Supporting Information

Cobalt Tungsten Oxide Hydroxide Hydrate (CTOHH) on DNA Scaffold: an Excellent Bi-functional Catalyst for Oxygen Evolution Reaction (OER) and Aromatic Alcohol Oxidation

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This file contains 36 pages in which the details of materials used in the electrode fabrication, fabrication of electrodes and instruments used for various characterizations are available. Supplementary figures include XRD, XPS, TEM, FE-SEM, EDS, elemental mapping, FT-IR, EDLC plots, Surface concentration calculation, surface concentration plots, general procedure for recycling, 1H NMR data, 13C NMR data of aromatic carbonyl compounds and comparison table for organic catalysis.
Materials and Instruments used for characterization and OER studies

Cobalt acetate (Co(Ac)$_2$), sodium tungstate were purchased from Sigma-Aldrich. Double-stranded Deoxyribonucleic acid (DNA) from Herring Testes with a base pair of around 50 k was obtained from Alfa-Aesar and used as received. The electrochemical analyzer AUT-86853 was used for all electrochemical characterizations. The UV-Visible (UV-Vis) absorption spectra were recorded in a Unico (model 4802) UV-Vis-NIR spectrophotometer equipped with a 1 cm quartz cuvette holder for liquid samples. The Fourier Transform Infrared (FT-IR) spectroscopy analysis was done with the model Nexus 670 (FT-IR), Centaurms 10X (Microscope) having spectral Range 4,000 to 400 cm$^{-1}$ with a MCT-B detector. The Hg/HgO reference and Pt counter electrodes were procured from CH instruments. Morphological characterizations was analyzed by HR-TEM, (Tecnai$^{TM}$ G$^2$ TF20) working at an accelerating voltage of 200 kV. Millipore water was used in electrochemical analysis. The XRD analysis was done with a scanning rate of 1° min$^{-1}$ in the 2$\theta$ range 10-90° using a Bruker X-ray powder diffractometer (XRD) with Cu K$_\alpha$ radiation ($\lambda = 0.154$ nm). X-ray photoelectron spectroscopic (XPS) analysis was performed using ESCALAB 250XI base system with UPS and XPS image mapping having Al K$\alpha$ as monochromatic X-ray source (Thermo Scientific, UK). FE-SEM analysis was performed using SUPRA 55VP, Gemini Column with air lock system (Carl Zeiss, Germany). The Scanning Electron Microscope (SEM) analysis as done with Tescan VEGA 3 SBH instrument with BrukerEasy EDS attached setup.

Materials and Methods for organic reactions

The alcohols 1a, 2a, 3a, 5a, 6a, 3c and deuterated solvents were purchased from Sigma Aldrich and 4a and 7a were purchased from TCI Chemicals and were used without purification. The alcohols 1c, 2c, 4c and 5c were prepared from corresponding carbonyl compounds. $^1$H and $^{13}$C NMR spectra were recorded on Bruker Avance-400 instrument and data given in the supporting information.
Figure S1. The XRD analysis of (a) CoWO₄ on DNA scaffold and (b) CoWO₄.
**Figure S2.** The high resolution spectra of (a) P 2p and (b) N 1s present in the synthesized CTOHH-DNA.
Figure S3. (a, b) TEM micrographs of CTOHH at high and low magnifications, (c, d) HR-TEM micrographs of CTOHH at high and low magnifications, (e) SAED pattern of CTOHH.
Figure S4. (a, b) TEM micrographs of CoWO$_4$ on DNA scaffold at high and low magnifications, (c) SAED pattern of CoWO$_4$ on DNA scaffold, (d, e) TEM micrographs of CoWO$_4$ at high and low magnifications, (f) SAED pattern of CoWO$_4$. 
Figure S5. (a,b) FE-SEM micrographs of CoWO$_4$ on DNA scaffold at high and low magnifications; (c,d) FE-SEM micrographs of CoWO$_4$ at high and low magnifications.
Figure S6. EDS analysis of (a) CTOHH-DNA and (b) CTOHH.
Figure S7. Elemental color mapping of CTOHH-DNA shows Cobalt (Co), Tungsten (W), Oxygen (O), Carbon (C) and Phosphorous (P).
Figure S8. FT-IR spectrum of only DNA (a) and chain-like CoWO$_4$ nanomaterials on DNA scaffold (b).
Figure S9. CVs of (a) CTOHH-DNA, (b) CTOHH, (c) CoWO$_4$ on DNA scaffold and (d) CoWO$_4$ for 2 $C_{dl}$ calculation.
**Determination of Surface concentration from the redox features of CV:**

Calculated area associated with the reduction of Co$^{3+}$ to Co$^{2+}$ for CTOHH-DNA = $1.16 \times 10^{-3}$ VA

Hence, the associated charge is $= \frac{1.16 \times 10^{-3} \text{VA}}{0.025 \text{Vs}^{-1}}$

$= 46.40 \text{ As}$

$= 46.40 \text{ C}$

Now, the number of electron transferred is $= \frac{46.40 \text{ C}}{1.602 \times 10^{-19} \text{ C}}$

$= 2.89 \times 10^{17}$

Since, the reduction of Co$^{3+}$ to Co$^{2+}$ is a single electron transfer reaction, the number electron calculated above is exactly the same as the number of surface active sites.

Hence.

The surface concentration of Co that participated in OER is $= 2.89 \times 10^{17}$

Similarly, we calculated remaining electrodes also.
Figure S10. CVs of (a) CTOHH-DNA, (b) CTOHH, (c) CoWO$_4$ on DNA scaffold and (d) CoWO$_4$ showing the area of redox features considered for the calculation of number of surface active sites.
Figure S11. (a-d) are the Post OER SEM images of CTOHH-DNA from lower to higher magnification respectively.
Figure S12. (a-c) are the Post OER HR-TEM images of CTOHH-DNA from lower to higher magnification respectively; (d) is the SAED pattern.
Table S1. Comparative loading of catalysts by comparing with the added active materials, PVDF and NMP for slurry preparation.

<table>
<thead>
<tr>
<th>S.No</th>
<th>Catalyst taken</th>
<th>Catalyst added mg</th>
<th>PVDF taken mg</th>
<th>NMP added μL</th>
<th>Final loading of the catalyst mg/cm²</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>CTOHH</td>
<td>1.3</td>
<td>0.3</td>
<td>15</td>
<td>1.4</td>
</tr>
<tr>
<td>2</td>
<td>CTOHH-DNA</td>
<td>1.2</td>
<td>0.3</td>
<td>15</td>
<td>1.3</td>
</tr>
</tbody>
</table>
Table S2: Substrate scope of oxidation of secondary benzyl alcohols to ketones.\(^a\)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Alcohols</th>
<th>Aldehydes</th>
<th>Yields(^b) (%)</th>
<th>Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="1c.png" alt="Image" /></td>
<td><img src="1d.png" alt="Image" /></td>
<td>87</td>
<td>91</td>
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<tr>
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<td><img src="5d.png" alt="Image" /></td>
<td>66</td>
<td>69</td>
</tr>
</tbody>
</table>

\(^a\)Reaction condition: Alcohol (0.75 mmol), CTOHH-DNA (50 mg) and K$_2$CO$_3$ (2 equiv.) in 0.5 mL toluene at 110 °C under O$_2$ (1 atm). \(^b\)Isolated yield.
Table S3: Comparison of our catalyst with other catalysts in terms of reaction conditions, oxidizing agent and recyclability.\textsuperscript{1-6}

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reaction conditions (solvent, temperature, time)</th>
<th>Oxidizing agent</th>
<th>Recyclability</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEMPO/H\textsubscript{5}PV\textsubscript{2}Mo\textsubscript{10}O\textsubscript{40}</td>
<td>Acetone, 100 °C, 18 h</td>
<td>O\textsubscript{2} (2 atm)</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>2,6-diisopropylphenyl/Coordinated Gold(1) Complex</td>
<td>Toluene, 90 °C, 10 h</td>
<td>O\textsubscript{2}</td>
<td>-</td>
<td>2</td>
</tr>
<tr>
<td>Vanadium Complex</td>
<td>DCE, 60 °C, 24 h, NEt\textsubscript{3}</td>
<td>O\textsubscript{2}</td>
<td>-</td>
<td>3</td>
</tr>
<tr>
<td>Polymer-incarcerated Gold nanocluster</td>
<td>BTF/H\textsubscript{2}O (1:1), RT, 5 h</td>
<td>O\textsubscript{2} (1 atm)</td>
<td>7 Times</td>
<td>4</td>
</tr>
<tr>
<td>V\textsubscript{2}O\textsubscript{5}</td>
<td>Toluene, K\textsubscript{2}CO\textsubscript{3} (3 equiv.), 100 °C, 13 h</td>
<td>O\textsubscript{2}</td>
<td>-</td>
<td>5</td>
</tr>
<tr>
<td>Fe-nano catalyst @SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3}</td>
<td>Solvent free, 120 °C, 24 h</td>
<td>TBHP</td>
<td>9 Times</td>
<td>6</td>
</tr>
<tr>
<td>CTOHH-DNA</td>
<td>Toluene, K\textsubscript{2}CO\textsubscript{3} (2 equiv.), 110 °C, 24 h</td>
<td>O\textsubscript{2} (1 atm)</td>
<td>5 Times</td>
<td>This work</td>
</tr>
</tbody>
</table>
General procedure for reusability test

Initial first cycle of the reaction was carried out by above mentioned procedure, thus aromatic alcohols (0.75 mmol) were taken in a 15 mL pressure tube containing 50 milligram of catalyst and K$_2$CO$_3$ (2 equivalents) in 0.5 mL of toluene. The reaction was degassed with nitrogen and pressurized by oxygen with 1 atmosphere. The resulting mixture was allowed to stir for 24 hours at 110 ºC. After completion of the reaction, catalyst was filtered and washed twice with ethyl acetate. The combined organic solvent was evaporated under reduced pressure and purified by column chromatography. The residual catalyst was dried under vacuum and reused for next cycle.

(D) Analytical data of Aromatic aldehydes

(1) 4-Methoxybenzaldehyde (1b)

![Structure of 4-Methoxybenzaldehyde]

The compound was obtained as colorless oil and obtained by an oxidation of (4-methoxyphenyl)methanol following general oxidation protocol. The obtained title compound matches with literature data $^7$.

$^1$H NMR (400 MHz, CDCl$_3$, 24 ºC): $\delta$ 9.88 (s, 1H), 7.83 (d, $J$ = 8.80 Hz, 2H), 6.99 (d, $J$ = 8.77 Hz, 2H), 3.88 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$, 24 ºC): $\delta$ 190.94, 164.75, 132.11, 130.11, 114.45, 55.70.

(2) 4-Methylbenzaldehyde (2b)

![Structure of 4-Methylbenzaldehyde]

The compound was obtained as colorless oil and obtained by an oxidation of (4-methylphenyl)methanol following general oxidation protocol. The obtained title compound matches with literature data $^8$.

$^1$H NMR (400 MHz, CDCl$_3$, 24 ºC): $\delta$ 9.94 (s, 1H), 7.75 (d, $J$ = 7.71 Hz, 2H), 7.30 (d, $J$ = 7.54 Hz, 2H), 2.41 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$, 24 ºC): $\delta$ 191.96, 155.52, 134.19, 129.81, 129.69, 21.81.

(3) 3-bromobenzaldehyde (3b)

![Structure of 3-bromobenzaldehyde]
The compound was obtained as light brown liquid and obtained by an oxidation of (3-bromophenyl)methanol following general oxidation protocol. The obtained title compound matches with literature data.  

\[ \text{H NMR (400 MHz, CDCl}_3\text{, 24 °C):} \delta 9.94 \text{ (s, 1H), 7.98 \text{ (s, 1H), 7.80-7.78 (m, 1H), 7.74-7.72 (m, 1H), 7.42-7.38 (m, 1H);} \]
\[ \text{C NMR (100 MHz, CDCl}_3\text{, 24 °C):} \delta 190.80, 138.08, 137.37, 132.41, 130.72, 128.46, 123.45. \]

(4) 3,4-Hydroxybenzaldehyde (4b)

The compound was obtained as light brown solid and obtained by an oxidation of 4-(hydroxymethyl)benzene-1,2-diol following general oxidation protocol. The obtained title compound matches with literature data.  

\[ \text{H NMR (400 MHz, DMSO-d}_6\text{, 24 °C):} \delta 10.79 \text{ (bs, 2H), 9.90 \text{ (s, 1H), 7.52 \text{ (d, J = 8.56 Hz, 1H), 6.41-6.38 (m, 1H), 6.33 \text{ (s, 1H);} \]
\[ \text{C NMR (100 MHz, CDCl}_3\text{, 24 °C):} \delta 191.14, 165.23, 163.31, 132.99, 115.25, 108.69, 102.25. \]

(5) 3-nitrobenzaldehyde (5b)

The compound was obtained as orange solid and obtained by an oxidation of (3-nitrophenyl)methanol following general oxidation protocol. The obtained title compound matches with literature data.  

\[ \text{H NMR (400 MHz, CDCl}_3\text{, 24 °C):} \delta 10.11-10.08 \text{ (m, 1H), 8.69-8.63 (m, 1H), 8.48-8.42 (m, 1H), 8.23-8.20 (m, 1H), 7.78-7.76 (m, 1H);} \]
\[ \text{C NMR (100 MHz, CDCl}_3\text{, 24 °C):} \delta 189.99, 189.86, 148.80, 137.47, 134.91, 134.78, 130.54, 130.50, 128.66, 128.62, 124.51, 124.32. \]
(6) 4-formylbenzonitrile (6b)

The compound was obtained as white solid and obtained by an oxidation of 4-(hydroxymethyl)benzonitrile following general oxidation protocol. The obtained title compound matches with literature data 11.

$^1$H NMR (400 MHz, CDCl$_3$, 24 °C): $\delta$ 9.98 (s, 1H), 7.88 (d, $J = 7.91$ Hz, 2H), 7.74 (d, $J = 7.95$ Hz, 2H);
$^{13}$C NMR (100 MHz, CDCl$_3$, 24 °C): $\delta$ 190.76, 138.82, 133.00, 129.99, 117.83, 117.68.

(7) 4-(Dimethylamino)benzaldehyde (7b)

The compound was obtained as white solid and obtained by an oxidation of (4-(dimethylamino)phenyl)methanol following general oxidation protocol. The obtained title compound matches with literature data 12.

$^1$H NMR (400 MHz, CDCl$_3$, 24 °C): $\delta$ 9.68-9.65 (m, 1H), 7.68-7.66 (m, 2H), 6.64-6.62 (m, 2H), 3.00 (s, 6H);
$^{13}$C NMR (100 MHz, CDCl$_3$, 24 °C): $\delta$ 190.11, 190.04, 154.25, 131.81, 124.98, 124.94, 110.88, 39.91, 39.88.

(E) Analytical data of ketones

(1) 1-(2-methoxyphenyl)ethanone (1d)

The compound was obtained as yellow liquid and obtained by an oxidation of 1-(2-methoxyphenyl)ethanol following general oxidation protocol. The obtained title compound matches with literature data 13.

$^1$H NMR (400 MHz, CDCl$_3$, 24 °C): $\delta$ 7.71-7.69 (m, 1H), 7.45-7.41 (m, 1H), 6.95-6.31 (m, 2H), 3.88-3.84 (m, 3H), 2.59-2.56 (m, 3H);
$^{13}$C NMR (100 MHz, CDCl$_3$, 24 °C): $\delta$ 199.89, 158.94, 133.71, 130.32, 128.25, 120.53, 111.63, 55.48, 31.82.
(2) 1-(2-bromophenyl) ethanone (2d)

The compound was obtained as white solid and obtained by an oxidation of 1-(2-bromophenyl)ethanol following general oxidation protocol. The obtained title compound matches with literature data\textsuperscript{14}.

$^1$H NMR (400 MHz, CDCl$_3$, 24 °C): $\delta$ 7.61-7.59 (m, 1H), 7.47-7.45 (m, 1H), 7.38-7.34 (m, 1H), 7.31-7.27 (m, 1H), 2.62 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$, 24 °C): $\delta$ 201.36, 141.48, 133.88, 131.85, 128.96, 127.50, 118.92, 30.35.

(3) 1-(4-chlorophenyl)ethanone (3d)

The compound was obtained as white solid and obtained by an oxidation of 1-(4-chlorophenyl)ethanol following general oxidation protocol. The obtained title compound matches with literature data\textsuperscript{15}.

$^1$H NMR (400 MHz, CDCl$_3$, 24 °C): $\delta$ 7.82 (d, $J = 8.12$ Hz, 2H), 7.36 (d, $J = 8.00$, 2H), 2.52 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$, 24 °C): $\delta$ 196.72, 139.48, 135.42, 129.70, 128.8, 26.49.

(4) 1-(4-hydroxyphenyl) ethanone (4d)

The compound was obtained as white solid and obtained by an oxidation of 4-(1-hydroxyethyl)phenol following general oxidation protocol. The obtained title compound matches with literature data\textsuperscript{16}.

$^1$H NMR (400 MHz, CDCl$_3$, 24 °C): $\delta$ 8.51 (bs, 1H), 7.92-7.90 (m, 2H), 6.97-6.95 (m, 2H), 2.59 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$, 24 °C): $\delta$ 199.25, 161.88, 131.43, 129.40, 115.75, 26.37.
(5) 1-(4-nitrophenyl)ethanone(5d)

The compound was obtained as pale yellow solid and obtained by an oxidation of 1-(4-nitrophenyl)ethanol following general oxidation protocol. The obtained title compound matches with literature data 17.

$^1$H NMR (400 MHz, CDCl$_3$, 24 °C): $\delta$ 8.25 (d, $J = 8.12$ Hz, 2H), 8.07 (d, $J = 8.20$ Hz, 2H), 2.64 (s, 3H);

$^{13}$C NMR (100 MHz, CDCl$_3$, 24 °C): $\delta$ 196.40, 150.36, 141.44, 129.35, 123.86, 26.99.
(F) $^1$H and $^{13}$C NMR spectra of aldehydes

**Figure S13.** $^1$H NMR spectrum of 4-methoxybenzaldehyde, 1b recorded in CDCl$_3$ (400 MHz)

**Figure S14.** $^{13}$C NMR spectrum of 4-methoxybenzaldehyde, 1b recorded in CDCl$_3$ (100 MHz)
Figure S15. $^1$H NMR spectrum of 4-methylbenzaldehyde, 2b recorded in CDCl$_3$ (400 MHz)

Figure S16. $^{13}$C NMR spectrum of 4-methylbenzaldehyde, 2b recorded in CDCl$_3$ (100 MHz)
Figure S18. $^1$H NMR spectrum of 3-bromobenzaldehyde, 3b recorded in CDCl$_3$ (400 MHz)

Figure S17. $^{13}$C NMR spectrum of 3-bromobenzaldehyde, 3b recorded in CDCl$_3$ (100 MHz)
**Figure S19.** $^1$H NMR spectrum of 3,4-dihydroxybenzaldehyde, 4b recorded in CDCl$_3$ (400 MHz)

**Figure S20.** $^{13}$C NMR spectrum of 3,4-dihydroxybenzaldehyde, 4b recorded in CDCl$_3$ (100 MHz)
Figure S21. $^1$H NMR spectrum of 3-nitrobenzaldehyde, 5b recorded in CDCl$_3$ (400 MHz)

Figure S22. $^{13}$H NMR spectrum of 3-nitrobenzaldehyde, 5b recorded in CDCl$_3$ (100 MHz)
Figure S23. $^1$H NMR spectrum of 4-formylbenzonitrile, 6b recorded in CDCl$_3$ (400 MHz)

Figure S24. $^{13}$C NMR spectrum of 4-formylbenzonitrile, 6b recorded in CDCl$_3$ (100 MHz)
Figure S25. $^1$H NMR spectrum of 4-(dimethylamino)benzaldehyde, 7b recorded in CDCl$_3$ (400 MHz)

Figure S26. $^{13}$C NMR spectrum of 4-(dimethylamino)benzaldehyde, 7b recorded in CDCl$_3$ (100 MHz)
(G) $^1$H and $^{13}$C NMR spectra of ketones

Figure S27. $^1$H NMR spectrum of 1-(2-methoxyphenyl)ethanone, 1d recorded in CDCl$_3$ (400 MHz)

Figure S28. $^{13}$C NMR spectrum of 1-(2-methoxyphenyl)ethanone, 1d recorded in CDCl$_3$ (100 MHz)
Figure S29. $^1$H NMR spectrum of 1-(2-bromophenyl)ethanone, 2d recorded in CDCl$_3$ (400 MHz)

Figure S30. $^{13}$C NMR spectrum of 1-(2-bromophenyl)ethanone, 2d recorded in CDCl$_3$ (100 MHz)
Figure S31. $^1$H NMR spectrum of 1-(4-chlorophenyl)ethanone, 3d recorded in CDCl$_3$ (400 MHz)

Figure S32. $^{13}$C NMR spectrum of 1-(4-chlorophenyl)ethanone, 3d recorded in CDCl$_3$ (100 MHz)
Figure S33. $^1$H NMR spectrum of 1-(4-hydroxyphenyl)ethanone, 4d recorded in CDCl$_3$ (400 MHz)

Figure S34. $^{13}$C NMR spectrum of 1-(4-hydroxyphenyl)ethanone, 4d recorded in CDCl$_3$ (100 MHz)
Figure S35. $^1$H NMR spectrum of 1-(4-nitrophenyl)ethanone, 5d recorded in CDCl$_3$ (400 MHz)

Figure S36. $^{13}$C NMR spectrum of 1-(4-nitrophenyl)ethanone, 5d recorded in CDCl$_3$ (100 MHz)
References


