

**Supporting Information:**

**Bimetallic cyclic redox couple in di-manganese copper oxide supported by nickel borate for boosted alkaline electrocatalytic oxygen evolution reaction**

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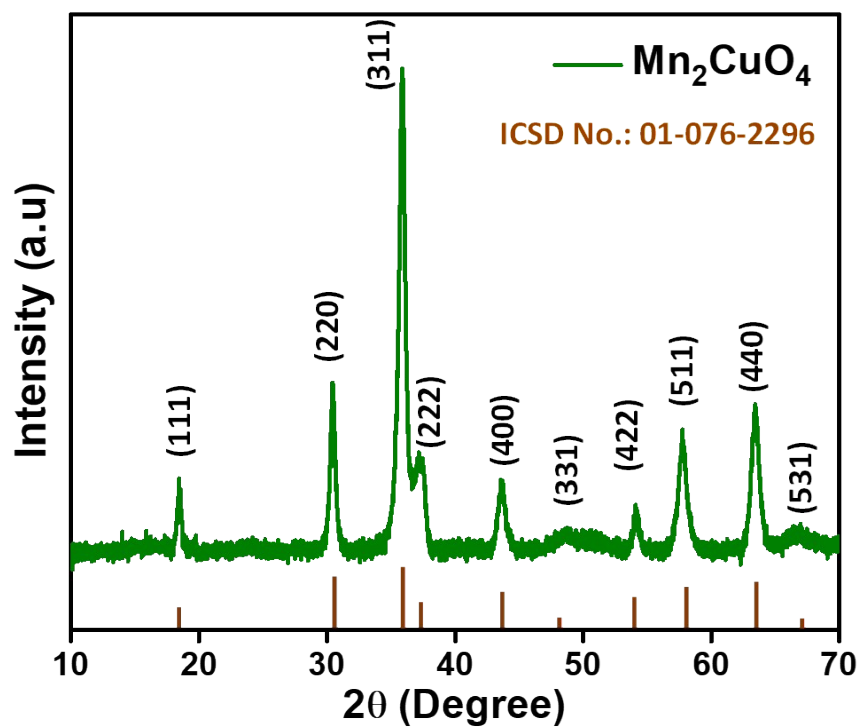
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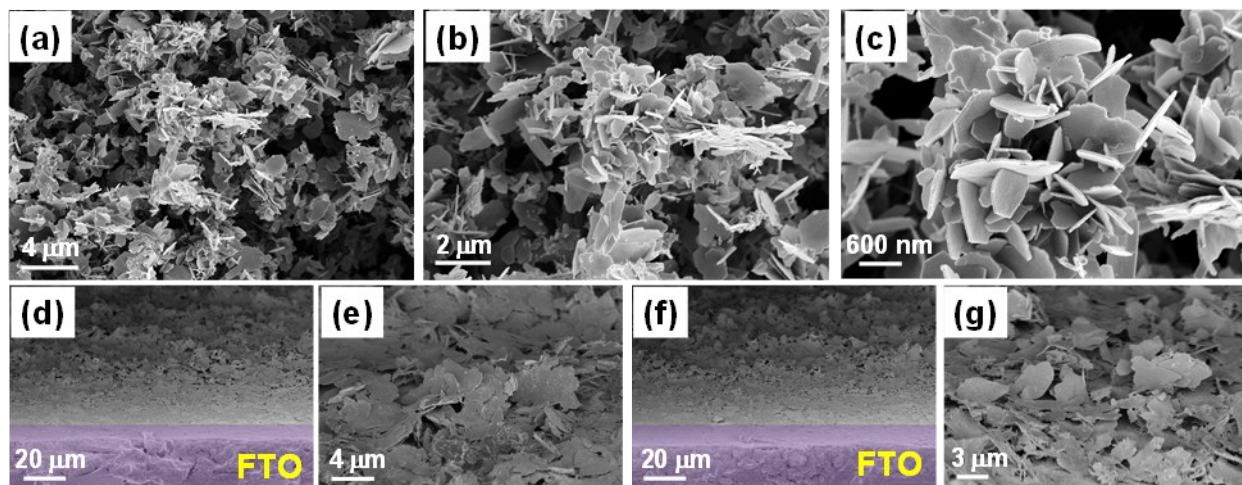
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## Materials Characterization

X-ray diffraction measurement was accomplished using a Rigaku Smartlab X-ray diffractometer with copper  $K_{\alpha}$  ( $\lambda=1.54 \text{ \AA}$ ) as source with 9 kW power. XRD patterns were recorded from  $2\theta$  ( $10 - 70^{\circ}$ ) keeping the scan rate fix at  $4^{\circ} \text{ s}^{-1}$ . To determine the morphological features of the samples, field emission scanning electron microscopy (FESEM) analysis was carried out using a Zeiss (model-Gemini and Sigma) instrument operated at 5kV. A JEOL (JEM-2100F) transmission electron microscope with an operating voltage of 200 kV was used for field emission transmission electron microscopy (FETEM) analysis of the samples. A CH Instruments model CHI760E, Inc., Austin, TX, was used to record the cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). Gas chromatography (GC) (Model-7820A, Agilent Technologies) was used to measure the evolved gasses and to calculate faradaic efficiency.

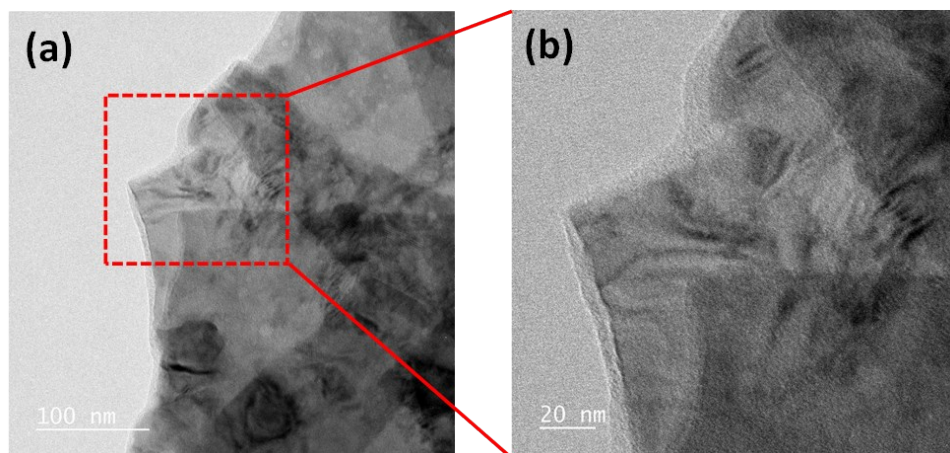


**Figure S1.** PXRD of the synthesized  $\text{Mn}_2\text{CuO}_4$  powder with all the peaks indexable to the cubic phase of di-manganese copper oxide (ICSD No. 01-076-2296)

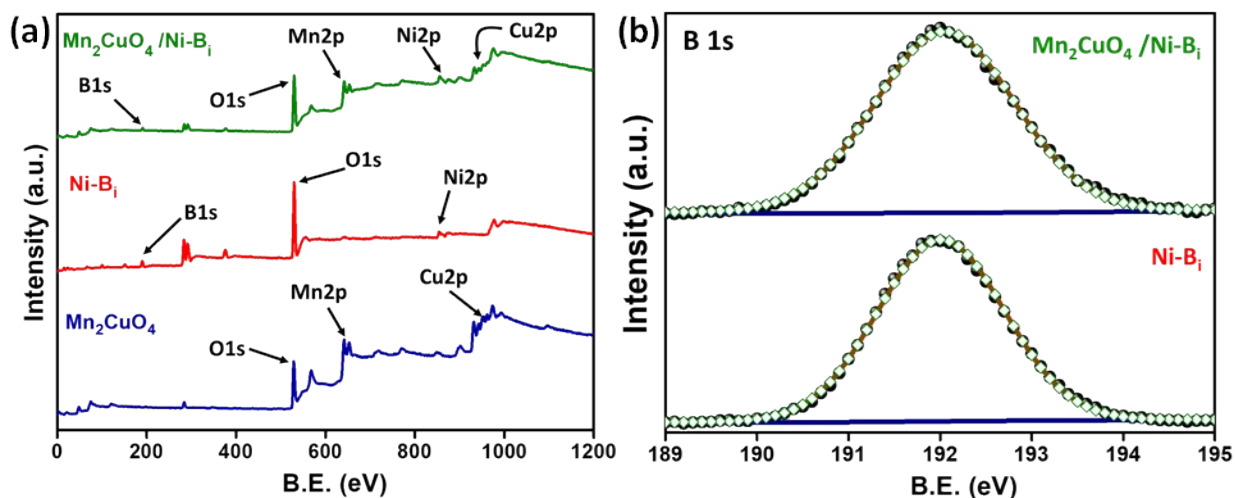


**Figure S2.** (a-c) FESEM images of the synthesized  $\text{Mn}_2\text{CuO}_4$  powder, cross-sectional view of the fabricated electrode of (d, e) bare  $\text{Mn}_2\text{CuO}_4$ , and (f, g)  $\text{Mn}_2\text{CuO}_4/\text{Ni-Bi}$

From the figure, it is clear that the morphology of the catalyst is intact upon the fabrication of bare and modified electrocatalyst over FTO.

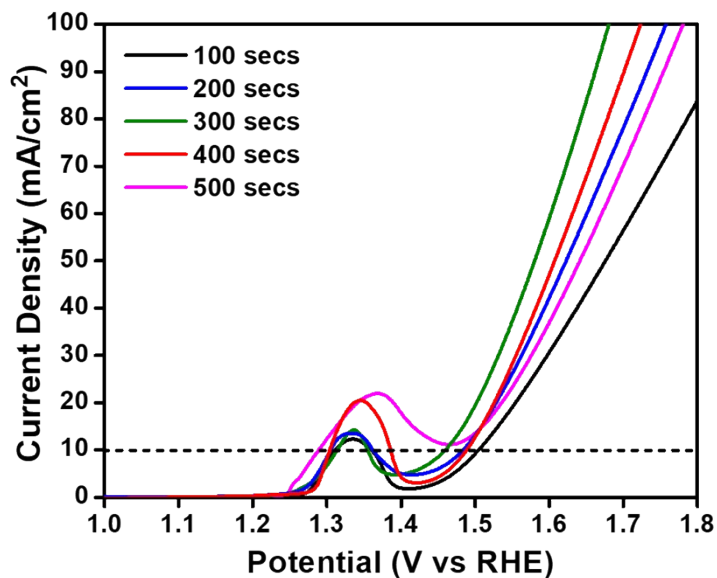


**Figure S3.** FETEM images of the composite  $\text{Mn}_2\text{CuO}_4/\text{Ni-B}_i$  showing the uniform deposition of nickel borate over the surface



**Figure S4.** (a) XPS survey spectra of  $\text{Mn}_2\text{CuO}_4$ ,  $\text{Ni-B}_i$ , and  $\text{Mn}_2\text{CuO}_4/\text{Ni-B}_i$  confirming the presence of all the respective elements, (b) 1s core-level spectra of boron for  $\text{Ni-B}_i$  and  $\text{Mn}_2\text{CuO}_4/\text{Ni-B}_i$

The XPS survey spectra (Fig. S4 (a)) of  $\text{Mn}_2\text{CuO}_4$ ,  $\text{Ni-B}_i$ , and  $\text{Mn}_2\text{CuO}_4/\text{Ni-B}_i$  shows the presence of the respective elements in the compounds. The 1s core-level spectra of boron are shown in Fig. S4 (b). The peak at a binding energy of 192.01 eV is for bare nickel borate, and for the composite,  $\text{Mn}_2\text{CuO}_4/\text{Ni-B}_i$ , the peak is shifted to 192.05 eV.<sup>1,2</sup> The shift in the peak position towards higher binding energy is due to the interaction of nickel borate with di-manganese copper oxide.



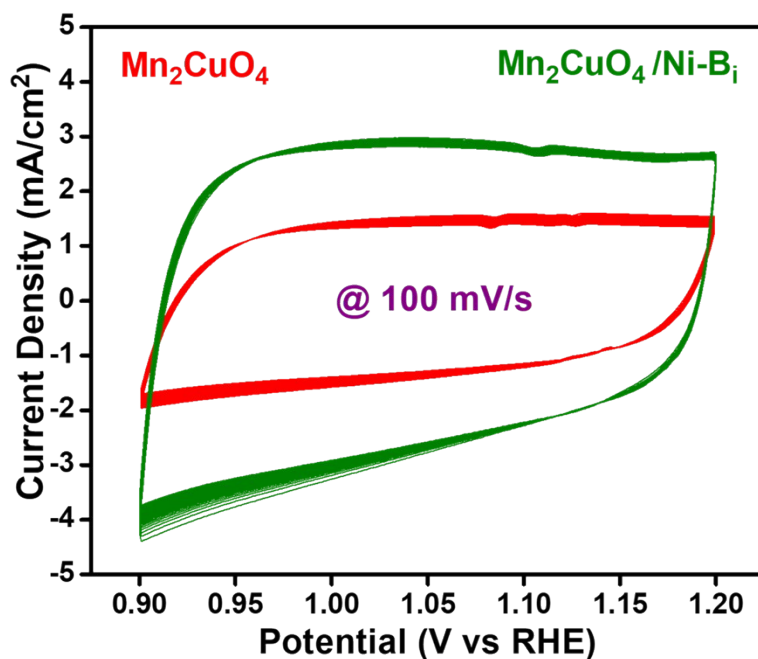
**Figure S5.** Linear sweep voltammograms (LSV) of  $\text{Mn}_2\text{CuO}_4/\text{Ni-B}_i$  for the optimization of nickel borate deposition over the  $\text{Mn}_2\text{CuO}_4$  surface

As can be seen from the figure, the performance of the electrocatalyst is dependent on the time of deposition of  $\text{Ni-B}_i$  over the  $\text{Mn}_2\text{CuO}_4$  surface. The optimum deposition time is found out to be 5 min (300 sec). The excessive deposition of  $\text{Ni-B}_i$  overcrowds the surface leading to the decrease in the active surface area for the catalytic reaction, henceforth the performance decreases with the increase in the deposition time (400 sec and 500 sec).

**Table S1.** The charge transfer resistance ( $R_{ct}$ ) values obtained by fitting the Nyquist plots

| Potential<br>(vs RHE) | Condition         | Compound                                            | $R_{ct}$ ( $\Omega$ ) |
|-----------------------|-------------------|-----------------------------------------------------|-----------------------|
| 1.5 V                 | Before cross-over | Mn <sub>2</sub> CuO <sub>4</sub> /Ni-B <sub>i</sub> | <b>144.9</b>          |
|                       |                   | RuO <sub>2</sub>                                    | 97.24                 |
| 1.55 V                | At cross-over     | Mn <sub>2</sub> CuO <sub>4</sub> /Ni-B <sub>i</sub> | 48.3                  |
|                       |                   | RuO <sub>2</sub>                                    | 49.54                 |
| 1.6 V                 | After cross-over  | Mn <sub>2</sub> CuO <sub>4</sub> /Ni-B <sub>i</sub> | <b>13.15</b>          |
|                       |                   | RuO <sub>2</sub>                                    | 23.47                 |





**Figure S6.** CV plots of 1000 cycles for testing the durability of  $\text{Mn}_2\text{CuO}_4$  and  $\text{Mn}_2\text{CuO}_4/\text{Ni-B}_i$  measured at a scan rate of 100 mV/s

From Fig. S6, it can be inferred that the durability of both bare  $\text{Mn}_2\text{CuO}_4$  and modified  $\text{Mn}_2\text{CuO}_4/\text{Ni-B}_i$  is high even after a continuous run of 1000 cycles. The high stability of both the catalyst is due to the self-healing redox cycle of bimetallic Cu and Mn in di-manganese copper oxide and Ni in nickel borate.

**Table S2.** Comparison between the recently developed electrocatalysts

| Catalyst                                                         | Electrolyte           | Overpotential<br>(mV) at specific<br>current density | Tafel slope<br>(mV/dec) | Reference        |
|------------------------------------------------------------------|-----------------------|------------------------------------------------------|-------------------------|------------------|
| <b>Mn<sub>2</sub>CuO<sub>4</sub></b>                             | <b>1M NaOH</b>        | <b>420 @ 10 mA/cm<sup>2</sup></b>                    | <b>104</b>              | <b>This work</b> |
| <b>Mn<sub>2</sub>CuO<sub>4</sub> /Ni-B<sub>i</sub></b>           | <b>1M NaOH</b>        | <b>230 @ 10 mA/cm<sup>2</sup></b>                    | <b>56</b>               | <b>This work</b> |
| Ni-B <sub>i</sub> /CC                                            | 0.1M K-B <sub>i</sub> | 470 @ 10 mA/cm <sup>2</sup>                          | 107                     | S1               |
| Ni-B <sub>i</sub> -P <sub>i</sub> /CC                            | 0.1M K-B <sub>i</sub> | 440 @ 10 mA/cm <sup>2</sup>                          | 139                     | S2               |
| IrO <sub>2</sub>                                                 | 0.1M KOH              | 450 @ 10 mA/cm <sup>2</sup>                          | 83                      | S3               |
| RuO <sub>2</sub>                                                 | 0.5M KOH              | 425 @ 10 mA/cm <sup>2</sup>                          | 55                      | S4               |
| Mn <sub>2</sub> O <sub>3</sub>                                   | 1M KOH                | 270 @ 10 mA/cm <sup>2</sup>                          | 85                      | S5               |
| Mn <sub>3</sub> O <sub>4</sub> -CoMn <sub>2</sub> O <sub>4</sub> | 0.1M KOH              | 310 @ 10 mA/cm <sup>2</sup>                          | 81                      | S6               |
| Co(PO <sub>3</sub> ) <sub>2</sub>                                | 0.1M NaPi             | 440 @ 8 mA/cm <sup>2</sup>                           | 74                      | S7               |
| Co <sub>3</sub> O <sub>4</sub>                                   | 0.1M KOH              | 400 @ 10 mA/cm <sup>2</sup>                          | 49                      | S8               |
| Mn <sub>x</sub> Co <sub>3-x</sub> O <sub>4</sub>                 | 0.1M KOH              | 350 @ 10 mA/cm <sup>2</sup>                          | 85                      | S9               |
| CoFe <sub>2</sub> O <sub>4</sub>                                 | 0.1M KOH              | 370 @ 10 mA/cm <sup>2</sup>                          | 82                      | S10              |
| MnCo <sub>2</sub> O <sub>4</sub>                                 | 1M KOH                | 327 @ 10 mA/cm <sup>2</sup>                          | 79                      | S11              |
| Mn <sub>2</sub> CoO <sub>4</sub>                                 | 1M KOH                | 399 @ 10 mA/cm <sup>2</sup>                          | 79                      | S11              |
| CuCo <sub>2</sub> O <sub>4</sub>                                 | 0.5M KOH              | 327 @ 10 mA/cm <sup>2</sup>                          | 74                      | S12              |
| NiCo <sub>2</sub> O <sub>4</sub>                                 | 0.1M KOH              | 320 @ 10 mA/cm <sup>2</sup>                          | 87                      | S12              |
| V-doped Co <sub>3</sub> O <sub>4</sub>                           | 1M KOH                | 294 @ 10 mA/cm <sup>2</sup>                          | 53                      | S13              |
| V-doped NiFe <sub>2</sub> O <sub>4</sub>                         | 1M KOH                | 270 @ 10 mA/cm <sup>2</sup>                          | 42                      | S13              |
| Co-B <sub>i</sub>                                                | 0.5M K-B <sub>i</sub> | 285 @ 10 mA/cm <sup>2</sup>                          | 166                     | S14              |

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