Iron and Manganese Codoped Cobalt Tungstates
Co$_{1-(x+y)}$Fe$_x$Mn$_y$WO$_4$ as Efficient Photoelectrocatalysts for Oxygen Evolution Reaction

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ABSTRACT: Photoelectrocatalysts are robust materials for the production of energy through different ways such as water splitting. Narrow optical band gaps and high overpotentials are limiting the development of photoelectrocatalysts. In this study, a series of Co$_{1-(x+y)}$Fe$_x$Mn$_y$WO$_4$ solid solutions of cobalt tungstate codoped with iron and manganese have been synthesized hydrothermally. The synthesized solid solutions have been characterized by powder XRD, UV−visible spectra, cyclic voltammetry (CV), and linear sweep voltammetry (LSV). They all crystallize in a wolframite-type monoclinic crystal system with space group $P_2_1/c$. Doping of iron and manganese leads to narrowing of the optical band gap of Co$_{1-(x+y)}$Fe$_x$Mn$_y$WO$_4$ from 2.60 to 2.04 eV. The electrocatalytic activity toward oxygen evolution reaction of all of the samples has been evaluated through LSV measurements. It is found that the sample named C5, which is codoped with manganese and iron, has the lowest onset potential and needs the lowest overpotential to attain the targeted 5 mA cm$^{-2}$ and standard 10 mA cm$^{-2}$ current densities as compared with all other synthesized samples. This study shows that the synthesized tungstates can be good candidates for the photoelectrocatalytic oxygen evolution reaction.

1. INTRODUCTION

Cost-effective and efficient energy production is the main concern of the modern age. The reason behind this is the huge consumption of finite reserves of fossil fuels. Therefore, it is necessary to find renewable resources for energy production. Among common methods, the electrochemical and photocatalytic reactions govern many systems such as fuel cells, metal air batteries, and water splitting systems. The main focus of these reactions is oxygen evolution reaction (OER), hydrogen evolution reaction (HER), oxygen reduction reaction (ORR), and photocatalytic water splitting. Visible-light-driven electrochemical water splitting is an outbreak for the production of energy from water. However, it is necessary to engineer and efficient materials that can govern both photocatalytic and electrocatalytic activities. To date, noble metal-based materials are considered the most efficient electrocatalysts for different reactions of water splitting. Although being highly expensive, noble metals are not promising for practical applications. On the other hand, earth-abundant transition metals and their oxides, hydroxides, and composites play a vital role in electrocatalysis. Extensive studies have been carried out on transition-metal tungstates due to their promising applications in various research areas such as photoluminescent materials, cathode materials, supercapacitors, microwave devices, multiferroics, and electrocatalysts. Particularly, transition-metal tungstates MWO$_4$ (M = Mn−Zn) with wolframite-type structures have gained much attraction because they show diverse catalytic properties driven by UV/visible light. These materials have been used in various applications such as water splitting, hydrodesulfurization, organic pollutant degradation. Theoretical studies show that CoWO$_4$, one of the transition-metal tungstates, can show high activities toward OER reactions. Other transition-metal tungstate materials showing direct band gap are reported to show a direct band gap near 2.20 eV. Other similar transition-metal tungstate materials showing direct band gap include MnWO$_4$. 

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with $E_p = 2.56$ eV, FeWO$_4$ with $E_p = 2.16$ eV, NiWO$_4$ with $E_p = 2.46$ eV, CuWO$_4$ with $E_p = 2.24$ eV, and ZnWO$_4$ with $E_p = 3.56$ eV.\textsuperscript{10,23} The smaller band gaps of catalysts make them able to absorb higher-wavelength light. This property thus makes catalysts active materials to utilize the major portion of the solar spectrum, in which the wavelength of radiations is high. Since the crystal structure of all members in MWO$_4$ (where M = Mn, Fe, Co, Ni, Cu, Zn) is similar, one transition metal can be doped with other transition metals, which in turn can tune the band gaps of the synthesized samples for better photoelectrochemical efficiency. For example, Han et al. doped cobalt in ZnWO$_4$, and the band gap is shifted from a higher value (3.56 eV) to a lower value (2.56 eV).\textsuperscript{22} In this article attempts were made to dope cobalt with iron and manganese using hydrothermal method. The synthesized samples were characterized to elucidate their structural, optical, and electrochemical properties. The band gap is shifted to lower values upon codoping of iron and manganese. The OER activity is also enhanced upon doping of iron and manganese. The details of these interesting findings are given below.

2. RESULTS AND DISCUSSIONS

2.1. Structural Evolution. Transition-metal tungstates synthesized by different methods almost show similar wolframite-type structures. The structural elucidation of the cobalt tungstate series was carried out using powder X-ray diffraction analysis. The XRD patterns of cobalt tungstates Co$_{1-(x+y)}$Fe$_x$Mn$_y$WO$_4$ which are named C1 to C5 (details are given in Experimental Section) are similar and can be indexed to monoclinic CoWO$_4$ with a wolframite-type structure with space group $P2_1/c$.\textsuperscript{24} having reference code number (JCPDS 15-0867) as shown Figure 1a. This implies that the structure of the solid solutions may be the same. Moreover, no impurity peaks were found in XRD patterns of all other samples in the series. It was found that the data can be refined with space group $P2_1/c$ and used as the beginning model for Rietveld refinement of the X-ray diffraction data of all other samples in the series. It was found that the data can be refined well with $R_p \leq 0.022$ and $R\beta \leq 0.012$.

The Rietveld refinement plots for the X-ray diffraction data of two selected samples, which are named C1 and C5, are shown in Figure 1b,c, and the refinement details are listed in Table 1. The occupancies of transition-metal ions that are doped in place of cobalt are given in footnotes to Table 1. A linear relationship between the unit cell volume and the concentration of $x + y$ can be seen in Figure 1d, which agrees
ionic radii of Fe$^{2+}$ (0.92 Å) and Mn$^{2+}$ (0.97 Å) in high spin state. Co$^{2+}$ is 0.88 Å in the high spin state. Co$^{2+}$ is replaced by Fe$^{2+}$ and Mn$^{2+}$, and the average six-coordinated ions, as described in the literature. CoWO$_4$ (C1) also alters the band gap. On the other hand, MnWO$_4$ and FeWO$_4$ show band gap values of about 2.5 and 2.16 eV, respectively. To further confirm that the synthesized samples are direct band gap semiconductors, eq 1 can be written as

$$\ln(\alpha h) = \ln A + m \ln(h - E_g)$$

where $\alpha$, $A$, and $E_g$ are constants, with $A$ being the absorption coefficient, $\alpha h$ the photonic energy, and $E_g$ the band gap. Here, $m$ exponent is a constant that reflects the nature of absorption, which is equal to $1/2$, $2$, $3/2$, or $3$ for direct allowed, indirect allowed, direct forbidden, and indirect forbidden transitions, respectively.

Different studies show that CoWO$_4$ found in amorphous and crystalline mesoporous and nonmesoporous forms displays a direct band gap $E_g$ of ~2.2~2.6 eV. The band gap increases just due to a change in the synthesis method of CoWO$_4$, which might result in defect creation in the samples. This implies that CoWO$_4$ synthesized by different methods may have variations in oxygen occupancies, which alters the band gap. On the other hand, MnWO$_4$ and FeWO$_4$ show band gap values of ~2.5 and 2.16 eV, respectively.

To further confirm that the synthesized samples are direct band gap semiconductors, eq 1 can be written as

$$\ln(\alpha h) = \ln A + m \ln(h - E_g)$$

Here, $m$ is the slope of the ln(\(\alpha h\)) vs ln(\(h - E_g\)) curve. The value of $E_g$ is determined by plotting d(ln(\(\alpha h\)))/d(h) vs \(h\). The strongest peaks observed in the particular energy values give a good approximation of the optical band gap $E_g$. As shown in Figure 3b, two values of $E_g$ are evidenced for each composition as $E_g1$ and $E_g2$ at ~1.88 and ~2.35 eV, respectively, which are used to find the values of $m$ from ln(\(\alpha h\)) vs ln(\(h - E_g\)) curves. Figure 4 shows that the linear fit of these curves always gives the same slope value near 0.5, which confirms that these materials show direct allowed band gaps.

Thus, the graph of (\(\alpha h\))^2 against photon energy $h$ is plotted to find the direct band gap of the samples. The optical band gaps have been determined by extrapolation of the linear portion of the (\(\alpha h\))^2 peaks to zero. Again, two values of $E_g$ are evidenced for each composition as $E_g1$ and $E_g2$, as shown in Figure 4.
The $E_g1$ values (shown in Figure 5a) are large first absorption bands, which are related to transition from oxygen anion to metallic cation. The $E_g2$ values are the smallest absorption bands ranging from 1.6 to 1.81 eV can be related to the $d-d$ energy transition between two metal cations. The $E_g1$ values are shown in Figure 5b, which is an expanded part of Figure 5a at lower energy ($h\nu$). The $E_g2$ values are shown in Figure 5b. Figure 5b at lower energy ($h\nu$). The $E_g1$ values are actually the representative band gap ($E_g$) values of cobalt tungstates. The estimated direct band gap ($E_g$) of CoWO$_4$ is 2.60 eV, which is in good agreement with the literature.\textsuperscript{10b} The band gap of the solid solutions Co$_{1-(x+y)}$Fe$_x$Mn$_y$WO$_4$ decreases with $x$ and $y$. Exceptionally, the smallest band gap of 2.04 eV is observed for sample C2, where 50% cobalt has been replaced with iron.\textsuperscript{10b} The band gap of the solid solutions Co$_{1-(x+y)}$Fe$_x$Mn$_y$WO$_4$ decreases with $x$ and $y$. Exceptionally, the smallest band gap of 2.04 eV is observed for sample C2, where 50% cobalt has been replaced with iron.\textsuperscript{10b} A comparison of band gaps ($E_g$) of synthesized samples and band gaps of similar kinds of tungstates is given in Table 2. This comparison indicates that the studied samples show a narrowing of band gap through codoping of iron and manganese with cobalt in CoWO$_4$. It is surprising that the doping of iron with cobalt decreases the band gap exceptionally to a lower value that is not found in any tungstate until now. This is mainly attributed to the mixing of 3d orbitals of cobalt and iron. Similarly, small band gaps of 2.1 and 2.2 eV have been observed for samples C4 and C5. This implies that the synthesized materials can be used as potential photocatalysts for water splitting and organic pollutant degradation.

**2.3. Electrochemical Properties.** The theoretical studies show that CoWO$_4$ should behave as an efficient electrocatalyst toward water splitting.\textsuperscript{20} However, the experimental studies show that CoWO$_4$ gives an overpotential of 810 mV to achieve the standard 10 mA cm$^{-2}$ current density.\textsuperscript{10b} The overpotential of CoWO$_4$ has been lowered by making a composite of CoWO$_4$ with Ni and graphitic carbon.\textsuperscript{16} Similarly, an overpotential of 400 mV to achieve the standard 10 mA cm$^{-2}$ current density has been observed for manganese-doped cobalt tungstate.\textsuperscript{29} Therefore, the electrochemical properties of as-synthesized samples toward the oxygen evolution reaction (OER) were studied by linear sweep voltammetry (LSV). The LSV curves are represented in Figure 6a. From LSV curves, it was observed that all of the synthesized samples successfully evolved oxygen via water splitting. Sample C5 showed the lowest onset potential toward the oxygen evolution reaction (OER) as compared to all other synthesized samples. For comparison, the overpotential that is required to achieve a current density of 5 mA cm$^{-2}$ was considered, which is represented by Figure 6b. It was observed that sample C5 required a very small overpotential of 410 mV to achieve 5 mA cm$^{-2}$ as compared with sample C1 ($\eta_5 = 550$ mV), sample C2 ($\eta_5 = 590$ mV), sample C3 ($\eta_5 = 580$ mV), and sample C4 ($\eta_5 = 490$ mV). It was further observed that samples C1, C4, and C5 were able to reach the standard 10 mA cm$^{-2}$ current density among all samples. Figure 6c represents that sample C5 needs only 460 mV overpotential to reach the 10 mA cm$^{-2}$ current density as compared to sample C1 ($\eta_{10} = 580$ mV) and sample C4 ($\eta_{10} = 540$ mV). This indicates that sample C5 has the greatest catalytic activity toward the oxygen evolution reaction (OER) with the lowest value of onset potential and it
generates the maximum current density and requires the lowest overpotential to reach 5 and 10 mA cm\(^{-2}\) current densities, respectively (Table 3).

To further understand the superior OER activity of sample C5, the Tafel plot was derived from measured LSV curves using eq 4.

\[ \eta = \alpha + b \log j \] (4)

where \(\eta\) is the overpotential, \(j\) is the current density, and \(b\) is the Tafel slope. Figure 6d represents the Tafel plot. The lowest Tafel slope (83 mV dec\(^{-1}\)) of sample F among the prepared samples indicated that it had the fastest electron transfer and was kinetically more favorable as compared to other samples. Figure 7 shows the basic mechanism of water splitting. In the case of the oxygen evolution reaction in basic

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Table 2. Comparison of Band Gaps of Synthesized Samples with Similar Kinds of Reported Tungstates\(^a\)

| catalyst         | synthesis method       | band gap \(E_g\) (eV) | references |
|------------------|------------------------|------------------------|------------|
| CoWO\(_4\)       | dissolution reaction   | 2.20                   | 10b        |
| CoWO\(_4\)       | coprecipitation reaction | 2.68               | 10c        |
| MnWO\(_4\)       | dissolution reaction   | 2.56                   | 10b        |
| NiWO\(_4\)       | dissolution reaction   | 2.46                   | 10b        |
| NiWO\(_4\)       | coprecipitation reaction | 2.95               | 10c        |
| CuWO\(_4\)       | dissolution reaction   | 2.24                   | 10b        |
| CuWO\(_4\)       | coprecipitation reaction | 2.41               | 10c        |
| ZnWO\(_4\)       | dissolution reaction   | 3.56                   | 10b        |
| FeWO\(_4\)       | hydrothermal           | 2.16                   | 23         |
| Zn\(_{1-x}\)Co\(_x\)WO\(_4\) (0≤x≤1) | hydrothermal           | 3.56–3.61             | 22         |
| α-Ag\(_{2-x}\)Zn\(_x\)WO\(_4\) (0≤x≤0.25) | hydrothermal           | 3.18–3.08             | 27         |
| C1               | hydrothermal           | 2.60                   | this work  |
| C2               | hydrothermal           | 2.04                   | this work  |
| C3               | hydrothermal           | 2.52                   | this work  |
| C4               | hydrothermal           | 2.10                   | this work  |
| C5               | hydrothermal           | 2.21                   | this work  |

\(^a\)The \(E_g\) values for synthesized samples taken in this comparison are the \(E_g^1\) values.

Table 3. Comparison of OER Activities of Synthesized Samples with Different Reported Materials

| catalyst         | onset potential (V) | over potential (mV) | tafel slope (mV dec\(^{-1}\)) | references |
|------------------|---------------------|---------------------|-------------------------------|------------|
| CoWO\(_4\)       | 810                 | 107                 | 28                            |            |
| CoMoO\(_4\)      | 765                 | 110                 | 28                            |            |
| 21 wt % W CoMoO\(_4\) | 680                 | 106                 | 28                            |            |
| CoWO\(_4\)/GC    | 388                 | 84                  | 29                            |            |
| CoWO\(_4\)/Ni    | 336                 | 84                  | 29                            |            |
| C5                | 1.6                 | 400                 | 84                            | this work  |

To further understand the superior OER activity of sample C5, the Tafel plot was derived from measured LSV curves using eq 4.

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Figure 6. (a) LSV curves, (b) overpotential required for 5 mA cm\(^{-2}\), (c) overpotential required for 10 mA cm\(^{-2}\), and (d) Tafel plot.
medium, which is half-reaction of water splitting and takes place at the anode, a four-step mechanism is proposed for oxygen evolution on the surface of the working electrode. During oxygen evolution, three crucial intermediates (MOH, MO, and MOOH) are formed,\(^3\) as shown in Figure 7a.

\[
\begin{align*}
M + OH^- &\rightarrow MOH \\
MOH + OH^- &\rightarrow MO + H_2O \\
MO + OH^- &\rightarrow MOOH + e^- \\
MOOH &\rightarrow M + O_2 + H^+ 
\end{align*}
\]

This indicates that on the surface of the anode evolution of oxygen gas and formation of H\(^+\) take place. H\(^+\) ions are transferred to the counter electrode via the electrolyte, where they undergo reduction and evolution of hydrogen gas takes place, as shown in Figure 7b. Abundant bubbling of oxygen and hydrogen gases is also observed on surfaces of the working electrode and counter electrode, respectively.

3. CONCLUSIONS

In this article, highly efficient iron and manganese codoped cobalt tungstate electrocatalysts Co\(_{1-x}\)Fe\(_x\)Mn\(_y\)WO\(_4\) have been reported. Single-phase iron and manganese codoped tungstates have been successfully synthesized by a hydrothermal method. Codoping of iron and manganese has increased charge separation and reduced the band gap under visible light irradiation. This indicates that the synthesized tungstates can be used as potential catalysts under visible light. An increase in electrocatalytic activity toward OER has been reported. Single-phase iron and manganese codoped electrocatalysts have shown better OER activity.

4. EXPERIMENTAL SECTION

The samples comprising the nominal chemical formula (Co\(_{1-x}\)Fe\(_x\)Mn\(_y\)WO\(_4\)) have been prepared using the hydrothermal method. The details of concentrations of metals in the nominal formula (Co\(_{1-x}\)Fe\(_x\)Mn\(_y\)WO\(_4\)) are given in the footnotes of Table 1. In a typical reaction, which is carried out for the synthesis of cobalt tungstate CoWO\(_4\), 2 mmol (0.477 g) CoCl\(_2\)-6H\(_2\)O and 2 mmol (0.6598 g) Na\(_2\)WO\(_4\)-2H\(_2\)O were dissolved in 10 mL of distilled water by continuous magnetic stirring for 10 min at room temperature. An acidic buffer solution was added to the above mixture to maintain the pH of the mixture at 5. This gives acidic nature to the reaction mixture. After that, the reaction mixture was poured into a stainless steel autoclave and heated at 160 °C in a muffle furnace for 24 h followed by slow cooling to attain room temperature. The powder product obtained from heat treatment was first washed with deionized water and then with analytical-grade ethanol to remove the impurities from the samples. The samples were centrifuged instead of filtering through filter paper to get maximum yield and to avoid the percolation of tiny particles of samples in the pores of the filter paper. The moisture content was eliminated by drying the samples at 60 °C for 24 h in air. A similar experimental process mentioned above for the synthesis of cobalt tungstate CoWO\(_4\) was utilized for the synthesis of the samples in the series of Co\(_{1-x}\)Fe\(_x\)Mn\(_y\)WO\(_4\). For this purpose, the stoichiometric amounts of salts of iron (FeSO\(_4\)) and manganese (MnCl\(_2\)-4H\(_2\)O) were added to cobalt tungstate and heated at 160 °C in the muffle furnace for 24 h followed by slow cooling to attain room temperature. The powder product was washed and centrifuged. The synthesized samples were subjected to different characterizations (Scheme 1).

Scheme 1. Schematic Diagram for the Synthesis of Co\(_{1-x}\)Fe\(_x\)Mn\(_y\)WO\(_4\)

The powder X-ray diffraction (PXRD) data were collected on a PANalytical X’Pert\(^3\) Powder diffractometer with Cu Kα (\(\lambda = 0.15405\) nm and \(\lambda = 0.15443\) nm) radiation (2θ range, 5–120° for 2 h; step, 0.0131) at 40 kV, 40 mA, and room temperature. The powder X-ray diffraction (PXRD) data were analyzed by refinement of the data using the Rietveld method\(^3\) with the help of GSAS software.\(^5\) The lattice parameters and unit cell volumes were calculated from the refinement of the PXRD data. The surface morphology of the materials was analyzed by SEM analysis using a SEM.

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The Tafel slope. The measurement was performed at a scan rate of 5 mV s\(^{-1}\). Glassy carbon is used for OER in 1 M aqueous KOH solution as the electrolyte. The RHE potential range was 1.0–1.82 V. The onset potential of the samples was calculated at 10 mA cm\(^{-2}\) current density. All of the potential data were converted into the reversible hydrogen electrode (RHE) potential by the following equation

\[
E_{\text{RHE}} = E_{\text{Ag/AgCl}}/\text{Sat. KCl} + 0.059 \text{pH} + 0.197
\]

The overpotential (\(\eta\)) of OER was calculated by the following equation

\[
\eta = E_{\text{RHE}} - 1.23
\]

The Tafel plot was used to calculate the Tafel slope by the following equation

\[
\eta = a + b \log j
\]

where \(\eta\) is the overpotential, \(j\) is the current density, and \(b\) is the Tafel slope.

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**Notes**

The authors declare no competing financial interest.

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