

1 Nanocrystalline NiWO₄-WO₃-WO_{2.9}
2 Composite strings: Fabrication,
3 Characterization and their Electrocatalytic
4 Performance for Hydrogen Evolution
5 Reaction

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26 **Abstract**

27

28 In this study, novel nano crystalline composite strings made from mixed nickel-tungsten oxides
29 ($\text{NiWO}_4\text{-WO}_3\text{-WO}_{2.9}$) have been fabricated. The $\text{NiWO}_4\text{-WO}_3$ fibers produced by the
30 electrospinning method were post treated in an argon atmosphere at 800°C which yielded
31 $\text{NiWO}_4\text{-WO}_3\text{-WO}_{2.9}$ nanocrystals attached together forming a string-like structure. The presence
32 of $\text{WO}_{2.9}$ phase was confirmed by both the XRD and TEM diffraction pattern analysis. String
33 morphology and structure were found to change with different post treatment conditions such
34 as by changing the calcination temperature from 550°C under oxygen to 800°C under pure argon
35 atmosphere. This material was investigated for electrocatalytic hydrogen evolution reaction
36 (HER) in 0.5 M H_2SO_4 and 0.1M KOH electrolytes. These composite strings showed good
37 electrocatalytic activity compared to the $\text{NiWO}_4\text{-WO}_3$ fibers reported previously [1]. It was
38 concluded that the presence of $\text{WO}_{2.9}$ phase increases the electrocatalytic activity of the catalyst
39 as compared to the $\text{NiWO}_4\text{-WO}_3$ fibers with over potentials as low as 40 mV and 50 mV in 0.5 M
40 H_2SO_4 and 0.1M KOH respectively.

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42 **Keywords:** Electrospinning, nickel tungstate, tungsten oxide, composite strings, hydrogen evolution
43 reaction.

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1. Introduction

In an effort to address the growing global energy demands, the quest for efficient electrocatalysts still continues, with new materials being investigated for hydrogen evolution reaction (HER) [2-6]. Hydrogen is a promising alternative to fossil fuels due to the numerous advantages it offers such as being pollution-free and sustainable [7]. Moreover, hydrogen production through water electrolysis has attracted much interest as hydrogen can be produced in high purity and large quantities [8]. At the same time, the generated gases from water electrolysis have proved useful in other applications such as self-cleaning membranes [9-11]. Several metal oxide electrocatalysts have been put forward for HER including NiO [12], WO₃ [13], ZnO [14] and MoO [15]. Nevertheless, the methods of producing catalytic fibers, nanorods, nanowires or string-like structures are gaining importance in recent literature studies [16]. Among these methods, electrospinning has stood out to be a versatile, flexible and cost effective method for metal oxide fibrous production. In electrospinning, a syringe is filled with the desired solution. The needle of the syringe is connected to a collector via high voltage. The electrical charge draws very fine fibers from the needle tip, which gets accumulated on the collector [17, 18]. Fabrication of metal oxide fiber like structures through the electrospinning method has attracted much interest, where it is being studied in various applications such as WO₃ fibers for gas sensing [19], NiO nanorods [20] and TiNb₂O₇ strings [21] for batteries, TiO₂ fibers for hydrogenation [22] and ZnO nanofibers for photocatalysis [23]. However, the research on fibrous electrocatalysts is still an emerging area with only few studies reported on the fabrication, characterization and application on electrocatalyst fibers for HER. Recently, Wang et al. [24] reported low Tafel slopes of about 34 mV/dec for CoSe₂ nanowires grown on carbon fiber paper. Chekin et al. [25] reported enhanced electrocatalytic activity of WO₃ nanorods when used in conjunction with carbon nanotubes (CNTs). A current density of 3.8 mA/cm² was reported as compared to commercial WO₃ particles registering a current density of 0.8 mA/cm² at a potential of -0.8 V. They also observed a low Tafel slope of 104 mV/dec for WO₃ nanorods compared to 130 mV/dec for WO₃ particles. The use of CNTs along with the electrocatalytic material may be attributed to CNTs superior catalytic

82 properties owing to its high electrical conductivity and better electron transport characteristics
83 [26, 27].

84 The electrospinning process offers an advantage of producing mixed oxides in the end
85 morphology structures [28, 29]. The electrospinning solution can be tailored to incorporate a
86 combination of different elemental salts. Several oxide mixtures including Ti-based mixed oxide
87 fibers [29], ZnO-NiO hybrid fibers [30] and ZnO-SnO₂ mixed oxide fibers [31] have been reported.
88 Wu et al. [32] reported a Tafel slope of 89 mV/dec in 0.5M H₂SO₄ electrolyte using electrospun
89 MnCo₂O₄ fibers when tested for HER. Recently, our group reported the fabrication of electrospun
90 mixed oxides WO₃-NiWO₄ and NiWO₄-WO₃-NiO composite fibers for HER, where fibers with
91 different compositions were produced by varying the electrospinning solution parameters [1] .
92 The presence of NiWO₄ phase in WO₃- NiWO₄ fibers enhanced the electrocatalytic activity for
93 HER when compared with pure WO₃ and NiO fibers. Low overpotentials of 80 mV and 60 mV in
94 0.5M H₂SO₄ and 0.1 KOH media respectively were reported. The composite fibers also registered
95 low Tafel slopes of 50.2 mV/dec and 41.9 mV/dec in 0.5M H₂SO₄ and 0.1 KOH media respectively.

96 With the ongoing efforts to find promising electrocatalysts, WO_{2.9} phase is reported to be
97 potential candidate [33]. The fabrication of WO_{2.9} phase has been reported in a few studies. Al-
98 Sharab et al. [34] synthesized WO_{2.9} fibers by evaporating WO₃ powder in a transmission electron
99 microscope (TEM) chamber using the electron beam. The same phase was synthesized [34]
100 under an inert gas condensation system, whereby the WO₃ powder was evaporated in a reduced
101 pressure chamber in the presence of an argon gas. Xu et al. [35] synthesized aligned WO_{2.9} fibers
102 via flame synthesis method utilizing a tungsten substrate. Li et al. [33] synthesized WO_{2.9}
103 nanoparticles by annealing ball milled commercial WO₃ particles in a tube furnace for one hour
104 under H₂-Ar atmosphere. They [33] also tested electrocatalytic activity for HER in 0.5M H₂SO₄
105 where the WO_{2.9} nanoparticles registered a low Tafel slope of 50 mV/dec and an overpotential of
106 70 mV.

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108 This study aims at fabricating NiWO₄-WO₃-WO_{2.9} composites in the string morphology using the
109 electrospinning method. Moreover, it is an effort to further improve the previously reported [1]

110 NiWO₄-WO₃ composite fibers for HER. To the best of our knowledge, no study on the direct
111 synthesis of this combination of composite fibers could be found in the literature.

112 **2. Materials and Methods**

113

114 2.1 Materials

115

116 The following salts, solvents, polymer, and acids were obtained from Sigma-Aldrich: nickel II
117 acetate (NiAc), ammonium metatungstate hydrate (AMT), ethanol ($\geq 99\%$), polyvinylpyrrolidone
118 (PVP, Mw = 1,300,000), sulfuric acid ($>90\%$) and potassium hydroxide (KOH). The salts, polymer
119 and solvents were used in their as-received form, while the acids were adjusted to their required
120 compositions. CNS was developed by Applied Nanostructured Solutions, LLC through a
121 continuous chemical vapor deposition process [36].

122 2.2 Fabrication of Mixed Nickel-Tungsten Oxide Nanocrystalline Strings

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124 Mixed NiWO₄-WO₃ composite fibers were prepared by the electrospinning method. A Nanon-
125 01A electrospinning setup (MECC, Japan) was used for this purpose. NiWO₄-WO₃ electrospun
126 fibers were produced by following the method reported earlier by Anis et al. [1]. NiAc and AMT
127 salts were first dissolved in deionized (DI) water. A clear salt solution was obtained. Following
128 this, PVP was added to facilitate the electrospinning process [37] by increasing the
129 electrospinning solution viscosity. The molar ratio of Ni: W was kept as 1:2. Electrospinning was
130 carried out using a stainless steel needle of gauge 22 at a 0.5 ml/h flow rate and 28 kV voltage.
131 The as-spun fibers were allowed to dry at 80°C for 6 h, after which they were calcined at 550°C
132 for 2 h. calcination was carried out to remove the PVP polymer and produce pure mixed metal
133 oxide fibers. For convenience, specimens prepared by mixing NiWO₄-WO₃ composite with Ni: W
134 of 1:2 molar ratios are designated as NW12. The NW12 fibers, after calcination at 550°C, were
135 further treated at 800°C under a pure argon atmosphere in a tube furnace for 60 minutes. The
136 pressure inside the tube was maintained at 0.03 MPa. The resulting fibrous material was
137 collected after the tube furnace cooling down to room temperature. The specimen processed
138 under these conditions is designated as NW12-Ar throughout the manuscript referring to NW12

139 fibers treated in argon atmosphere. Another as-spun specimen was heat treated directly at 800°C
140 in air, without calcination at 550°C, to compare their electrocatalytic activity with the other
141 catalytic fibers fabricated in this study. This specimen is designated as NW12-O. The symbol O
142 signifies the presence of oxygen.

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144 2.3 Mixed Nickel-Tungsten Oxide Nanocrystalline String Characterization

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146 Nova Nano Scanning electron microscopy (high resolution SEM, FEI) operating at 10 kV and a high
147 resolution transmission electron microscope (HRTEM) (Tecnai F20, FEI), operating at 200kV were
148 used to study the mixed metal oxide fiber morphology. SEM energy dispersive X-ray (EDS)
149 detector was used for elemental analysis. For SEM analysis, the fibers were directly deposited
150 onto the SEM stub, while for TEM, the sample was sonicated for 15 minutes before deposition
151 on a copper grid. Structural analysis was performed through an X-ray diffractometer (PANalytical,
152 Emperean). Ni-filtered $\text{CuK}\alpha$ ($\lambda = 1.5056 \text{ \AA}$) radiations were used in the range of $10\text{-}90^\circ 2\theta$, with
153 45 kV and 40 mA voltage and current.

154

155 2.4 Electrochemical Characterization

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157 The catalytic composite strings were dispersed in ethanol, after which carbon nano structures
158 (CNS) was added and dispersed through sonication using a BRANSON 1510 model until a uniform
159 suspension was obtained. Metal oxide electrocatalysts are often used in conjunction with CNTs
160 or CNS for superior catalytic properties due to their high electrical conductivity and better
161 electron transport [26, 27]. Fiber to CNS ratio (by weight) was kept as 80:20. To prepare the
162 working electrode, a clean glassy carbon electrode (GCE) was coated with a fixed volume of the
163 suspension by the drop casting. A mass loading of 0.1 mg/cm^2 catalyst was used in this study.
164 Following this, the electrode was further dried in an oven at 50°C for 30 minutes.

165

166 The metal oxide composite string was tested as an electrocatalyst for HER in acidic and alkaline
167 media as H_3O^+ and OH^- are two of the most conductive ions [38]. A three-electrode system was

168 used [1] to test the electrocatalytic performance of NW12, NW12-O and NW12-Ar strings in 0.5M
169 H₂SO₄ and 0.1M KOH solutions. This was performed using an Autolab302N
170 potentiostat/galvanostat, where linear polarization (LP) graphs were obtained at a scan rate of
171 50mV/s. The reference and counter electrode were Ag|AgCl|KCl3.5M and a platinum wire
172 respectively. The potentials are reported with reference to a reversible hydrogen electrode
173 (RHE).

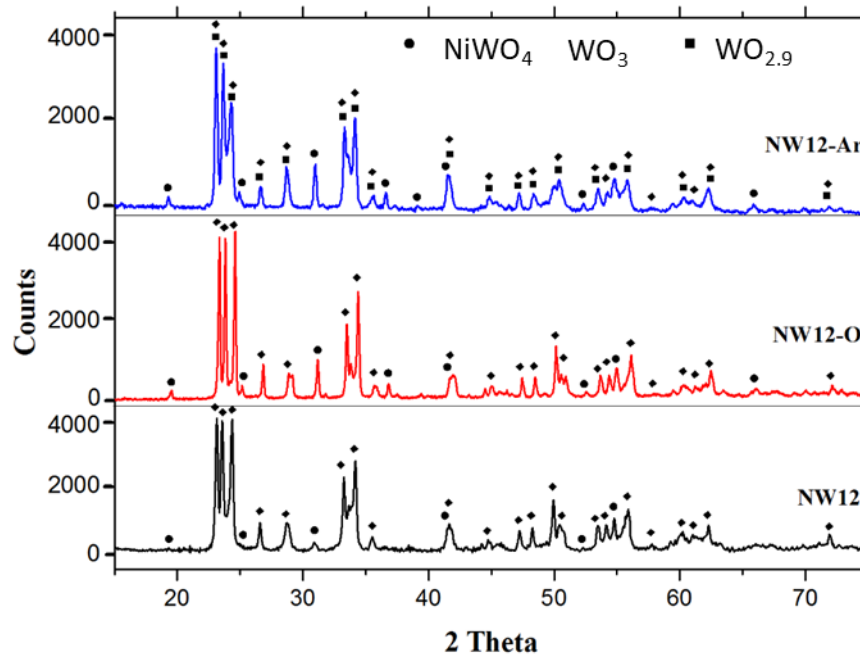
174 3. Results

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176 3.1 Structural and Morphological Characterization of the Mixed Metal Oxides

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178 The experimental XRD patterns were analyzed in X'pert Highscore software using Rietveld
179 refinement [39]. Standard patterns for the expected phases were acquired from Pearson's Crystal
180 Structure Database for Inorganic Compounds [40] and used for phase identification. Figure 1
181 shows the XRD patterns of NW12, NW12-O and NW12-Ar samples. The peaks of both NiWO₄
182 (monoclinic structure, MgWO₄ prototype, *P12/c1* space group and 13 space group number with
183 $a=4.599\text{\AA}$, $b=5.669\text{\AA}$ and $c=4.913\text{\AA}$ lattice parameters) and room temperature WO₃ (triclinic
184 structure, WO₃ prototype, *P-1* space group and 2 space group number with $a=7.375\text{\AA}$, $b=7.507\text{\AA}$
185 and $c=7.710\text{\AA}$ lattice parameters) compounds could be positively identified in all samples.
186 However, the pattern of the annealed sample at 800°C under argon (NW12-Ar) showed few
187 differences than other two patterns. The difference was due to the presence of WO_{2.9} compound,
188 which is believed to have monoclinic structure, WO_{2.9} prototype, *P12/m1* space group and 10
189 space group number with $a=7.316\text{\AA}$, $b=7.534\text{\AA}$ and $c=10.557\text{\AA}$ lattice parameters. Detailed
190 crystallographic data of the identified phases in all samples are provided in Table 1. The XRD
191 pattern refinement for NW12-Ar sample was challenging, because many of WO₃ and WO_{2.9} peaks
192 were found overlapping. Nevertheless, the phase identification in this work was successful and
193 conforms with the O-W binary phase diagram [41] data.



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Figure 1: XRD patterns of NW12, NW12-O and NW12-Ar samples

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Table 1: Crystallographic data of the detected phases in the current study

Phase	Crystallographic system	Prototype	Space group	Lattice parameters (Å)			Angles (°)		
				<i>a</i>	<i>b</i>	<i>c</i>	α	<i>B</i>	γ
WO₃	Triclinic	WO ₃	<i>P</i> -1	7.375	7.507	7.710	89.97	89.63	89.86
WO_{2.9}	Monoclinic	WO _{2.9}	<i>P</i> 12/ <i>m</i> 1	7.316	7.534	10.557		133.19	
NiWO₄	Monoclinic	MgWO ₄	<i>P</i> 12/ <i>C</i> 1	4.599	5.669	4.913		89.94	

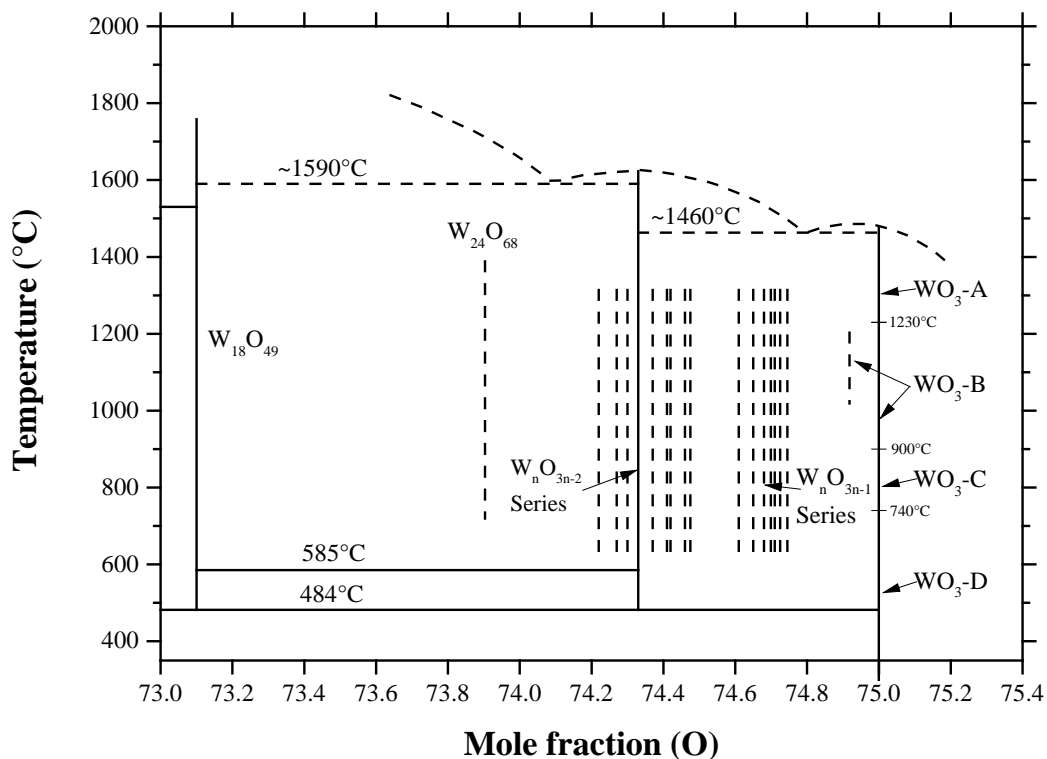
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199 Figure 2 shows the O-W binary phase diagram in a condensed system at 0.1 MPa [41]. Several
 200 compounds exist in a very narrow composition range (73-75 at. % O). These compounds are
 201 W₁₈O₄₉, W₂₄O₆₈, W_{*n*}O_{3*n*-2} series, W_{*n*}O_{3*n*-1} series and WO₃. Therefore, any deviation in oxygen
 202 composition below 75 at. % will lead to different phase formation. For instance, NW12-Ar and
 203 NW12-O samples were both annealed at 800°C in argon and oxygen atmospheres, respectively.

204 The phase content of NW12-Ar was maintained as NiWO₄, WO₃ and WO_{2.9}, while the oxygen
 205 concentration increased upon annealing and thus WO₃ grew on the expense of WO_{2.9} to have
 206 only WO₃ and NiWO₄ in NW12-O sample. In principle, both WO_{2.9} and WO₃ phases exist as
 207 stoichiometric compositions. Figure 3 is drawn to describe the crystal structure and diffraction
 208 pattern of these two compounds.

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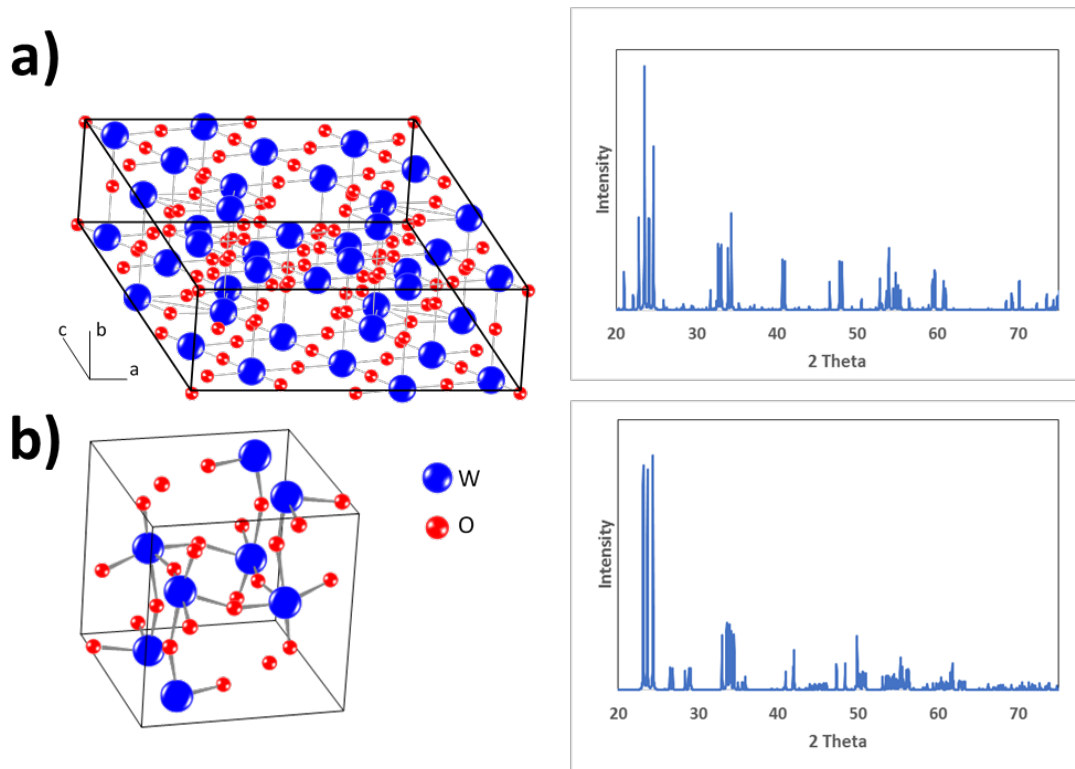
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211

212 Figure 2: The O-W binary phase diagram in a condensed condition at 0.1 MPa.

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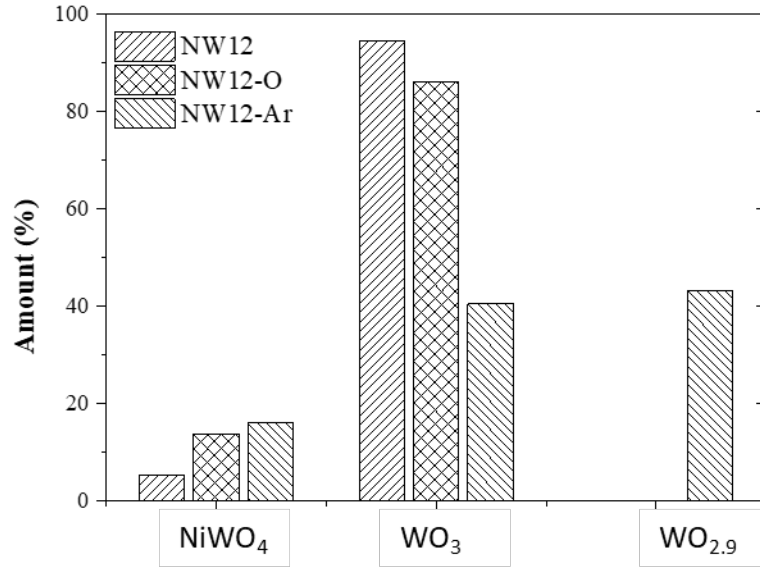
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Figure 3: Unit cells and standard XRD patterns of (a) $\text{WO}_{2.9}$ and (b) WO_3 .

216

217 In order to calculate the relative amounts of all detected phases, Rietveld refinement [39] was
 218 performed, which is based on the best fit with the measured patterns using a least square
 219 approach. The bar chart in Figure 4 summarizes the relative amounts of the detected phases by
 220 XRD analysis. Details on the fitting procedure are included in the supplementary information.



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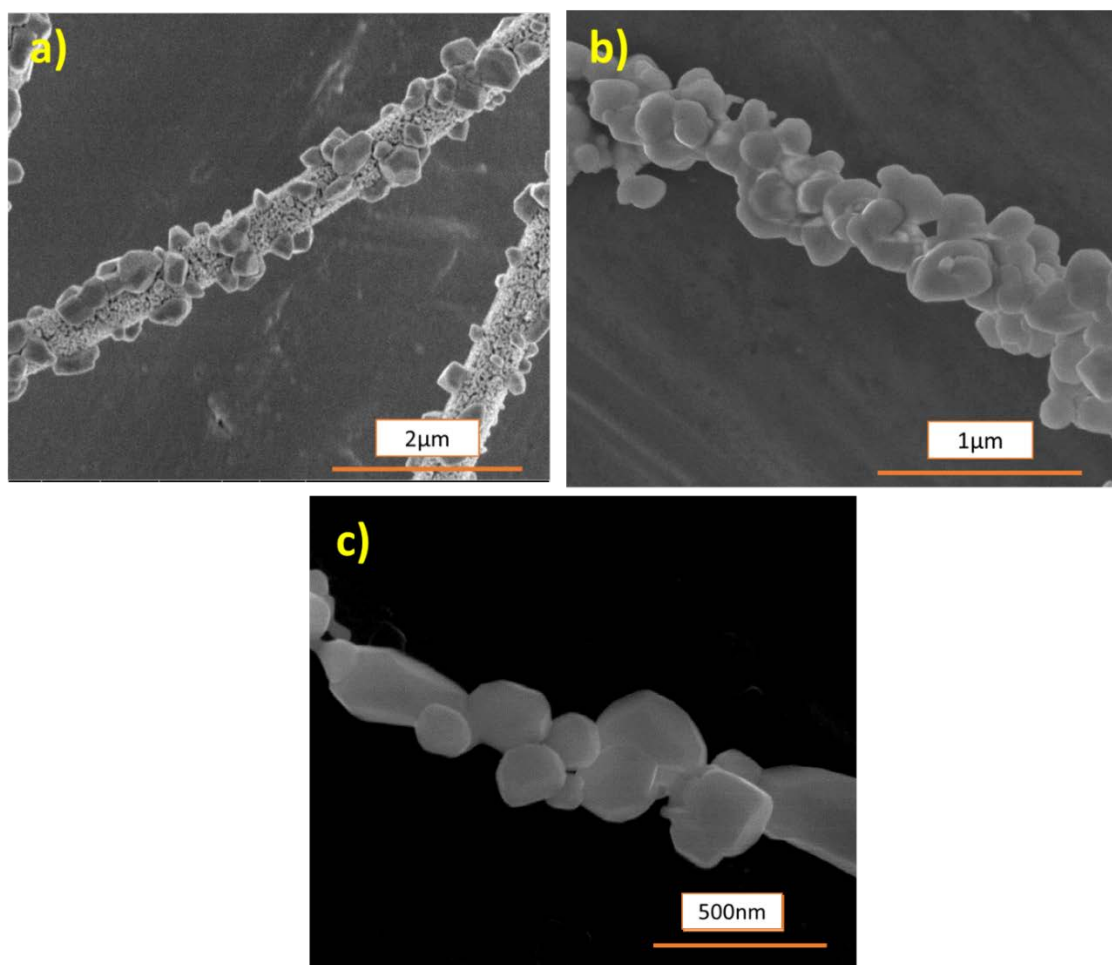
222 Figure 4: Bar chart represents the relative amounts of detected phases for NW12, NW12-O and
 223 NW12-Ar specimens.

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225 The amount of NiWO₄ was relatively high (16.1%) in NW12-Ar as compared to 5.3 and 13.8% in
 226 NW12 and NW12-O, respectively. While, WO₃ was dominant in NW12 sample due to the reasons
 227 discussed in a previous study published by Anis et al. [1]. The amounts of WO₃ and WO_{2.9} were
 228 about 40.6% and 43.3%, respectively, in NW12-Ar. The approach of treating O-W samples under
 229 various atmospheres including hydrogen [33] and argon [34] has been reported, whereby WO_{2.9}
 230 phase was obtained. However, different atmospheric variations including the gas type and
 231 pressure maintained in the tube chamber might produce phases with different compositions.
 232 Hence, this opens new research areas to further study the effect of different conditions on WO_{2.9}
 233 phase formation.

234 Figure 5 shows the HR-SEM images of NW12, NW12-O and NW12-Ar. Fiber like morphology was
 235 observed for NW12 (Figure 5a), similar to the one reported in [1]. Large tungsten crystals can be
 236 observed along the fiber, while the fiber itself is made from tiny particles composed of both
 237 NiWO₄ and WO₃ [42]. A change in composite fiber morphology occurred when the as-spun fibers
 238 were treated at 800°C in air instead of 550°C. The morphology of the fibers changed from fibrous
 239 to more like 'strings' as shown in Figure 5b. Larger crystals compared to NW12 were observed in
 240 this case. The high temperature provided the driving force for the small crystals to grow through

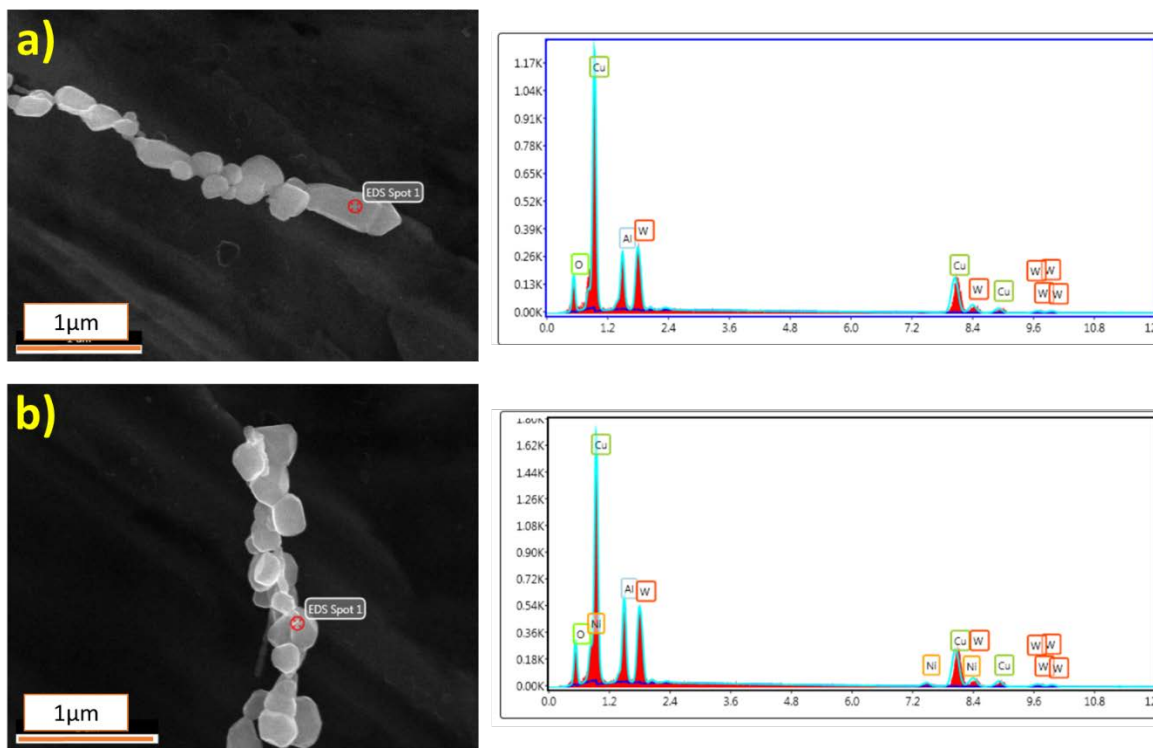
241 the diffusion process [42]. When the NW12 fibers were treated at 800°C under an argon
242 atmosphere, again a 'string-like' morphology was observed. The nanocrystals can be seen to be
243 attached together to form a string in Figure 5c. These morphological differences are attributed
244 to the different phase contents as concluded from the XRD analysis. Figure 6 shows the SEM
245 image of NW12-Ar and their corresponding EDS spectrums. Figure 6a shows the EDS spectrum
246 corresponding to the spot location on a single crystal, while Figure 6b shows the spectrum
247 corresponding to a spot along the fiber in NW12-Ar sample. EDS analyses revealed that the fibers
248 consist of Ni, W and O, while the pure tungsten oxide crystal consists of only W and O elements.
249 The small Ni signals are due to the presence of NiWO₄ phase along the string. The copper peak
250 corresponds to the copper tape on which the material was placed, while the Al peak corresponds
251 to the Al stub used during the SEM analysis.



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253

Figure 5: HR-SEM images of (a) NW12, (b) NW12-O and (c) NW12-Ar.

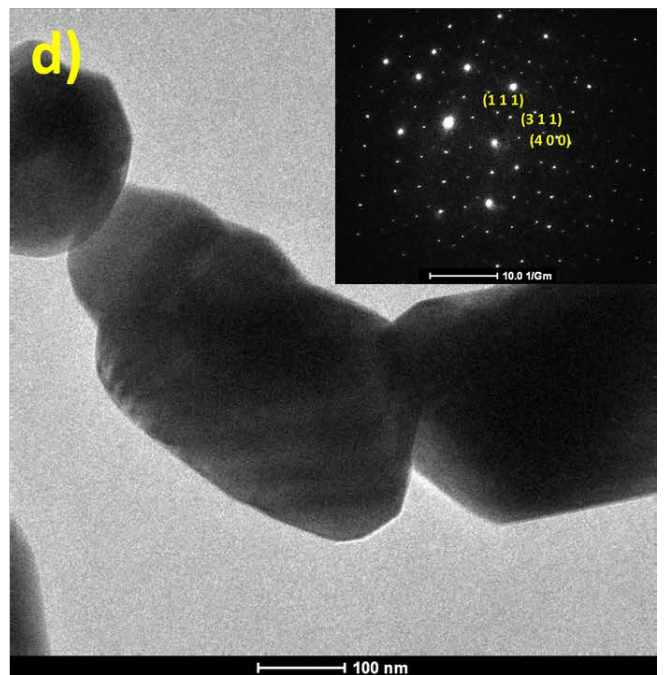
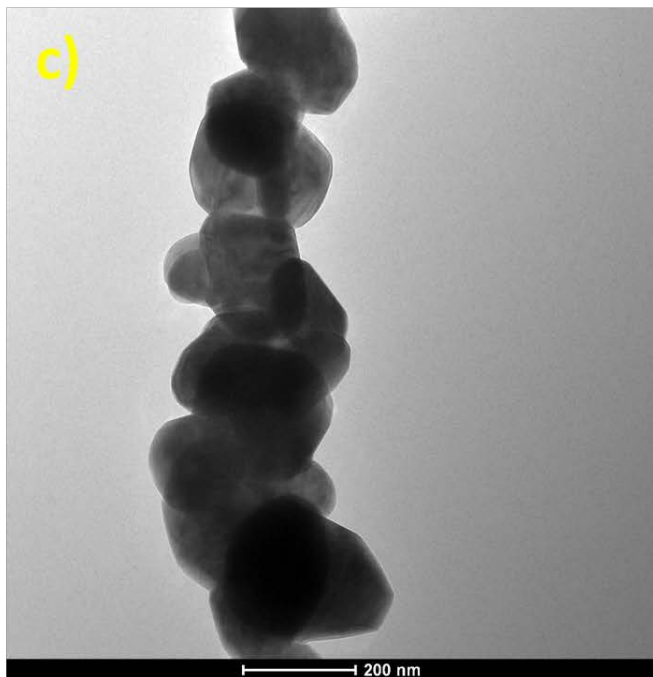
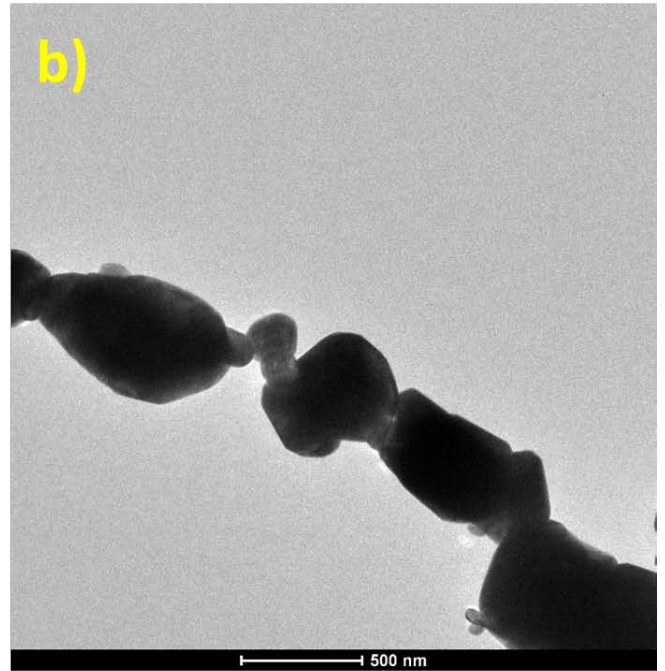
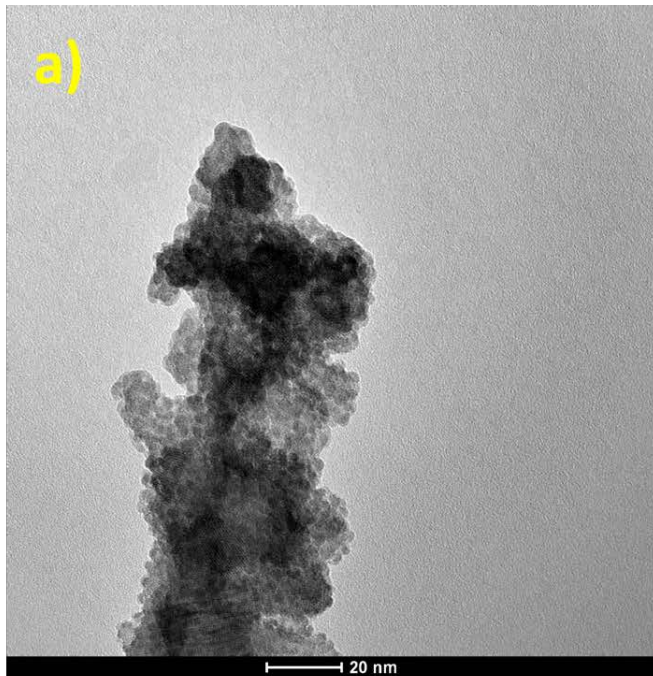


254
 255 Figure 6: HRSEM images for NW12-AR and their corresponding EDS spectrums. The spectrum
 256 particularly corresponds to the EDS spots shown in the SEM images (a) at the single crystal and
 257 (b) along the string with a few crystals overlapping.

258

259 Both SEM and TEM provided valuable structural and compositional information for the
 260 composite strings. While SEM gave us an indication of the overall fiber morphology, owing to
 261 bulk EDS analysis, it was not possible to conclude the precise location of the phases in the
 262 composite string. Thus, TEM was use for this purpose. Figure 7 shows TEM images of NW12,
 263 NW12-O and NW12-Ar. The TEM images provide greater insight on fiber morphology, which are
 264 indeed made from crystals of different sizes depending upon their post treatment procedures.
 265 Figure 7a shows the morphology of NiWO₄-WO₃ composite fibers with Ni: W molar ratio of 1:2.
 266 The fiber is seen to be made from very small particles which are essentially much smaller than
 267 10nm in size. However, when the same as-spun fibers were calcined at 800°C, larger crystals are
 268 observed (Figure 7b) on the expense of the smaller ones. Clearly, crystal growth has occurred.
 269 Similar is observed for the NW12-Ar (Figures 7c and 7d) which are composed of large crystals.
 270 String morphology does not change much when the NW12 fibers are post treated in either Argon

271 at 800°C or directly annealed at 800°C in air. The SAED spot pattern in Figure 7d corresponds to
272 the WO_{2.9} phase indicating the monoclinic symmetry (space group *P12/m1*) with lattice
273 parameters $a=7.316 \text{ \AA}$, $b=7.534 \text{ \AA}$, $c=10.557 \text{ \AA}$ and $\beta=133.19^\circ$. The selected area diffraction
274 (SAED) pattern of WO_{2.9} has been coincided with another pattern from adjacent crystals. The
275 planes labelled in the inset are (1 1 1), (3 1 1) and (4 0 0) corresponding to d-spacings of 3.11 Å,
276 1.48 Å and 1.33 Å, respectively.



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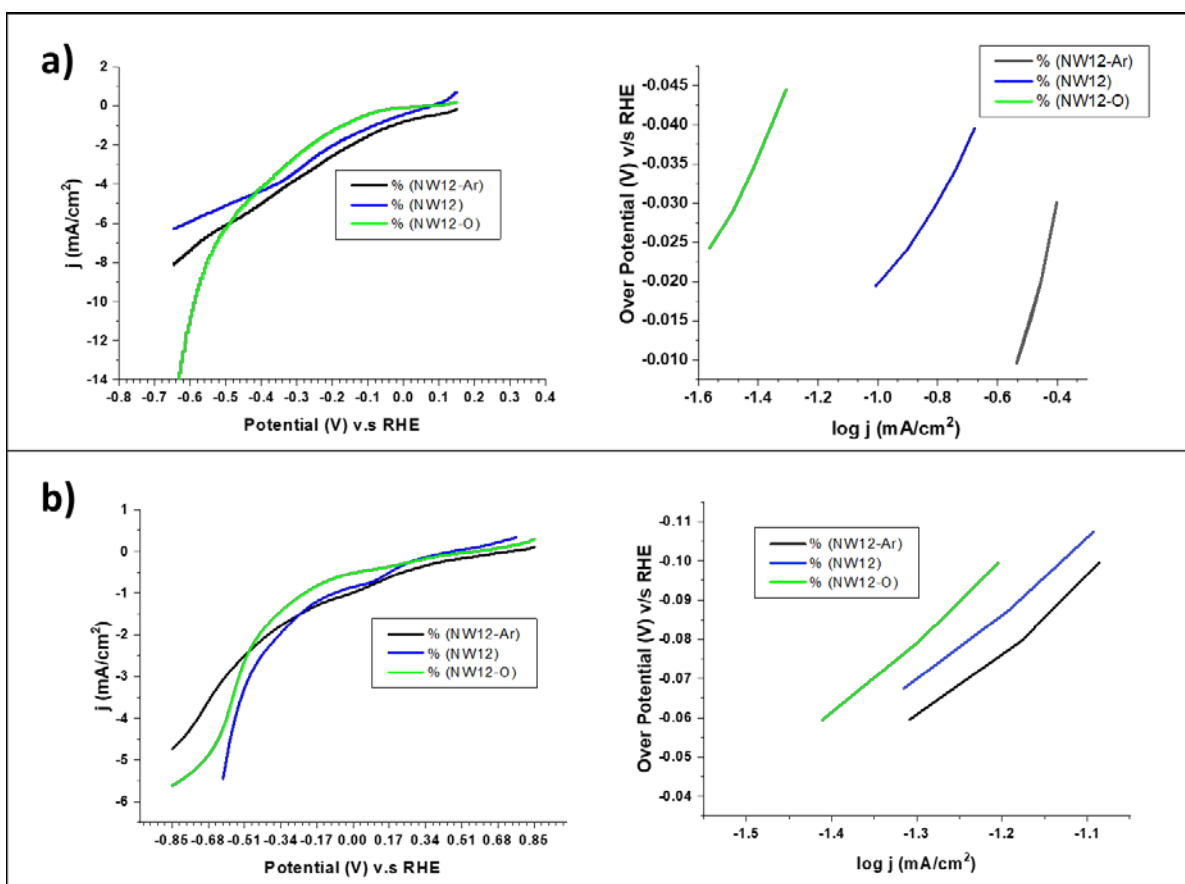
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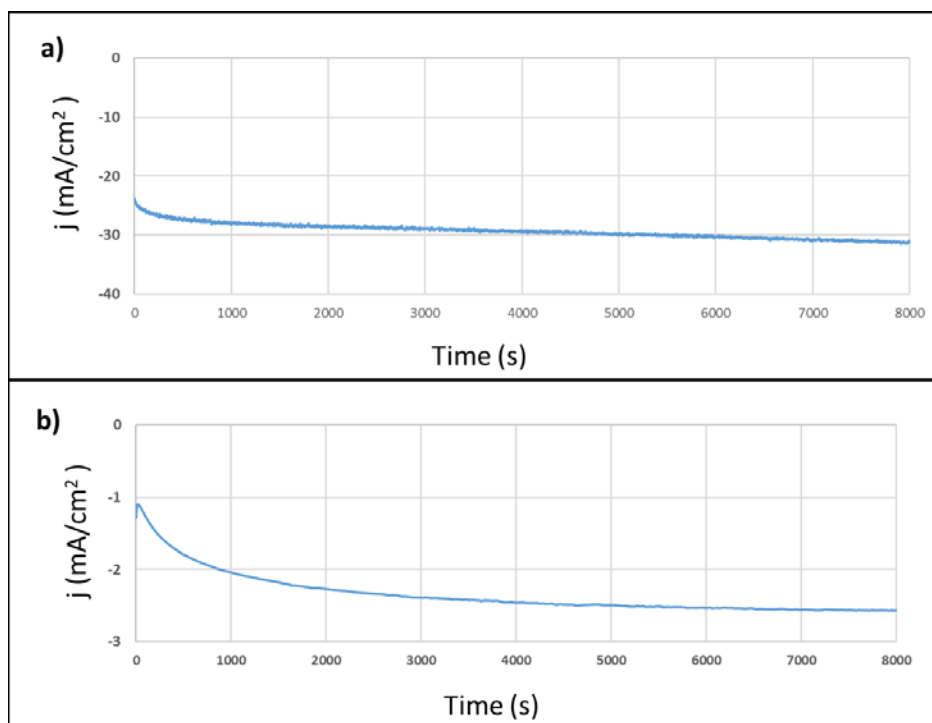
Figure 7: HR-TEM images of (a) NW12, (b) NW12-O and (c) NW12-Ar (d) NW12-Ar string along with corresponding SAED pattern in inset.

283 3.2 Electrocatalytic Activity of the Mixed Metal Oxides in Acidic and Alkaline Media
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285 NW12-Ar and NW12-O were studied for their hydrogen evolution electrocatalytic properties in
286 both acidic and alkaline media. Their electrocatalytic properties have been compared with
287 pristine NiO and WO₃ fibers for comparison, as well as with NW12 to study the effect of WO_{2.9}
288 phase on HER. NW12-O was tested to confirm the reason for the enhanced electrocatalytic
289 performance, whether due the presence of WO_{2.9} or the large amount of NiWO₄ phase (≈16 %)
290 in the nanocrystalline string. All over-potentials for hydrogen evolution were measured at a
291 current density of -1 mA/cm² in both 0.5 M H₂SO₄ and 0.1M KOH media unless otherwise stated.
292 The GCE shows negligible electrocatalytic activity as already established in the literature with
293 high over potentials greater than 500mV [1, 25]. Therefore, any electrocatalytic activity is from
294 the material fiber or string indeed.



295
296 Figure 8: Polarization curves and their corresponding Tafel slopes for NW12-Ar, NW12 and
297 NW12-O in (a) 0.5M H₂SO₄ and (b) 0.1M KOH.



298

299 Figure 9: catalyst stability over time - chronoamperometric response curves of NW12-Ar at a
 300 constant overpotential of -150 mV for HER in a 0.5 M H₂SO₄ and b 0.1 M KOH.

301
 302 Linear polarization (LP) curves for NW12-Ar, NW12 and NW12-O are compared in Figure 8. Figure
 303 8a compares the LP curves and Tafel plots for HER in 0.5 M H₂SO₄ while Figure 8b compares it in
 304 0.1M KOH. Table 2 summarizes the Tafel slopes and over potentials for the composite metal
 305 oxides in this study and compares it with pristine WO₃ and NiO fibers carried out in a previous
 306 study [1]. The highest Tafel slopes are reported for NiO in both electrolytes while low Tafel slopes
 307 are registered for the composite fibers, especially for NW12-Ar. Figure 9 shows the catalyst
 308 strings, NW12-Ar stability in both 0.5 M H₂SO₄ and 0.1 M.

309

310 4. Discussion

311

312 Thus far, the most promising electrocatalyst for hydrogen evolution reported in the literature is
 313 platinum [38] with very low over potentials observed in both acidic and alkaline media of about
 314 10mV [1, 43]. This makes platinum the most valued material for HER at present. Table 2

315 compared the over potentials and Tafel slopes for NW12, NW12-O, NW12-Ar, pure WO₃ and NiO
316 electrospun fibers. NiO was found to have poor electrocatalytic properties on its own. WO₃ also
317 registered high over potential and Tafel slope as compared to the composite fibers.

318 Interestingly, there is a correlation between the morphology and composition of the fibers to
319 their electrocatalytic activity. On comparing the NW12 fibers to the NW12-O strings, at first it can
320 be expected that NW12-O may perform better due to higher percentage of NiWO₄ phase (~14
321 wt. %) as opposed to just about 5 wt. % in NW12 fibers. This anticipation is due to the fact that
322 the presence of NiWO₄ phase along with WO₃ has already been proven to be beneficial for HER
323 [1]. However, large over potentials are registered for NW12-O, 220 mV and 240 mV in acidic and
324 alkaline media respectively. The over potential for NW12-O in 0.5M H₂SO₄ is in fact greater than
325 that reported for pristine WO₃ fibers. A possible explanation for this is the morphology of NW12-
326 O. At high temperatures, the crystal size increases and the fiber morphology changes to a string
327 made from randomly shaped particles as could be seen in Figures 5 and 7. This can be attributed
328 to a higher calcination temperature of 800°C used for the as-spun fibers. The NW12 over
329 potentials (82mV and 60mV in 0.5M H₂SO₄ and 0.1M KOH respectively) and Tafel slopes (55.0
330 mV/dec and 39.9 mV/dec in 0.5M H₂SO₄ and 0.1M KOH respectively) reported in this work are
331 quite similar to the ones previously reported in [1]. This is due to a similar electrochemical setup,
332 together with similar mass loadings used.

333 An over potential of 40mV is observed for NW12-Ar. This is much lower compared to the over
334 potential for NW12-O, signifying the presence of WO_{2.9} phase in the fiber which is stipulated to
335 play a critical role in the electrocatalytic activity for HER. Likewise, a low over potential of 50 mV
336 is registered for NW12-Ar in 0.1M KOH electrolyte compared to 60 mV for NW12. However, a
337 greater Tafel slope of 45 mV/dec is observed for NW12-Ar compared to 39.9 mV/dec for NW12
338 fibers. Nevertheless, there is not a significant difference between the two values. It should be
339 noted that different values of overpotentials and Tafel slopes are registered for the same material
340 in the two different electrolytes due to the difference in kinetics [1, 13].

341 Literature studies reported over potentials and Tafel slopes of various electrocatalysts in
342 different electrolyte media with different mass loadings [44, 45]. Hence, a direct comparison with

343 the literature data becomes difficult due to overall different working cell conditions and
344 electrode preparations. In this study, 0.1 mg/cm² mass loading for the catalyst was used, which
345 was similar to the one in our previous reported study [1] on mixed nickel-tungsten oxide and pure
346 WO₃ and NiO electrospun fibers for HER in 0.5M H₂SO₄ and 0.1M KOH. Mass loading of catalyst
347 indeed plays a crucial role as a higher mass loading usually leads to greater current [12]. The
348 WO_{2.9} nano particles for HER in acidic media [33] gave an over potential of 70 mV and a Tafel
349 slope of 50 mV/dec with a mass loading of 0.285 mg/cm². Many of the phosphide electrocatalysts
350 such as FeP [46] and CoP [47] have also reported to register low over potentials. For example,
351 CoP nanowires gave an overpotential of about 38mV and a Tafel slope of 51 mV/dec in acidic
352 media. However, the mass loading utilized was 0.92 mg/cm². Similarly, FeP nanoparticles [46]
353 gave overpotential of 55 mV in acidic media with a mass loading of 3.2 mg/cm² which is quite
354 higher than the one reported in this study. The low over potentials and Tafel slopes of NW12-Ar
355 fibers in both acidic and alkaline media attests to its potential for HER activity.

356 NW12-Ar also have good stability under longer times in both acidic and alkaline media, as shown
357 in Figure 9. Under an overpotential of 150 mV, the current density of the catalyst was seen to
358 increase initially with time, after which it maintained a constant value at -30 mA/cm² and -2.6
359 mA/cm² in 0.5M H₂SO₄ and 0.1M KOH respectively. The initial increase in current density is
360 attributed to the time dependent wetting of CNS, where the initial hydrophobicity of CNS,
361 decreases from 105° to 0° in 15 minutes [10].

362

363 The current study provides a further insight on mixed oxide fibrous materials and their change in
364 morphology upon post treatment, which is still limited in literature. Furthermore, it paves way
365 for synthesizing composite strings with the simple electrospinning technique whereby simple
366 post treatment steps can produce different compositions. Lastly, NW12-Ar can be further
367 explored for their potential applications besides electrocatalysis, such as in photoelectrochemical
368 reactions, similar to the way NW12 fibers were tested [42].

369

370

371

Table 2: Comparison of electrocatalytic parameters for NW12-Ar, NW12 and NW12-O.

<u>Material</u>	<u>0.5M H2SO4</u>		<u>Reference</u>
	Over potential (mV)	Tafel Slope (mV/dec)	
NW12	82	55.0	This work
NW12-O	220	70.1	This work
NW12-Ar	40	69.0	This work
WO₃	150	140.5	[1]
NiO	480	269.6	[1]
<u>0.1M KOH</u>			
	Over potential (mV)	Tafel Slope (mV/dec)	
NW12	60	39.9	This work
NW12-O	240	128.2	This work
NW12-Ar	50	45.0	This work
WO₃	270	134.8	[1]
NiO	410	258.4	[1]

372

373 5. Conclusion

374

375 Post treatment of electrospun WO₃- NiWO₄ fibers in an inert atmosphere at 800°C, produced
 376 WO₃-NiWO₄-WO_{2.9} composite strings. Morphology and structural characteristics were studied
 377 through various techniques. The change in morphology and composition brought about a change
 378 in the electrocatalytic properties of the nanocrystalline string altogether. When tested for HER,
 379 WO₃- NiWO₄-WO_{2.9} strings gave a low over potential in both acidic and alkaline media. The
 380 presence of WO_{2.9} phase was responsible for this improvement which was further confirmed by
 381 testing the as spun WO₃- NiWO₄ fibers calcined directly at 800°C under air. The fibers calcined at

382 800°C under air produced a higher percentage of NiWO₄ phase but it failed to register promising
383 electrocatalytic activity, hence attesting that WO_{2.9} indeed plays a crucial electrocatalytic role.

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391 **Conflicts of Interest**

392 None.

393 **References**

- 394
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