(α₁−1) cm ²)	α ₁	R ₂ (Ω cm ²)	Q _{CPE2} (F s ^(α₂−1) cm ²)	α ₂
SnO ₂	1.5	2.034	71.75	0.72 × 10 ^{−3}	0.831	891.9	0.23 × 10 ^{−3}	0.95
SnO ₂ CuO	1.5	2.179	2.91	48.56 × 10 ^{−3}	0.463	203	6.88 × 10 ^{−3}	0.90

4. Discussion

The advantage of the synthesis method is that the structural and morphological properties can be easily tuned by adjusting the ratio of ethylene glycol: water in the solvent and the microwave irradiation time. For example, in previous work, our research group fabricated ZnOCu nanocomposites in a two-step process using an ethylene glycol-rich solvent that favors the growth of metallic Cu clusters [57].

The electrochemical measurements reveal that the SnO₂/CuO composite is electroactive for ethanol-assisted water electrolysis. An interesting result was the compound's ability to manage more current densities as the ethanol concentration increased. This is important because other materials tend to reduce their activity due to the strong intermediaries adsorption, reducing the active area for replenishing electroactive species. The better performance of the SnO₂/CuO for the assisted water electrolysis is mainly attributed to the synergistic effect between the SnO₂ and CuO that drastically reduces the charge transfer resistance. On the other hand, although the proposed composite is very simple with limited capacity to achieve water electrolysis at low overpotentials, this can be used as co-catalysis to produce valuable by-products from the oxidation of organic molecules such as acetic acid, acetaldehyde, and others. Moreover, it can support many engineering applications, such as sensors and energy conversion devices. Finally, Table 2 compares the SnO₂/CuO and similar materials reported in the literature. It can be seen that the developed composite has comparable performance for assisted water electrolysis with some of the reported ones.

Table 2. Comparative performances of OER from synthesized SnO₂/CuO electrocatalyst and the electrode materials reported in the literature.

Catalyst	Scan Rate	Current Density	Electrolyte	Reference
CM-ZnO	50 mV s ^{−1}	10 mA cm ^{−2} at 1.7 V vs. RHE	2 mol L ^{−1} C ₂ H ₅ OH + 1 mol L ^{−1} KOH	[53]
Cu ₂ O/PPY/CPE	50 mV s ^{−1}	10 mA cm ^{−2} at 1.7 V vs. RHE	5 mol L ^{−1} C ₂ H ₅ OH + 0.1 mol L ^{−1} KOH	[58]
ZnOCu	20 mV s ^{−1}	10 mA cm ^{−2} at 1.56 V vs. RHE	0.5 mol L ^{−1} C ₂ H ₅ OH + 0.5 mol L ^{−1} KOH	[57]
Ni ₆ MnO ₈	50 mV s ^{−1}	10 mA cm ^{−2} at 1.6 V vs. RHE	1 mol L ^{−1} C ₂ H ₅ OH + 1 mol L ^{−1} KOH	[52]
SnO ₂ /CuO	20 mV s ^{−1}	10 mA cm ^{−2} at 1.62 V vs. RHE	1 mol L ^{−1} C ₂ H ₅ OH + 0.5 mol L ^{−1} NaOH	This work

5. Conclusions

Here, we demonstrate the facile approach to preparing SnO₂/CuO nanoheterostructures as effective electrocatalysts for hybrid water splitting. The XRD study confirmed the successful reduction of the chemical precursors forming oxidized composites. Furthermore, the XRD analysis shows that the composite has a very small crystallite size of 3.5 nm. The Raman and FTIR spectra confirm the successful reduction of SnO₂ and CuO. The electrochemical measurements toward the hybrid water splitting in the presence of ethanol show that the SnO₂/CuO composite is active for the assisted oxygen evolution reaction, having a big difference from the commercial SnO₂ compound.

Thus, this work provides a feasible pathway to design free noble-metal electrocatalysts using simple and low-cost equipment. Furthermore, the adopted synthesis method is scalable and can be used to produce advanced composites. This is important because the recent scientific reports in the field of materials proposed implementing a complex synthesis method in which, in some cases, more than three consecutive syntheses need to be made. In addition, several of them use sophisticated equipment and non-scalable synthesis.

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