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Facial Eco-Friendly Synthesis of Copper Oxide Nanoparticles Using Chia Seeds Extract and Evaluation of Its Electrochemical Activity

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Abstract: In the current study, copper oxide nanoparticles (CuO NPs) were synthesized using chia seed extract in a simple, rapid, and eco-friendly manner for the first time. The synthesized CuO NPs were characterized using different analytical techniques. The images of field emission scanning electron microscopy revealed that the CuO NPs were triangular and pyramid in structure, with a mean particle size of 61.5 nm. The absorption peak of the synthesized CuO NPs was measured using ultraviolet-visible spectroscopy and was recorded at a wavelength of 291 nm. The results of energy-dispersive X-ray analysis confirmed that the CuO NPs synthesized using chia seed extract yielded high-purity CuO NPs. Moreover, the X-ray diffraction analysis indicated the highly crystalline nature of the CuO NPs, and the X-ray photoelectron spectroscopy results indicated that the CuO NPs were prepared successfully. Additionally, electrochemical impedance spectroscopy measurements revealed excellent electrocatalytic conductivity and fast electron transfer at the electrode/electrolyte interface of the synthesized CuO NP-modified glassy carbon electrode.

Keywords: green synthesis; CuO nanoparticles; chia extract; metal oxide; characterization

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1. Introduction

In recent decades, nanoscale materials (1–100 nm) have been utilized for a diverse range of applications owing to their distinctive chemical, mechanical and electrochemical properties, which clearly distinguish these materials from those with large molecules [1–4]. Metal oxide nanoparticles (MONPs) such as TiO_2, ZnO, NiO, Fe_2O_3, and CuO have been applied in the biological, medical, and environmental fields [5–10]. Therefore, different chemical and physical methodologies have been developed to prepare them. Such synthetic methods have, however, generated other challenges for scientific communities, as they are time-consuming and expensive; moreover, they also involve the release of toxic reagents into the environment, causing significant pollution [11–14]. Therefore, to mitigate these issues, researchers have focused on employing alternative eco-friendly approaches, such as the usage of plant extracts or microorganisms, to synthesize MONPs [15–21].

Copper oxide NPs (CuO NPs) are regarded as unique and inexpensive MONPs. They have a small bandgap (~1.7 eV) and high surface area, in addition to exhibiting high catalytic activity [2,22]. Consequently, they are widely used in the environmental, industrial, medical, chemical, and physical fields [19,23,24]. For example, they are employed as catalysts and antimicrobial agents; they are also used in solar energy systems, electrochemical and gas sensors, and for water purification [25–27].

Nevertheless, several chemical methods have been investigated to synthesize CuO NPs using toxic and corrosive reducing agents such as ethylene glycol, hydrazine, and sodium tartrate [28,29]. In addition, microorganisms, e.g., yeast, bacteria, and fungi have been utilized to prepare CuO NPs in the literature [30,31]. To date, there has been an increase in reports on the synthesis of CuO NPs using plant extracts such as *Gloriosa superba* L., Aloe Vera leaf, coffee powder, and fruit peel extract [23,32–34]. Thus, green synthetic

CuO NPs using plant extracts are considered a good alternative to hazard reagents, high costs, and time-consuming methods.

This is, to our knowledge, the first study on the synthesis of CuO NPs using chia seed extract, which reports it as a safe, efficient, rapid, and eco-friendly method. Chia (*Salvia hispanica* L.) is a member of the Lamiaceae family, typical of an annual herbaceous plant. Further, it is well-known worldwide owing to its medicinal properties and significant benefits to human health. It is considered a rich source of dietary fiber, oil, and omega-3-linolenic acid. However, the natural antioxidants, such as flavonoids, phenolic compounds, caffeic acid, kaempferol, and chlorogenic acid [16] as shown in Figure 1, contained in chia seeds extract play an important role in the synthesis of these CuO NPs; specifically, they help eliminate any toxic reagents and are inexpensive. These compounds also act as capping and reducing agents to successfully reduce copper ions to CuO NPs in a facile manner. Therefore, the aim of this work is to synthesize CuO NPs using a simple, eco-friendly route and perform chemical and electrochemical characterizations of the synthesized nanoparticles.

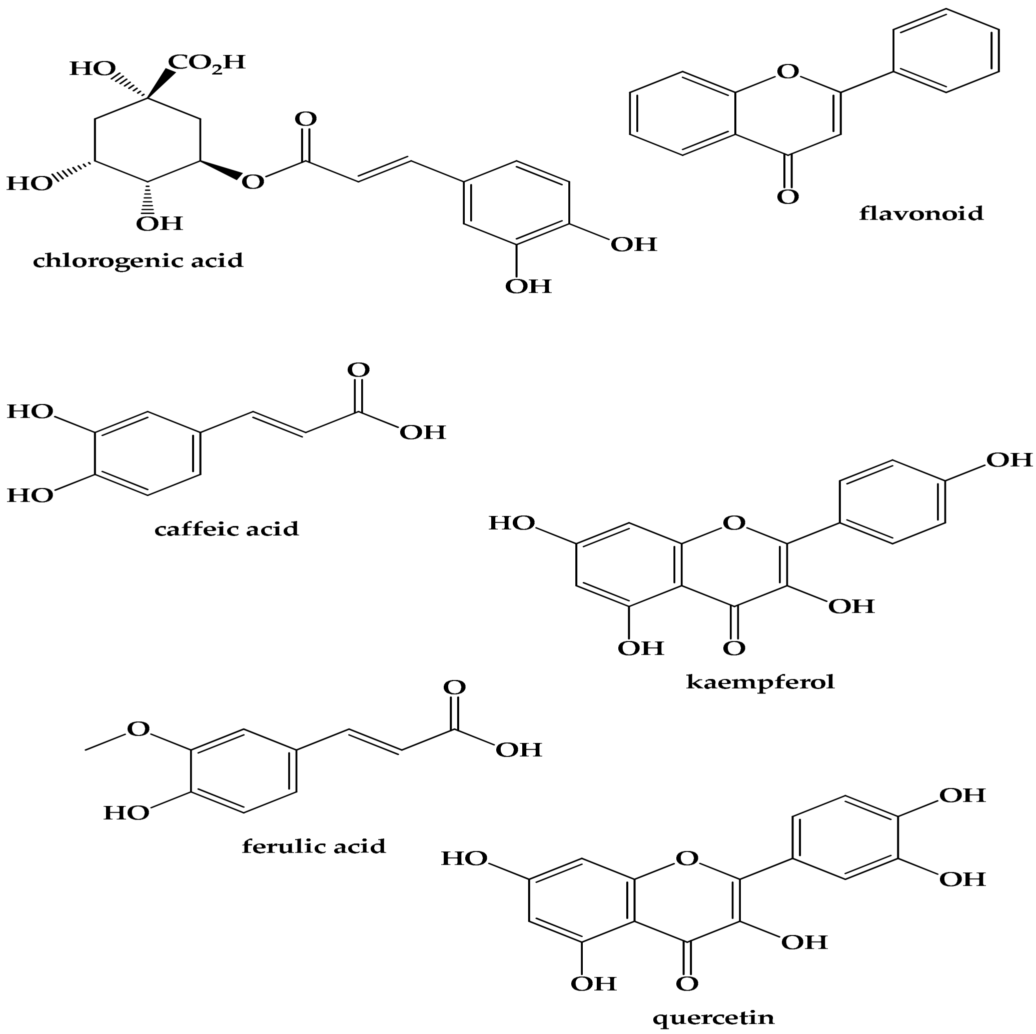

Figure 1. The chemical structure of some antioxidant compounds in chia seed extract.

2. Experimental

2.1. Materials and Preparation of Seed Extracts

Copper chloride ($CuCl_2.2H_2O$) was purchased from Sigma Aldrich Chemicals Ltd. and used as received; additionally, double-distilled water was used in this study. Chia seeds (*Salvia hispanica* L.) were purchased from a local market and first washed using tap water. Then, they were washed using double-distilled water to remove dust particles and impurities. They were subsequently dried under ambient conditions for three days. The seed extract was prepared by mixing 5 g of dried seeds with 100 mL of double-distilled water and boiling at 50 °C for 20 min. The seed extract was filtered and retained for further experiments.

2.2. Green Synthesis of the CuO NPs

$CuCl_2.2H_2O$ (10 g) was dissolved in double-distilled water (100 mL) in a flask. The solution was then boiled on a hot plate for 5 min at 30 °C. Then, 20 mL of the seed extract was added to the salt solution, along with vigorous stirring. The solution color changed from light green to dark brownish during the reaction, indicating the formation of CuO NPs. Then, the solution was centrifuged at 15000 rpm for 20 min. The synthesized CuO NPs were washed several times with double-distilled water and dried for 12 h in the oven at 80 °C. After that, the dried NPs were annealed in a muffle furnace at 300 °C for 3 h [21] to achieve stable CuO NPs. Finally, the synthesized CuO NPs were stored in a glass vial for characterization.

2.3. Characterization of the Synthesized CuO NPs

The morphological study and elemental composition of the synthesized CuO NPs were examined using field emission scanning electron microscopy (JSM-7100F FESEM JEOL USA) and energy-dispersive X-ray (EDX) analysis. The X-ray diffraction (XRD) patterns of the powdered CuO NPs were accomplished using a Scanting XDS 2000 diffractometer equipped with a Cu Kα radiation source. The absorption band of the synthesized CuO NPs was obtained using an ultraviolet-visible-near infrared (UV-vis-NIR) spectrometer (Lambda 750, Perkin Elmer) in the wavelength range of 200–800 nm. X-ray photoelectron spectroscopy (XPS) analysis was performed using a PHI 5000VersaProbeII, ULVAC-PHI Inc. instrument. Electrochemical impedance spectroscopy (EIS) was performed at 25 °C using an SP-200 potentiostat/galvanostat (Bio-Logic Science Instruments, France) equipped with EC-Lab software for data analysis. Three electrodes were utilized, including a glassy carbon (GC) electrode or the synthesized CuO NP-modified GC electrode as the working electrode, an Ag/AgCl electrode (saturated KCl) as the reference electrode, and a Pt electrode as the counter-electrode. The Nyquist plots were recorded in 0.1 mol L^{-1} KCl containing 2 mmol L^{-1} $[Fe(CN)_6]^{3-/4-}$, at the open-circuit potential over a frequency range of 0.1 Hz to 100 kHz under an AC amplitude of 10 mV.

3. Results and Discussion

3.1. Study of the Morphology of CuO NPs

The surface morphology of the synthesized CuO NPs using chia seed extract was analyzed using FESEM, as shown in Figure 2. The FESEM images (Figure 2a–d) clearly show a well-defined triangular pyramid shape with different sizes of the synthesized CuO NPs. It is also evident that the CuO NPs agglomerate at low and high magnifications. Overall, the average particle size of the CuO NPs synthesized using chia seed extract was approximately 61.5 nm.

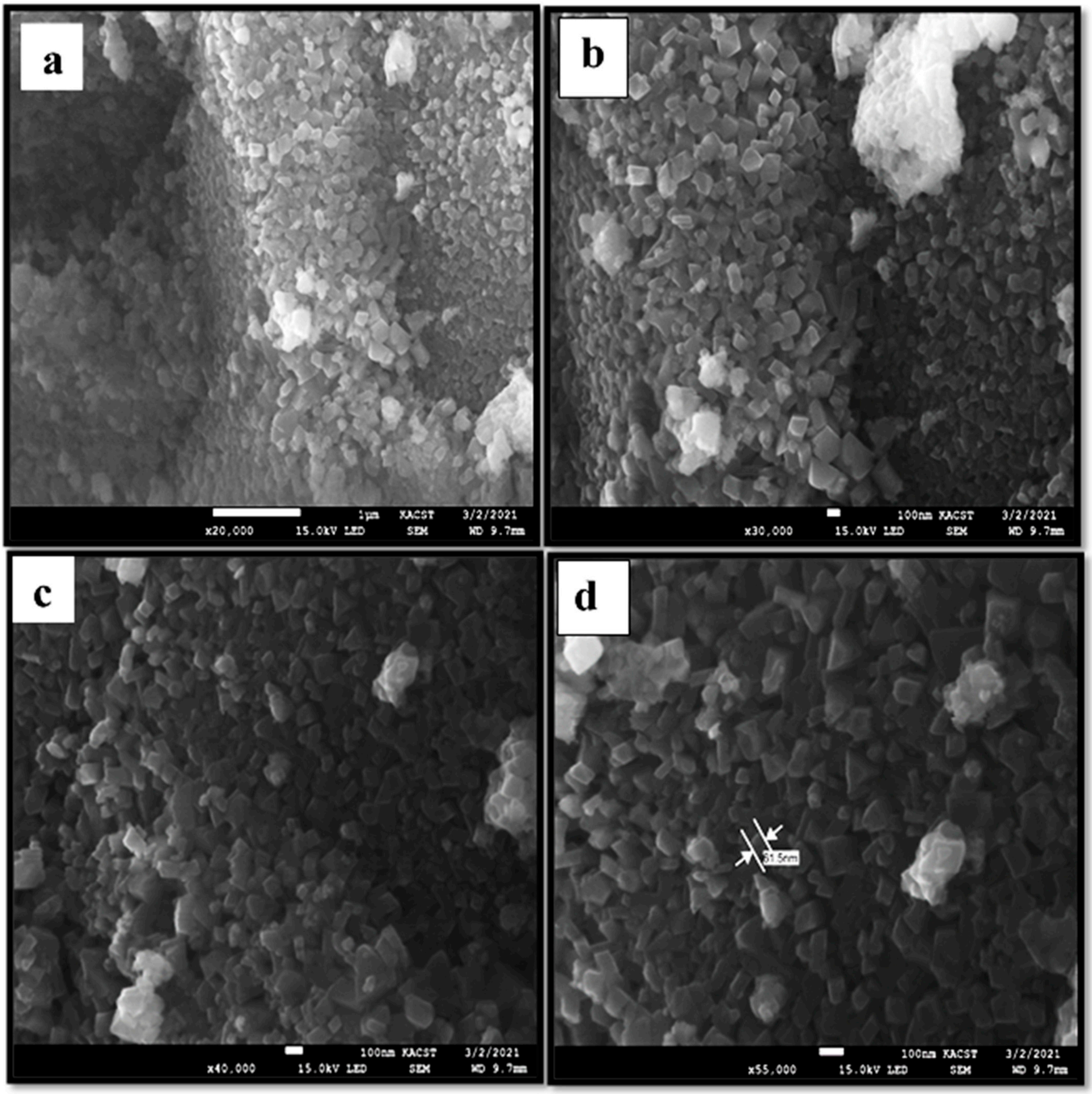

Figure 2. FESEM images of the synthesized CuO NPs at different magnifications.

3.2. EDX Spectrum

EDX analysis of the synthesized CuO NPs was used to confirm their elemental composition and purity (Figure 3). The copper peaks centered on 1 keV and 8 keV and the oxygen peak centered on 0.5 keV [21], as shown in Figure 3. The weight present compositions of Cu and O were 79.9% and 20.1%, respectively. The EDX spectrum revealed the high purity of the synthesized CuO NPs.

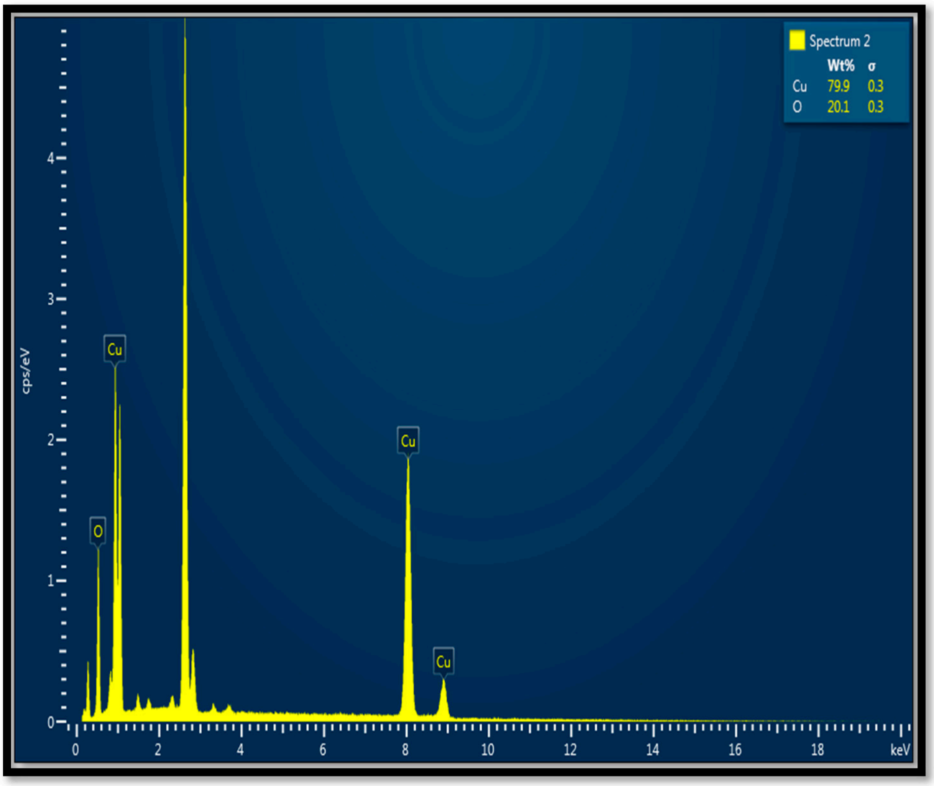

Figure 3. EDX spectrum of the synthesized CuO NPs.

3.3. X-ray Diffraction (XRD)

Figure 4a,b displays the XRD analysis of the experimental synthesized CuO NPs using chia seed extract and a comparison with its simulation data. According to the XRD pattern, there are significant diffraction peaks at 2θ (32.4°, 35.5°, 38.6°, 48.7°, 53.4°, 58.1°, 61.2°, 65.9°, 67.6°, 72.2°, and 74.7°), which correspond to (1 1 0) (1 1 1), (1 1 1), (2 0 2), (0 2 0), (2 0 2), (1 1 3), (0 2 2), (2 2 0), (3 1 2) and (2 0 3) planes. These diffraction peaks are interrelated with the Joint Committee on Powder Diffraction Standards (JCPDS) database. Further, from the distinct sharp peaks in the CuO NPs spectrum, the average crystalline size was estimated from Debye Scherer's equation and found to be approximately 46−55 nm. Comparing the experimental synthesis of CuO NPs to the respect simulation data, there is no variation in peak positions. These results demonstrate that the CuO NPs were free of any impurities. Additionally, the results indicate the successful preparation of the monoclinic CuO NPs using chia seed extract, and the highly crystalline nature of the prepared NPs [21].

3.4. UV-Vis Analysis:

The UV-vis spectrum was obtained in the wavelength range of 200–800 nm (Figure 5). During the chemical reaction between chia seed extract and copper chloride salt, the color changed from light green to dark brownish, indicating that the reaction was successful. This result was further confirmed by the distinct broad peak at approximately 291 nm [20], indicating the formation of CuO NPs. Moreover, as reported in the literature [16,35], the absorbance of chia seed extract and copper chloride salt were recorded in the range 400−450 nm and 235 nm, respectively.

However, the mechanism of the formation of and reduction in CuO NPs could be attributed to the ability of free radicals in flavonoids, phenolic compounds, and chlorogenic acid in chia seeds extract, to reduce copper ions to CuO NPs. These organic compounds also might act as capping and stabilizing agents, which play a role in the crystalline growth of CuO NPs into a well-defined triangular pyramid shape [16].

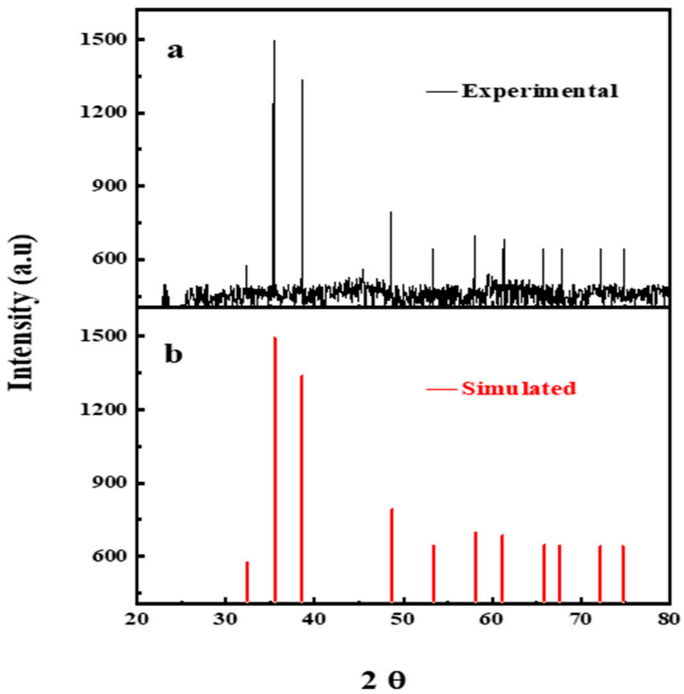

Figure 4. XRD spectrum of (**a**) of the synthesized CuO NPs experimentally and (**b**) in comparison with the simulated peaks.

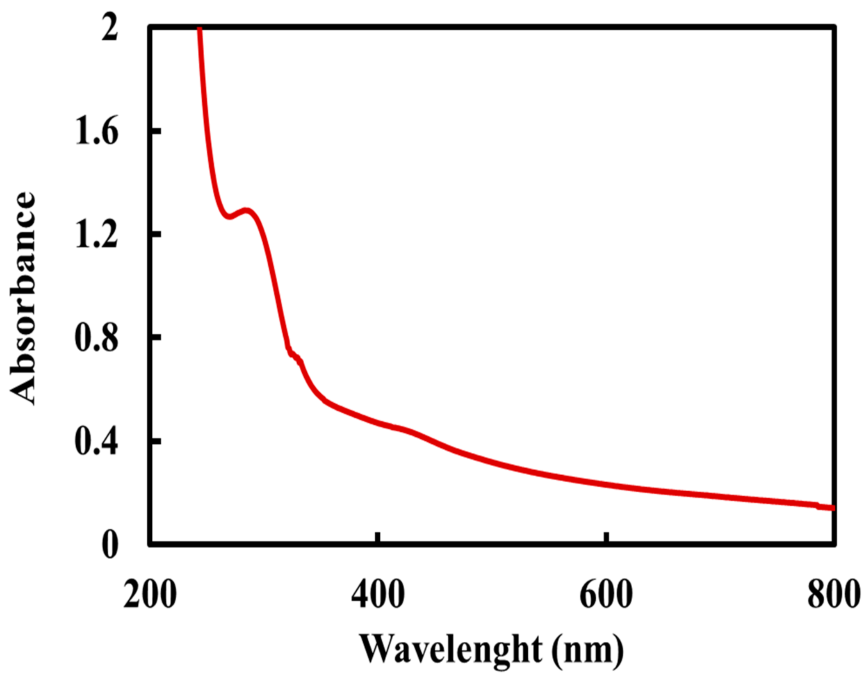

Figure 5. UV-vis absorption spectrum of the synthesized CuO NPs.

3.5. X-ray Photoelectron Spectroscopy (XPS)

XPS analysis was utilized to identify the elemental composition of the synthesized CuO NPs. Figure 6a,b shows their XPS spectra. The spectra were calibrated considering the binding energy (BE) of 284.5 eV for a C 1s electron. According to the XPS spectra, the BEs of 938.5 and 957.5 eV match Cu $2p_{3/2}$ and Cu $2p_{1/2}$, respectively, and the BE at 535 eV match O 1s [36,37]. This result revealed that the synthesized material obtained comprises pure CuO NPs without any impurities, and the EDX results were in good agreement.

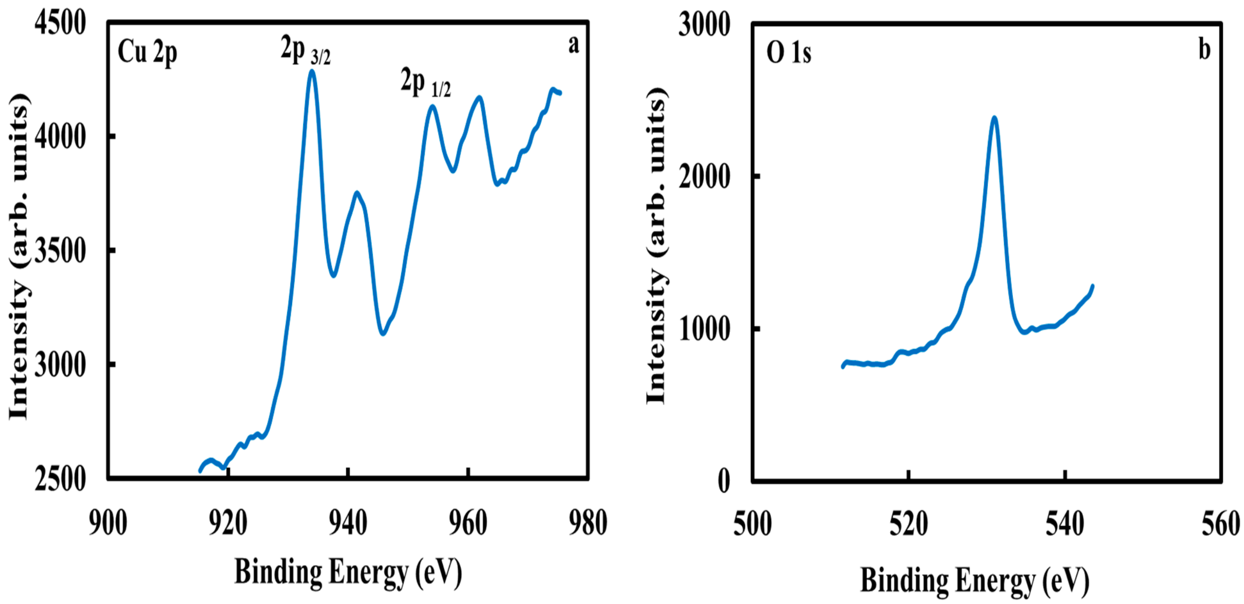

Figure 6. (**a**,**b**) XPS spectra of the synthesized CuO NPs.

3.6. Electrochemical Impedance Spectroscopy (EIS):

Figure 7 shows the EIS spectra of the bare GC electrode and the synthesized CuO NP-modified GC electrode. As depicted in the Nyquist plot form, there was a decrease in the semi-circular region's diameter after modification of the GC electrode with the synthesized CuO NPs, as compared with that of the bare GC electrode. The lower charge transfer resistance of the synthesized CuO NP-modified GC electrode enhanced the electrical conductivity and electron transfer at the electrode/electrolyte interface. Therefore, this result indicates that the synthesized CuO NPs may be utilized as electrochemical sensors.

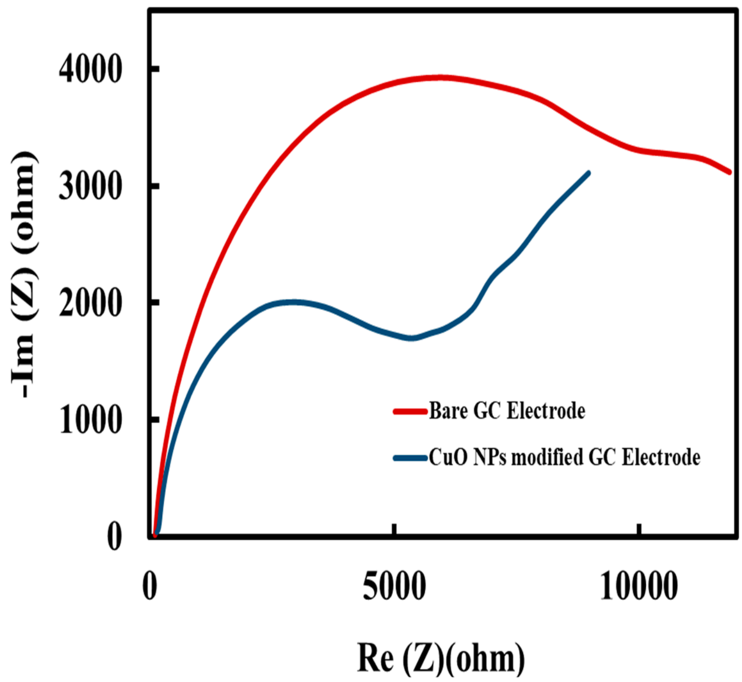

Figure 7. Nyquist plot of bare GC and the synthesized CuO NPs modified GC electrode, respectively.

4. Conclusions

In this study, CuO NPs were successfully synthesized using chia seed extract through an eco-friendly approach. The synthesized CuO NPs were characterized using FESEM, EDX, UV-vis spectroscopy, XRD, and XPS. The advantages of this work lie in the simple, fast, efficient, and eco-friendly synthesis of the CuO NPs using an aqueous extract of chia seeds, without the use of any hazardous reagents or tedious and expensive methods. The antioxidant compounds present in chia seeds extract acted as reducing and capping agents in the synthesis of the CuO NPs. The characterization outcomes show that the prepared CuO NPs were crystalline in nature, exhibited good electrical conductivity, and were high-purity MONPs. Additionally, the average synthesized nanoparticles' size was found to be 61.5 nm. Thus, the green CuO synthesized using chia seed extract could have potential for application in electrochemical sensing, as well as other environmental and antimicrobial applications.

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