ABSTRACT: Nonphotocatalytic water splitting through oxygen-deficient, mesoporous metal oxide design-based hydroelectric cells (HECs) is a well-known phenomenon. To exploit more power from HECs, a metal oxide with more oxygen deficiency is desirable. In this study, oxygen-deficient mesoporous SnO₂ via a sol–gel method and its composites with reduced graphene oxide (rGO) have been presented. Raman spectra of SnO₂-rGO nanocomposites revealed an increase in the oxygen vacancies, while the X-ray diffraction (XRD) pattern confirmed the strain formation in the nanocomposite lattice owing to defect formation. The X-ray photoemission spectroscopy (XPS) results also indicated the presence of oxygen vacancies on the surface of SnO₂, whereas Brunauer–Emmett–Teller (BET) measurements revealed that adding rGO into SnO₂ increased the surface area from 44.54 to 84.00 m² g⁻¹. The water molecules are chemidissociated on the oxygen-deficient mesoporous surface of the pellet followed by physiodissociation at the mesopores. The redox reaction of the dissociated ions at the Zn anode and the Ag inert cathode produces current in the outer circuit. Interestingly, adding few drops of water into a SnO₂-rGO-based HEC resulted in a short-circuit current of 148 mA with an open-cell voltage of 1.0 V. The maximum power delivered by the SnO₂-rGO-based HEC is 148 mW. The addition of rGO into SnO₂ boosts the peak current remarkably from 68 to 148 mA, which is the highest reported current generated by a hydroelectric cell.

INTRODUCTION

Oxide materials have gained popularity in recent years due to their high chemical stability and ease of processing.¹⁻³ Porous ceramic materials are widely used for a variety of applications in both research and industry. Because of their extensive properties such as high structural integrity, good thermal capacity, and harsh environmental stability, oxide-based porous ceramic humidity sensors have been known to provide a better response than polymer-based sensors.⁴ The important feature of a porous oxide ceramic material is that water molecules can easily pass through the pores, and vacancies result in a more effective surface area.⁵ Oxygen vacancies act as trapping centers for electrons and holes that define the physicochemical properties of oxide materials. Recently, defects like oxygen vacancies and porosity in a variety of metal oxides have been used to generate green electricity via water molecule dissociation in a hydroelectric cell (HEC) without the use of any electrolyte/light/alkali/temperature.⁶,⁷ In comparison with other metal oxides, tin oxide (SnO₂) has been studied extensively for applications such as catalytic breakdown, gas sensing, and organic molecule detection. These applications take advantage of the intrinsically defective chemical structure of tin oxide.⁸ Its use in industry is encouraged by its relative abundance, cheap cost availability, environmental friendliness, faster response time, and improved chemical stability. Tin oxide has been successfully employed in a range of modern applications due to its intrinsic defects, low electrical resistance, great optical transparency, and tunable valency of the tin cation.⁹⁻¹³ The use of oxygen-deficient SnO₂ in the form of green power generation using a hydroelectric cell (HEC) technology was recently reported.⁷ At ambient temperature, the device adsors water molecules on defective surfaces and spontaneously chemidissociates them into H⁺ and OH⁻ ions. Nanopores in the cell operate as trapping sites for hopping protons, generating a high electric field inside the nanopore and allowing physisorbed water molecules to split for a long time.⁶,¹⁴ Surface defect states including oxygen vacancies, interstitials, and unsaturated surface bonds have been found to increase active sites for water molecule attraction and chemidissociation reactions. Metal ion doping has been discovered to be particularly successful in increasing defect concentration, which has improved the current generation of SnO₂-based HEC. Apart from this, several
carbon-based nanomaterials are also used to enhance the electrical properties of SnO$_2$.\textsuperscript{15}

The importance of graphene-based metal oxide nanocomposites in science and technology is immense, and it holds enormous promise for energy conversion devices. Mixing SnO$_2$ with rGO improves adsorption by introducing grain boundaries, interfaces, and surface imperfections. Several articles on the production and use of SnO$_2$-rGO nanocomposites have been published to date. According to Gui, the presence of the oxygen vacancy enhances gas sensing performance toward NO$_2$ in the SnO$_2$/rGO heterostructure at room temperature.\textsuperscript{16} Using a simple hydrothermal process, Van Tuan et al. demonstrated that SnO$_2$/rGO nanocomposites have significantly improved photocatalytic capabilities.\textsuperscript{17}

In the present study, SnO$_2$-rGO nanocomposites have been studied first time in the context of hydroelectric cells. We have synthesized SnO$_2$ and SnO$_2$-rGO nanocomposites using a simple and convenient sol–gel approach. To increase the conductivity as well as the electric power output of SnO$_2$-rGO is added. This research suggests SnO$_2$-rGO nanocomposite as a potential candidate for green energy production through a hydroelectric cell.

### EXPERIMENTAL SECTION

**Material Used.** Graphite fine powder (98%), stannous chloride dihydrate (SnCl$_2$·2H$_2$O), ethylene glycol (C$_2$H$_4$O$_2$), citric acid (C$_6$H$_8$O$_7$), sulfuric acid, dilute hydrogen chloride, hydrogen peroxide (extra pure, 30% w/v, H$_2$O$_2$), potassium permanganate, hydrazine monohydrate, absolute ethanol (99.9%, CH$_3$CH$_2$OH), and sodium hydroxide were used for the synthesis. All of the compounds were of analytical grade and were utilized exactly as received. In the synthesis, deionized (DI) water was employed.
Figure 2. (a) Rietveld analysis of SnO₂ nanoparticles; (b) room-temperature X-ray diffraction patterns of SnO₂, GO, rGO, and SnO₂-rGO nanocomposites; and (c–e) structural model of SnO₂.

**Synthesis of GO.** Graphene oxide was made using a modified Hummer’s technique. Natural graphite powder (2 g) was mixed with concentrated H₂SO₄ (90 mL) in a beaker, which was agitated and chilled to 5 °C in an ice–water bath for 2 h. KMnO₄ (9 g) was progressively added to the graphitic solution at a temperature below 20 °C, then heated at 35 °C for 4 h while stirring. The mixture was stirred for 30 min at 98 °C after being diluted with DI water (200 mL). The reaction was stopped by adding a 30% H₂O₂ solution at a temperature below 20 °C. The solution was then stirred for 3 h at 70 °C under constant stirring. The nitrogen adsorption–desorption isotherm was recorded via the Brunauer–Emmett–Teller (BET) technique. The nitrogen adsorption–desorption isotherm was recorded via the Brunauer–Emmett–Teller (BET) technique. Raman spectra from a laser Raman spectrometer (Wi Tec alpha 300 RA) at a laser excitation wavelength of 532 nm were used to confirm the purity of the samples. X-ray photoelectron spectroscopy (XPS) at room temperature was used to analyze the chemical states of the elements and oxygen vacancies in synthesized samples. Surface morphology, elemental mapping, and particle size measurements were completed using field emission scanning electron microscopy (FESEM JEOL), scanning electron microscopy (SEM JSM6390LV), and transmission electron microscopy (JEM-1400 TEM), respectively. The nitrogen adsorption–desorption isotherm was recorded via the Brunauer–Emmett–Teller (BET) technique (Quantachrome) used to assess the pore size distribution, surface area, and pore volume. A hydraulic press machine was used to compress the produced powders into 2.0 × 2.0 cm² pellets (6 ton pressure). One side of the pellet was painted in a comb pattern with conducting silver paste, and the other side was covered with a 0.3 mm thick anode zinc plate. By adjusting external loads, a pulse source meter (Keithley-2400) was utilized to depict V–I polarization properties of the fabricated cell. The Nyquist plot of wet cells was accomplished using a CHI760E Electrochemical workstation within a frequency range of 0.1 to 10⁵ Hz.

**RESULTS AND DISCUSSION**

**Structural Characterization.** The components and crystalline phase of as-prepared SnO₂ and SnO₂-rGO nanocomposites are investigated using XRD. The obtained
diffraction pattern has been found in good agreement with JCPSD file no. 41-1445 for the rutile phase of tetragonal SnO₂ structure with space group P4₁/mmm. No distinctive peaks of additional contaminants were identified in the XRD pattern of SnO₂-rGO nanoparticles. FULLPROF suite software was used to perform Rietveld refinement of the X-ray data of the SnO₂ sample. Figure 2a delineates the Rietveld refinement of X-ray diffraction at room temperature for the SnO₂ sample. The lattice parameters of the unit cell a = b = 4.756 Å, c = 3.194 Å, and the volume of the unit cell V = 72.256 Å³ for pure SnO₂ were found to be in good agreement with the literature using Rietveld refinement. Six atoms make up the unit cell. As illustrated in Figure 2c–e, each tin Sn⁴⁺ ion is in the center of an extremely regular octahedron created by six oxygen ions, while each O²⁻ is surrounded by three Sn⁴⁺ positioned at the vertices of an isosceles triangle. The XRD patterns in Figure 2b of as-prepared SnO₂ and SnO₂-rGO nanocomposites are observed to be similar, with diffraction peak intensities decreasing, showing strain in the SnO₂ lattice caused by electrostatic interaction between the rGO sheet and SnO₂ nanoparticles.²³−²⁵

According to Debye Scherrer’s formula,²⁶ the average crystallite size (D) of our compound was calculated from the full-width at half maximum (FWHM) of the most prominent peak (110).

Debye Scherrer’s formula is given as

$$D = \frac{0.9\lambda}{\beta \cos \theta}$$

where λ is the X-ray wavelength (λ = 0.154 nm), β is the full-width at half maximum (FWHM) intensity, and θ is the diffraction angle.

For lattice strain²⁷

$$\varepsilon = \frac{\beta_{\text{ad}}}{4} \tan \theta$$

where ε is the strain, β_{ad} is the FWHM of the most intense (110) peak, and θ is the Bragg angle.

It can be seen that the peaks of pure SnO₂ are narrower than that of SnO₂ nanocrystals in the SnO₂-rGO composite, indicating the high crystallinity and larger crystal size of pristine SnO₂. It has been proved that the presence of rGO can modify the growth of SnO₂ grains.²⁸ Due to the confinement effect of the graphene sheet, the particle size of SnO₂ in the SnO₂-rGO composite is much smaller than that of pure SnO₂.²⁹,³⁰ The Sn–O bond length fluctuates due to lattice strain produced by the development of oxygen vacancies (Table 1).

### Table 1. Structural Properties of SnO₂ and SnO₂-rGO Using the (110) Diffraction Plane

| samples  | FWHM (β) (degree) | diffraction angle (2θ) (degree) | crystallite size (nm) | lattice strain |
|----------|-------------------|--------------------------------|----------------------|---------------|
| SnO₂     | 0.51              | 26.47                          | 16                   | 0.009         |
| SnO₂−rGO | 1.13              | 26.56                          | 8                    | 0.021         |

**Raman Analysis.** The microstructure and defect characteristics of SnO₂-rGO nanocomposites were studied using Raman spectroscopy. The Raman spectra of GO, rGO, and SnO₂-rGO nanocomposites at room temperature are shown in Figure 3. The D band and the G band are two significant distinctive bands that are assigned to graphene. A one-phonon defect-assisted process of vibrations of k-point phonons of A_{1g} symmetry gives rise to the diamondoid (D) band, demonstrating the presence of disorder and defects introduced by functional groups in the graphene planes. The E₃₂ phonon of sp²-hybridized carbon atoms of isolated double bonds in the graphene plane gives birth to the graphite (G) band.³³ It is observed that there is a shift in Raman peak positions, which confirms the bond formation between SnO₂ nanoparticles and graphene layers.³⁴-³⁵ The degree of defects in synthesized samples is determined by the ratio of D and G band intensity (I_D/I_G). I_D/I_G ratios for SnO₂-rGO (1.07) are higher than graphene oxide (0.83) and rGO (1.01), indicating the reduction in the sp² carbon domain and a greater number of defects caused by the growth of grain boundaries, vacancies, amorphous carbon species, and the attachment of SnO₂ nanoparticles on the rGO plane.³⁶−³⁸

**XPS Analysis.** The chemical state and surface compositions on the surface of prepared SnO₂ and SnO₂-rGO nanocomposites were studied using X-ray photoelectron spectroscopy (XPS). Figure 4a–d delineates the XPS spectra of the synthesized samples. The survey spectra (Figure 4a,b) demonstrate the primary constituents of SnO₂ and SnO₂-rGO samples, which are Sn, O, and C.

Three peaks at 529.4, 531.6, and 533.1 eV are observed in the high-resolution O 1s XPS spectra (Figure 4c). The 529.4 eV peak is attributed to lattice oxygen (Sn=O), the 531.6 eV peak is attributed to the oxygen-deficient region, and the third peak is attributed to chemisorbed oxygen species and –OH groups on the surface.³⁹,⁴⁰ The C 1s spectrum is shown in Figure 4d. The broad band may be separated into three XPS peaks centered at 284.9, 286.8, and 287.9 eV, which correspond to C–C, C–O, and C=O groups of rGO, respectively.⁴¹–⁴³ We can conclude that the SnO₂-rGO sample obtained via a sol–gel process consists of rGO and SnO₂ species with more oxygen vacancies and OH groups.

**Morphological Analysis.** The surface morphology of the prepared samples was investigated using the FESEM technique. Figure 5a–c displays the FESEM images of as-prepared SnO₂ nanoparticles, SnO₂-rGO nanocomposites, and rGO nanosheets. Figure 5a,b shows the FESEM images of the surface morphology of SnO₂ NPs and SnO₂-rGO nanocomposites. The spherical-shaped SnO₂ nanoparticles with approximately uniform size are shown in this FESEM picture.⁴⁴ In SnO₂-rGO nanocomposites, it is shown that the rGO sheets are immersed in clusters of SnO₂ nanoparticles. The structure of rGO nanosheets can be observed as a carbon layer, as shown in Figure 5c.

![Figure 3. Raman spectra of synthesized GO, rGO, and SnO₂-rGO nanocomposites.](https://doi.org/10.1021/acs.omega.2c04553)
Figure 4. X-ray photoelectron spectroscopy. (a, b) Survey scan of SnO$_2$ and SnO$_2$-rGO. High-resolution XPS spectra of (c) O 1s and (d) C 1s for SnO$_2$-rGO.

Figure 5. (a−c) FESEM of SnO$_2$, SnO$_2$-rGO, and rGO; (d) TEM image of the SnO$_2$-rGO nanocomposite; (e) particle size distribution histogram of the SnO$_2$-rGO nanocomposite; and (f−j) EDX spectra and mapping of the SnO$_2$-rGO nanocomposite.

SnO$_2$ nanoparticles scattered on the surface of nanosheet-like graphene layers in a SnO$_2$-rGO nanocomposite were also exhibited in the low-magnification TEM image in Figure 5d. Further, the particle size distribution histogram for
the SnO$_2$-rGO nanocomposite obtained from the TEM image, as shown in inset Figure 5e, is in the range of 7–8 nm, which is very close to the value calculated through XRD data. The signals of Sn, O, and C in the SnO$_2$-rGO nanocomposite are observed in the energy dispersive X-ray (EDX) spectrum in Figure 5f. To confirm the distribution of Sn (blue color), O (green color), and C (red color) onto the surface, elemental mapping of the area was carried out, as shown in Figure 5g–j.

**BET Analysis.** The Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods were used to measure the porosity and specific surface area of SnO$_2$ and SnO$_2$-rGO samples. Figure 6a–d shows the nitrogen adsorption/desorption isotherms and the BJH pore size distribution plot of pure SnO$_2$ and SnO$_2$-rGO nanocomposites. According to IUPAC standards, the resulting isotherm curves are type IV isotherms following an H3-type hysteresis loop, which is compatible with the De Boer classification, indicating that the materials are mesoporous. $^{37}$ The pore volume, surface area, and pore size of pure SnO$_2$ and SnO$_2$-rGO nanocomposites are listed in Table 2. The addition of rGO in SnO$_2$ produces more oxygen vacancies, which is also confirmed by XPS. A large surface area produces a large number of surface dangling bonds with associated oxygen vacancies. This increased surface area not only offers additional active sites but also provides effective transport channels for reactant molecules. $^{40–50}$

The BJH plots for the determination of the pore volume and the radius are delineated in Figure 6c,d. The average pore radius for pure SnO$_2$ and SnO$_2$-rGO was obtained nearly equal to 17.078 and 19.103 Å, respectively. The total pore volume increases from 0.084 cm$^3$ g$^{-1}$ (SnO$_2$) to 0.209 cm$^3$ g$^{-1}$ (SnO$_2$-rGO), suggesting the formation of additional pores.

The overall pore volume increases from 0.084 cm$^3$ g$^{-1}$ for SnO$_2$ to 0.209 cm$^3$ g$^{-1}$ for SnO$_2$-rGO, indicating the development of extra pores caused by the reduction of GO to rGO caused by the removal of various oxygen functional groups from the nanocomposites. $^{30}$ The observed results suggest that synthesized samples to fabricate HEC cells are highly mesoporous in nature because of oxygen vacancies

**Performance of SnO$_2$ and SnO$_2$-rGO Nanocomposites.** As illustrated in Figure 7a–d, the performance of SnO$_2$-based hydroelectric cells was assessed using voltage–current polarization (V–I) plots. With distinct working regions of HEC, the voltage drop across the external variable load is given as a function of current. The short-circuit current $I_{sc}$ and open-cell voltage $V_{oc}$ of SnO$_2$-based HEC showed a 68 mA current and 1.1 V open-cell voltage and SnO$_2$-rGO nanocomposite cells showed 148 mA current and 1.0 V open-cell voltage, respectively, as shown in Table 3. The maximum power output is reported at 93 mA by a Sb–SnO$_2$-based HEC among other metal oxides like ZnO, SnO$_2$, MgO, Al$_2$O$_3$, SiO$_2$, and TiO$_2$. $^{7,51}$

Table 4 presents a comparison of current and voltage generated by different HECs. It is observed that the metal oxide’s surface has unsaturated metal cations M$^{δ+}$ and oxygen vacancies V$^{δ−}$ on the surface. $^{7}$ This M$^{δ+}$–V$^{δ−}$ pair is known as active defect pair sites for adsorption as well as for chemidissociation of water molecules. $^{52}$ In SnO$_2$-rGO, the unsaturated metal cations and oxygen vacancies (as confirmed by the XPS, BET, and Raman spectroscopy) attract oxygen from a water molecule. These oxygen vacancies trap the electrons and attract hydroxyl ions of water molecules. This water molecule dissociates into hydronium and hydroxide ions when it approaches the defect pairs of electronegative surface cations and oxygen vacancies. Hydroxide ions create chemical bonds with unsaturated cations on the surface, and a

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Table 2. Data of the Average Surface Area, Pore Volume, and Pore Radius of SnO$_2$ and SnO$_2$-rGO Nanocomposites

| samples       | surface area (m$^2$ g$^{-1}$) | pore volume (cm$^3$ g$^{-1}$) | pore radius (Å) |
|---------------|-------------------------------|-------------------------------|-----------------|
| SnO$_2$       | 44.536                        | 0.084                         | 17.078          |
| SnO$_2$-rGO   | 84.008                        | 0.209                         | 19.103          |

Figure 6. (a–d) N$_2$ adsorption–desorption isotherm and the BJH pore size distribution plot of SnO$_2$ and SnO$_2$-rGO nanocomposites.
A chemisorbed layer of OH\(^-\) ions physisorbs the water molecules with the help of hydrogen bonding. Hydronium ion hopping occurs inside the open nanopores on the surface due to hydrogen bonding traps. The physisorbed water molecules in hydronium and hydroxide ions are further dissociated by the concentrated trapped ions, which provide enough electric potential. As a result of the Grotthuss chain reaction, hydronium ions migrate toward the cathode. The following are the electrochemical half-reactions that should occur on the electrode and the SnO\(_2\)-rGO surface.

At the metal-oxide surface,

\[
M^{\delta^+} - V^{\delta^-} + H_2O \rightarrow M - OH + H^+ 
\]

At the Zn surface,

\[
Zn \rightarrow Zn^{2+} + 2e^-; E = -0.76 \text{ V} \\
Zn + 2(OH)^- \rightarrow Zn(OH)_2 + 2e^- 
\]

At the Ag surface,

\[
2H_2O^+ + 2e^- \rightarrow H_2O + H_2; E = +0.22 \text{ V} 
\]

SnO\(_2\)-rGO HEC generates a higher offload current in comparison to SnO\(_2\) HEC. It is due to more surface energy generated by the unsaturated surface cations and oxygen vacancies formation in SnO\(_2\)-rGO, which is validated by XPS and BET results. Thus, SnO\(_2\)-rGO requires less activation energy for water molecule dissociation, which results in a higher current value.

Typical polarization zones are shown in the \(V-I\) polarization curves for SnO\(_2\) and SnO\(_2\)-rGO HECs at various load levels in Figure 7. The breakdown of water (H\(_2\)O) molecules into H\(_3\)O\(^+\) and OH ions, as well as redox processes at electrodes, generate current and voltage in HECs.\(^{35}\) The \(V-I\) curves are divided into three portions, AB, BC, and CD (as shown in Figure 7), which explain the different types of polarization losses used to characterize the cell’s operational zones.\(^{36,37}\) The open-circuit voltage of the cell at an infinite load was denoted by point A. The activation loss, which is prevalent in the lower current density regions, is given by the region AB. The activation loss is directly related to the rate of the electrochemical reaction. This loss is responsible for the delay in the initiation of the water dissociation process on the mesoporous surface and in

Table 3. Obtained Parameters of Fabricated Hydroelectric Cells

| samples      | \(I_{sc}\) (mA) | \(V_{oc}\) (volts) | ideal power (mW) | \(P_{max}\) = \(V_{oc}\) × \(I_{sc}\) |
|--------------|-----------------|-------------------|------------------|------------------|
| SnO\(_2\)    | 68              | 1.1               | 74               |                  |
| SnO\(_2\)-rGO| 148             | 1.0               | 148              |                  |

Table 4. Comparison of Different HECs

| HECs          | current (mA) | voltage (volts) | refs |
|---------------|--------------|-----------------|------|
| SnO\(_2\)     | 22.2         | 0.75            | 7    |
| Mg–SnO\(_2\)  | 41.69        | 0.78            | 14   |
| Co–SnO\(_2\)  | 77.52        | 0.45            | 14   |
| Li–SnO\(_2\)  | 70           | 0.98            | 53   |
| Sb–SnO\(_2\)  | 93           | 1.43            | 54   |
| CeO\(_2\)-rGO | 21.3         | 0.83            | 30   |
| TiO\(_2\)     | 2.3          | 0.90            | 7    |
| SiO\(_2\)     | 1.1          | 0.96            | 7    |
| ZnO           | 5.0          | 0.90            | 7    |
| MgO           | 1.5          | 0.94            | 7    |
| Al\(_2\)O\(_3\)| 6.5          | 0.93            | 7    |
| SnO\(_2\)-rGO | 148          | 1.0             | present work |

At the metal-oxide surface,

\[
M^{\delta^+} - V^{\delta^-} + H_2O \rightarrow M - OH + H^+ 
\]

At the Zn surface,

\[
Zn \rightarrow Zn^{2+} + 2e^-; E = -0.76 \text{ V} \\
Zn + 2(OH)^- \rightarrow Zn(OH)_2 + 2e^- 
\]

At the Ag surface,

\[
2H_2O^+ + 2e^- \rightarrow H_2O + H_2; E = +0.22 \text{ V} 
\]
the collection of ions by the respective electrodes. Pure SnO\(_2\) showed that a high activation loss may be due to low defect density dissociating a small number of water molecules, which, in turn, require more energy for the charge transfer reaction to proceed. The Ohmic region (BC) represented the internal resistance of the hydroelectric cell material to ion flow along with electron flow resistance offered by cell electrodes. It is observed that a large linear Ohmic region is useful for HEC operation observed in the SnO\(_2\)-rGO cell, which signifies the low internal resistance of the cell material. This may be because of increased defect centers, which promote the ion transfer via H\(_2\)O\(^+\) hopping and migration of OH\(^-\) via oxygen vacancies.

The mass transport loss/concentration loss, which is present in the higher current density zones, is represented by CD. The higher concentration loss is observed for SnO\(_2\)-rGO, which accounts for a higher concentration of dissociated ions and a limited amount of charge transport at highly active electrodes. The active linear region and the high current value obtained for SnO\(_2\)-rGO HEC are beneficial for facile, portable, and low-cost electricity generation by dissociation of the water molecule.

In the present study, cells’ maximum powers were calculated to be 74 and 148 mW for SnO\(_2\) and SnO\(_2\)-rGO-based HECs, respectively. The maximum power of 148 mW obtained for a SnO\(_2\)-rGO HEC cell with an area of 4.0 cm\(^2\) is higher among all reported HECs, as shown in Table 4. The addition of GO to SnO\(_2\) enhances the current magnitude from 68 mA for SnO\(_2\) to 148 mA for SnO\(_2\)-rGO. The improved oxygen vacancies and the surface area increase the water dissociation, resulting in an increase in the current. Because of the facile charge transfer between rGO and SnO\(_2\), the barrier to OH\(^-\) diffusion via grain boundaries is reduced, resulting in a lower Ohmic loss. The current HEC’s potential is higher than previously reported HECs, indicating that the redox reaction and the water dissociation rates are balanced.

The charge transport mechanism within hydroelectric cells has been observed by the Nyquist impedance response of fabricated HECs. Figure 8a,b shows the Nyquist plots of wet SnO\(_2\) and SnO\(_2\)-rGO HEC cells, respectively. In the given frequency range, both graphs in Figure 8a,b exhibit a single semicircular curve. It is observed that the addition of rGO in SnO\(_2\) decreased the series resistance by approximately 10 times, revealing high OH\(^-\) and H\(_2\)O\(^+\) conduction in the SnO\(_2\)-rGO cell because of which the current magnitude increased. In the case of a pure SnO\(_2\) cell, a semicircular arc at a high frequency illustrated the cell’s internal resistance of approximately 13 \(\Omega\), as obtained by the fitting curve in Figure 8a. The hydronium ions transfer toward the respective electrodes via a hopping mechanism, and hydroxide ions move via defects, which decreases the internal resistance of the cell. The highly reduced internal resistance is observed for SnO\(_2\)-rGO (\(~8\ \Omega\)) due to the high concentration of defects, which provide a conduction path for the dissociated ions.

In the wet condition, SnO\(_2\) cells have the highest impedance. The value of impedance was reduced for the SnO\(_2\)-rGO cell when GO was added to SnO\(_2\). This decrease in impedance suggests that electrons move from the surface of SnO\(_2\) nanoparticles to defects sites on the rGO surface generated during GO reduction in nanocomposites. The impedance of water-soaked cells dramatically drops to \(~30\ \Omega\) for the SnO\(_2\)-rGO cell as compared to \(~100\ \Omega\) for the SnO\(_2\) cell. The plots indicate diminished semicircular loops in the high and intermediate frequencies. The water dissociation in nanocomposite HECs led to a dramatic drop in resistance, allowing ionic flow. Because of the high proton conductivity in GO, the conductivity of nanocomposite-based HEC increased after wetting, as seen in the Nyquist plot. Adding GO content into SnO\(_2\) lowers grain boundary resistance, allowing facile hydroxyl ion migration through grain boundaries when compared to the pure SnO\(_2\) cell.

### CONCLUSIONS

In summary, the oxygen-deficient mesoporous SnO\(_2\) and SnO\(_2\)-rGO nanocomposites were synthesized via a sol–gel method. The addition of rGO into a SnO\(_2\) lattice induced oxygen deficiency as evidenced by XPS and Raman spectroscopy studies. The amount of water molecule dissociation/splitting in SnO\(_2\)-rGO nanocomposites was boosted by an increase in oxygen vacancies, Sn\(^{3+}\) surface ions, and increased surface area. The addition of rGO into SnO\(_2\) increased the conductivity of hydroxyl ions via migration. The SnO\(_2\)-rGO-based HEC delivers the highest reported current of 148 mA and a voltage of 1.0 V. The ability to build vast amounts of oxygen-deficient SnO\(_2\) and achieve a high current density with such a simple approach has enormous potential to replace solar cells and fuel cells.

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The text includes a figure (Figure 8) with Nyquist equivalent circuit fits for wet SnO\(_2\) and wet SnO\(_2\)-rGO hydroelectric cells, with an analogous circuit for simulating their Nyquist spectra.
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Author Contributions
Aarti contributed to the methodology, data curation, and writing—original draft; P.C. contributed to supervision; A.G. contributed to conceptualization, editing, validation, and supervision; J.S. contributed to editing and data analysis; and R.K.K. contributed to conceptualization, results, and discussion.

Notes
The authors declare no competing financial interest.

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