

## Supporting Information

### An advanced sandwich-type architecture of MnCo<sub>2</sub>O<sub>4</sub>@N-C@MnO<sub>2</sub> as an efficient electrode material for a high-energy density hybrid asymmetric solid-state supercapacitor

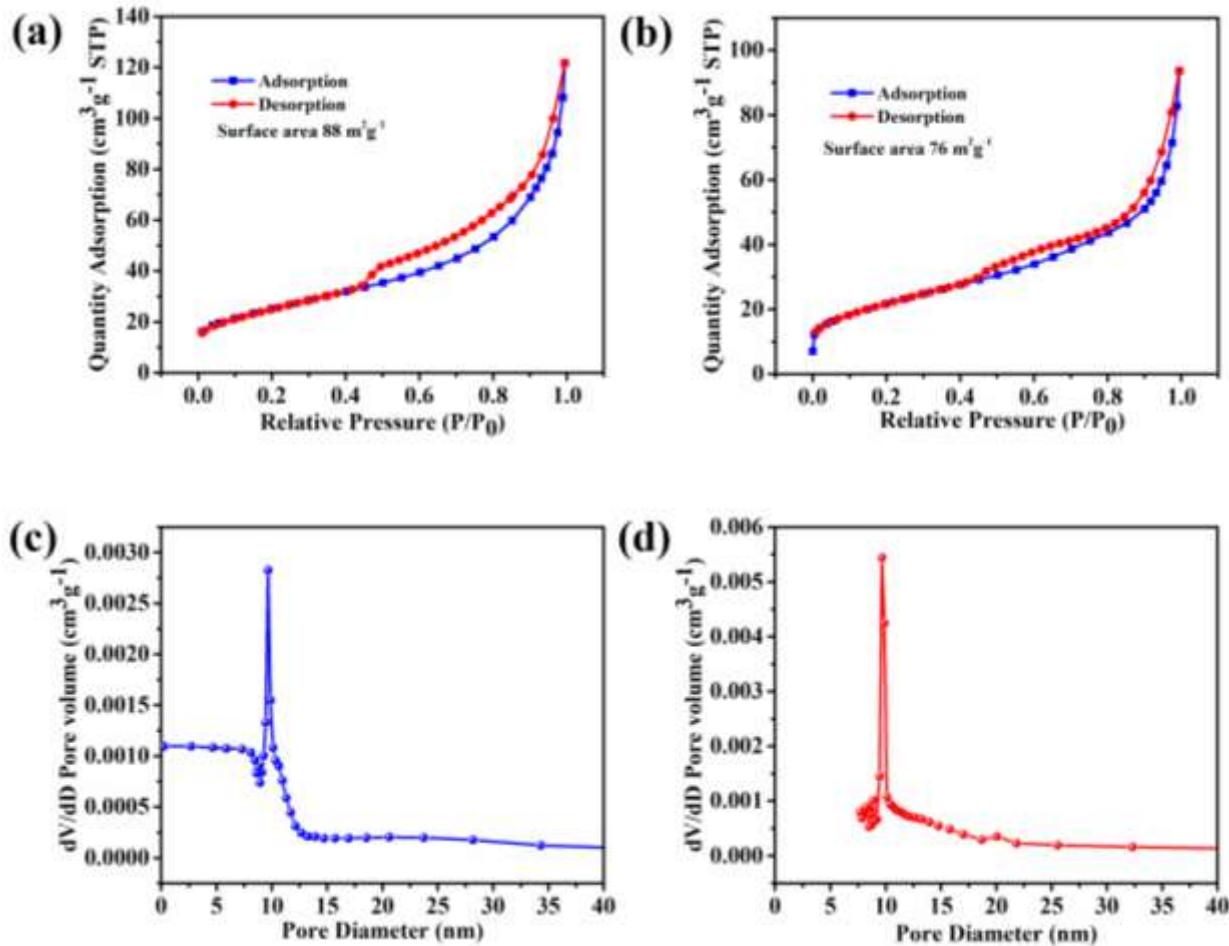
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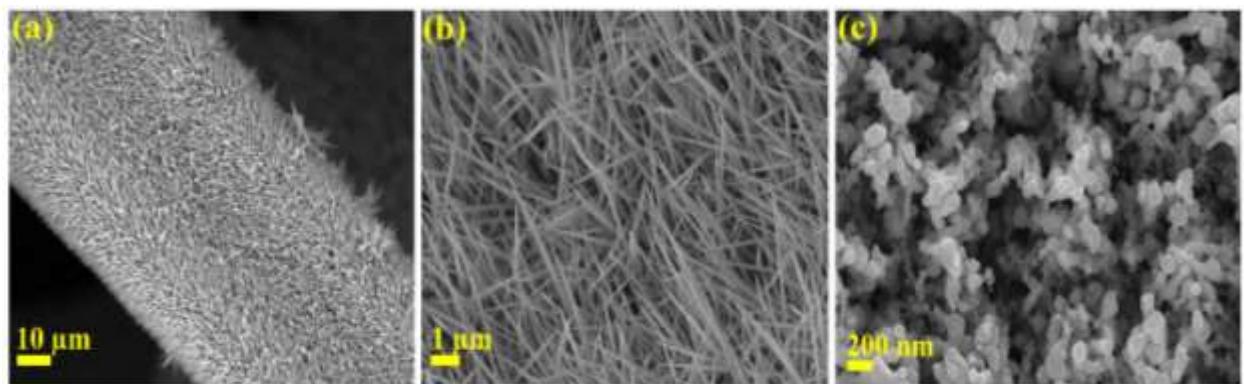
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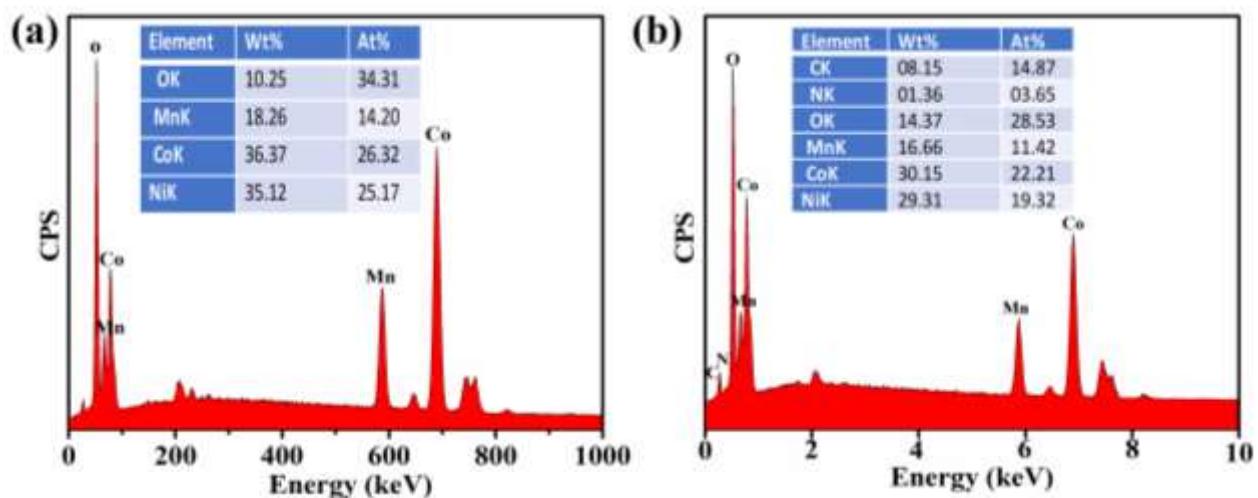
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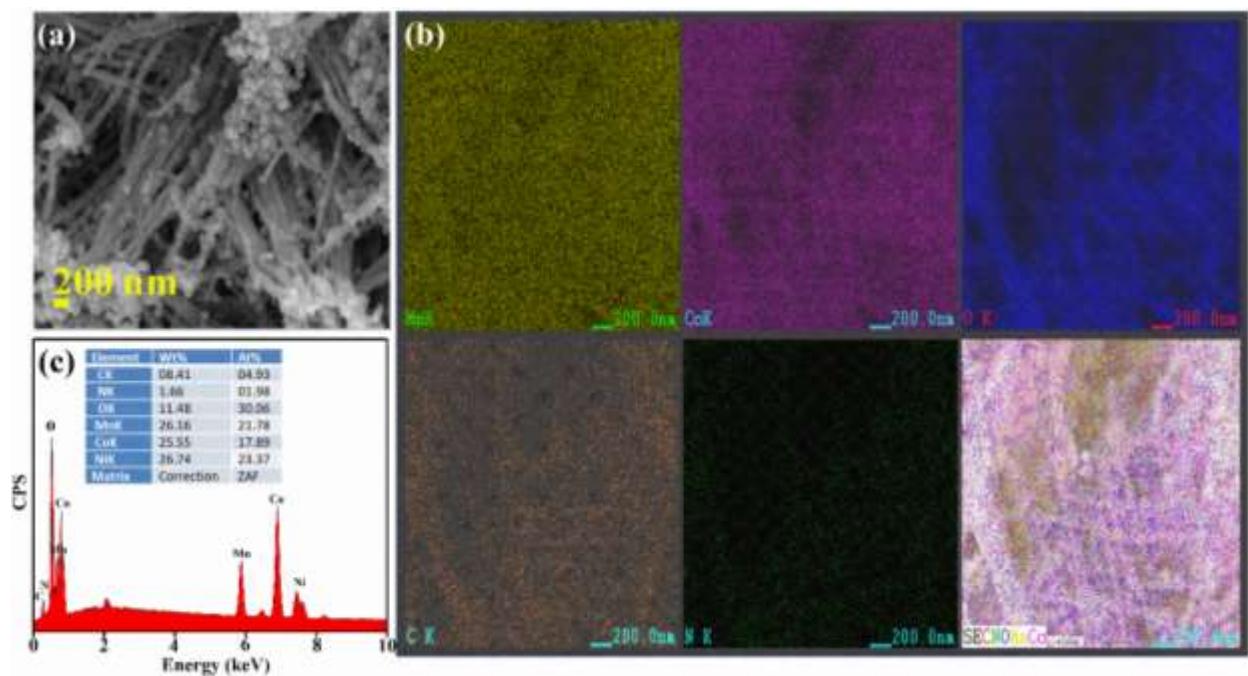
**Figure S1.** N<sub>2</sub> adsorption-desorption isotherm of (a) MnCo<sub>2</sub>O<sub>4</sub>@N-C, (b) MnCo<sub>2</sub>O<sub>4</sub> and Pore size distribution (c) MnCo<sub>2</sub>O<sub>4</sub>@N-C, (d) MnCo<sub>2</sub>O<sub>4</sub>.



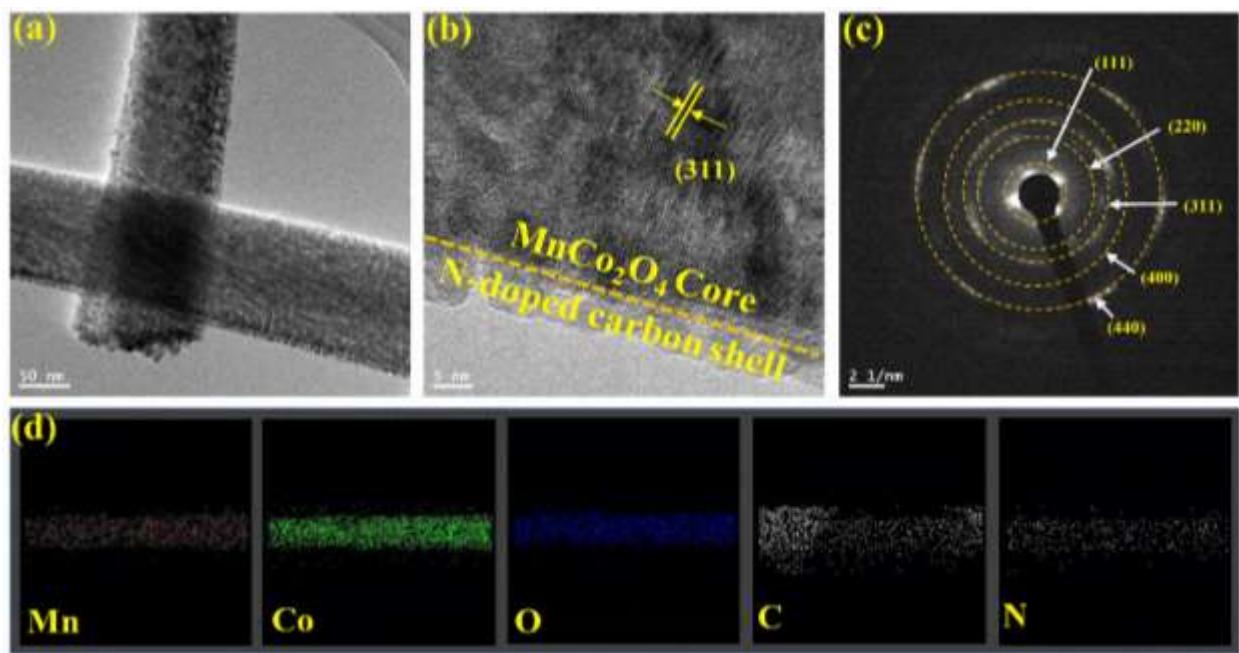
**Figure S2.** Low and high magnification FE-SEM images of (a and b)  $\text{MnCo}_2\text{O}_4$  calcined under argon atmosphere (c)  $\text{MnCo}_2\text{O}_4$  calcined under air atmosphere.



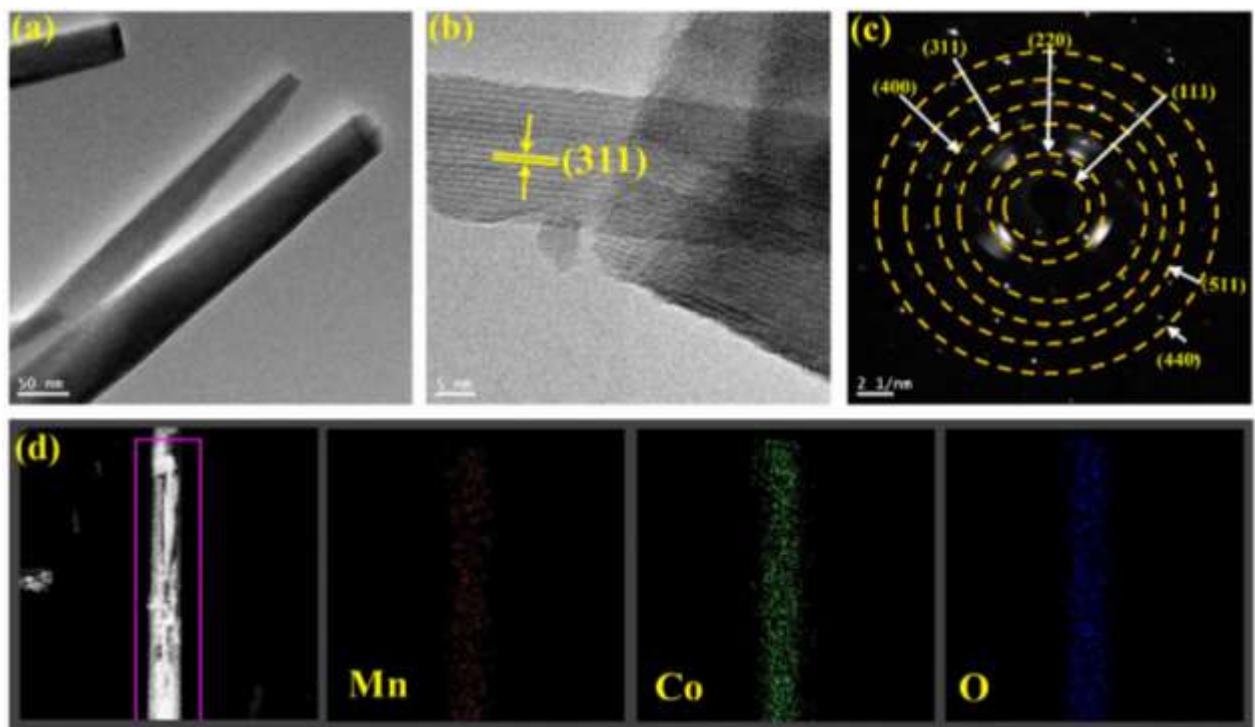
**Figure S3.** EDAX spectra of (a) MnCo<sub>2</sub>O<sub>4</sub> nanowire (b) MnCo<sub>2</sub>O<sub>4</sub>@N-C core@shell.



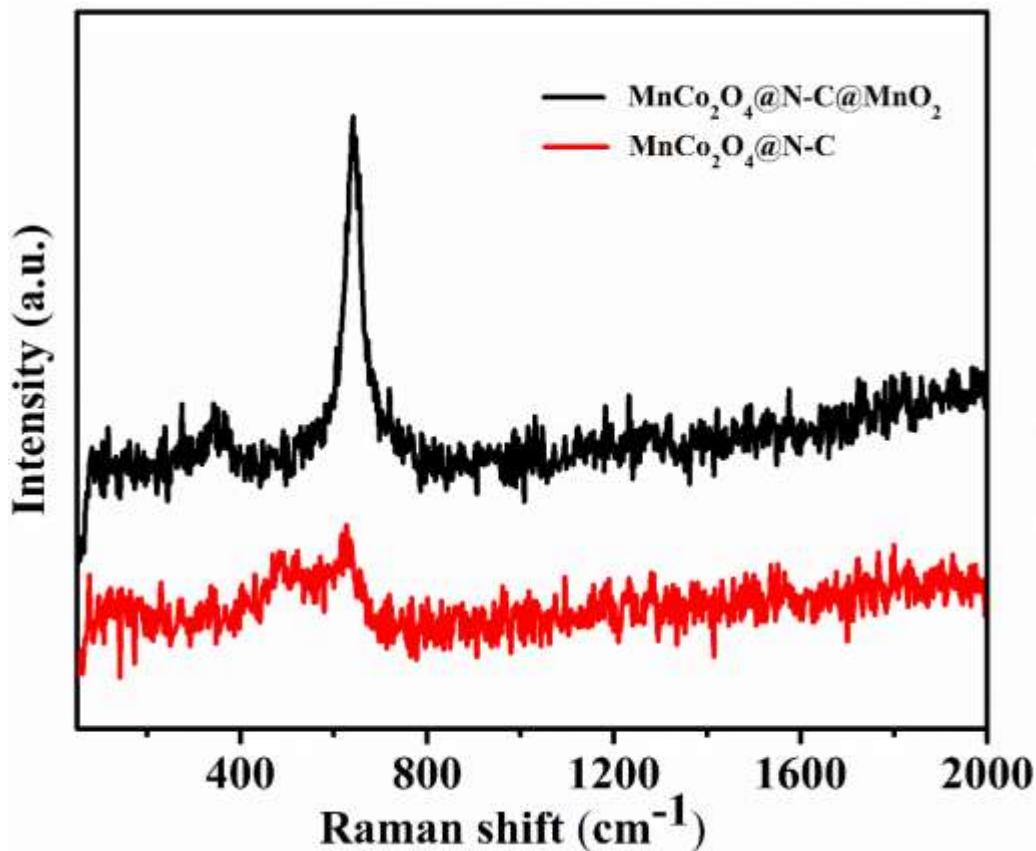
**Figure S4.** (a and b) The Color mapping spectra (c) EDAX of MnCo<sub>2</sub>O<sub>4</sub>@N-C@MnO<sub>2</sub> nanowire.



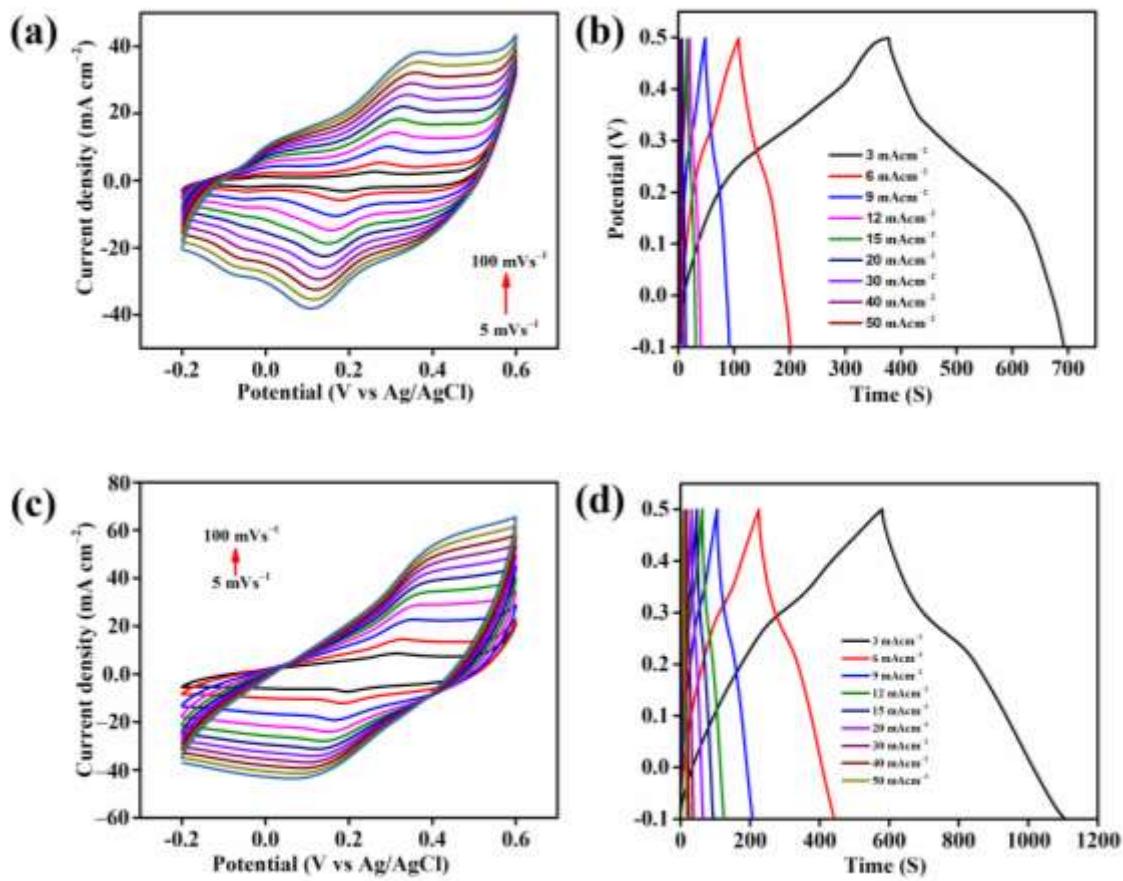
**Figure S5.** (a and b) High magnification HR-TEM, (c) SAED pattern and (d) color mapping of  $MnCo_2O_4$ @N-C core@shell.



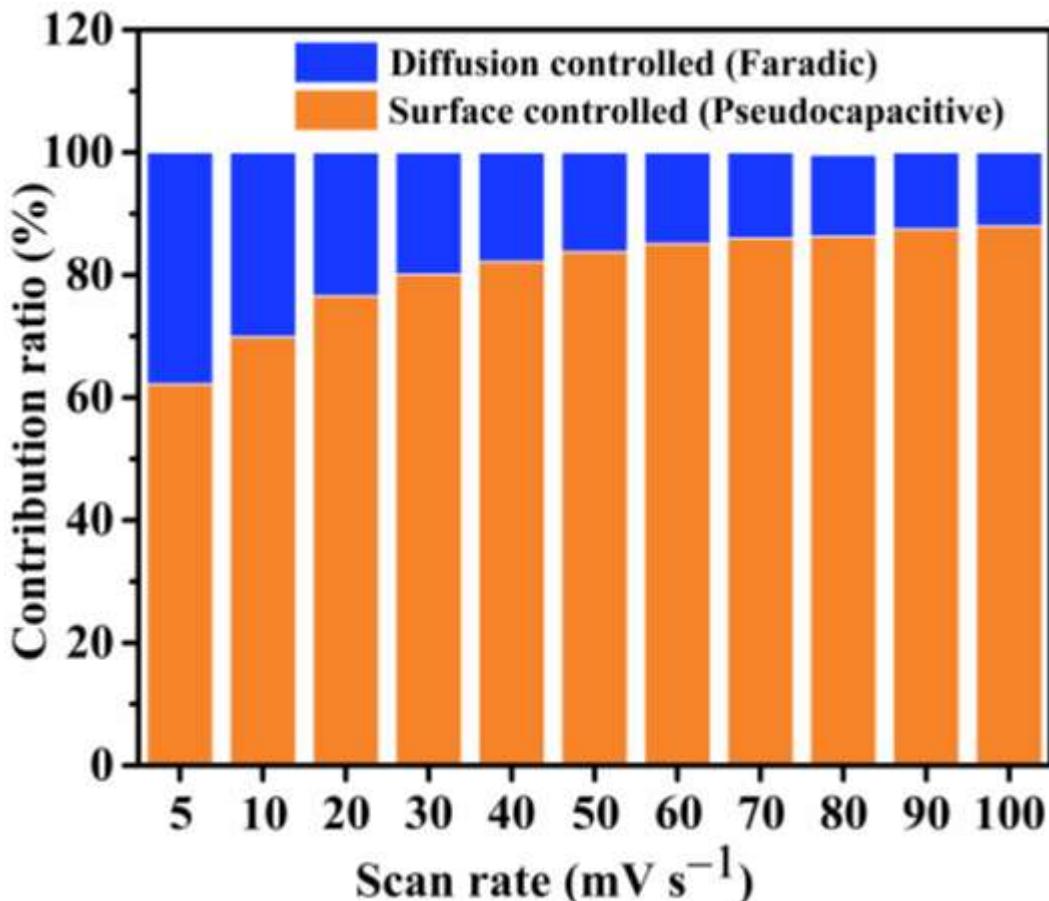
**Figure S6.** (a and b) High magnification HR-TEM, (c) SAED pattern and (d) color mapping of  $\text{MnCo}_2\text{O}_4$ .



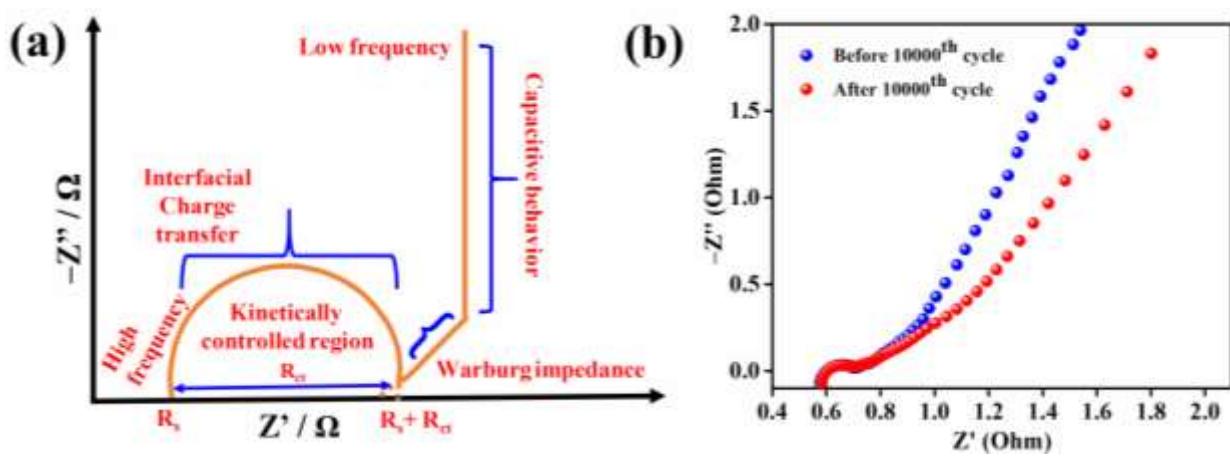
**Figure S7.** The Raman spectrum of  $\text{MnCo}_2\text{O}_4@\text{N-C}@{\text{MnO}}_2$  and  $\text{MnCo}_2\text{O}_4@\text{N-C}$ .



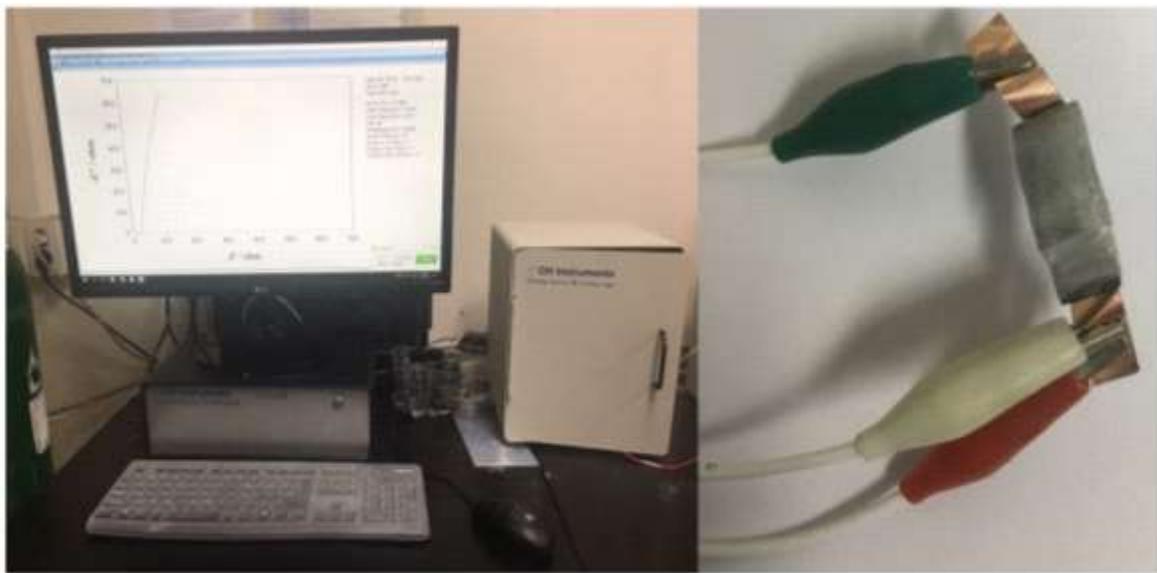
**Figure S8.** CV and GCD plot of (a, b) pure 1D  $\text{MnCo}_2\text{O}_4$  and (c, d)  $\text{MnCo}_2\text{O}_4@\text{N-C}$ .



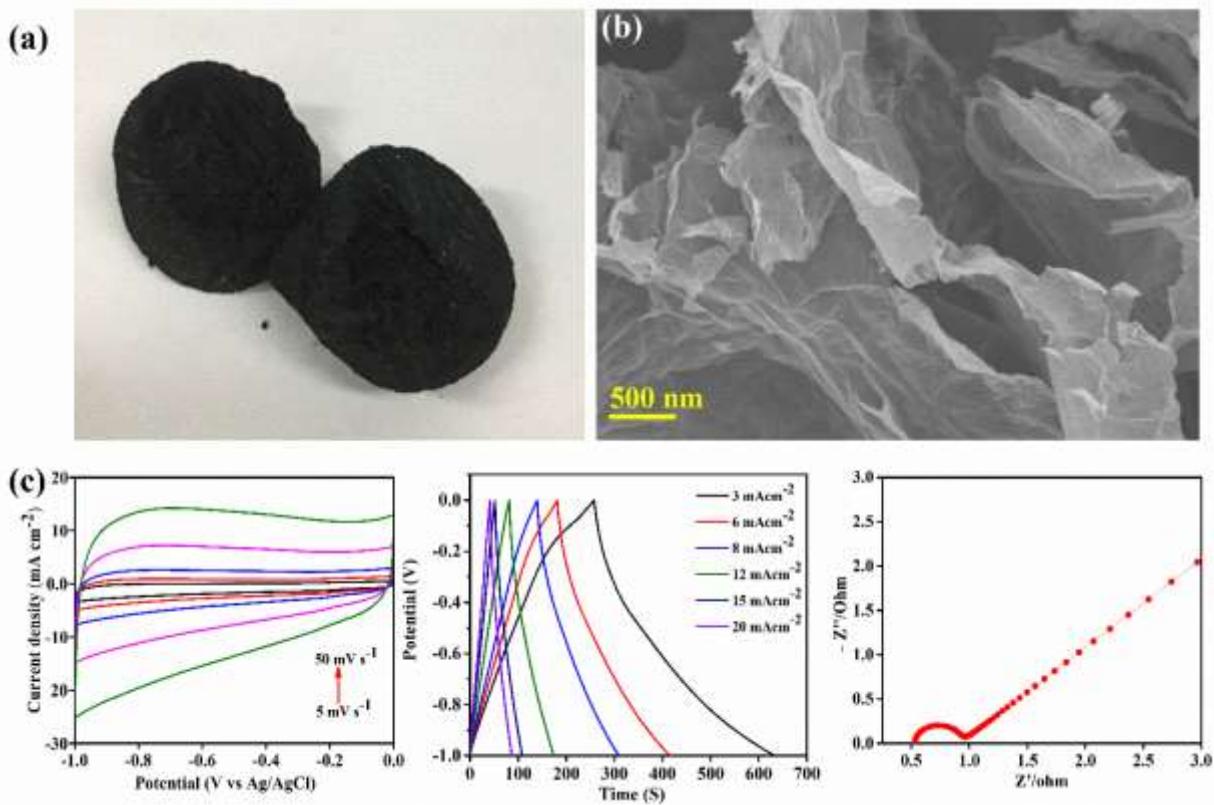
**Figure S9.** Bar chart showing the percentage of Faradic and pseudocapacitive contribution in at different scan rates of  $\text{MnCo}_2\text{O}_4@\text{N-C@MnO}_2$ .



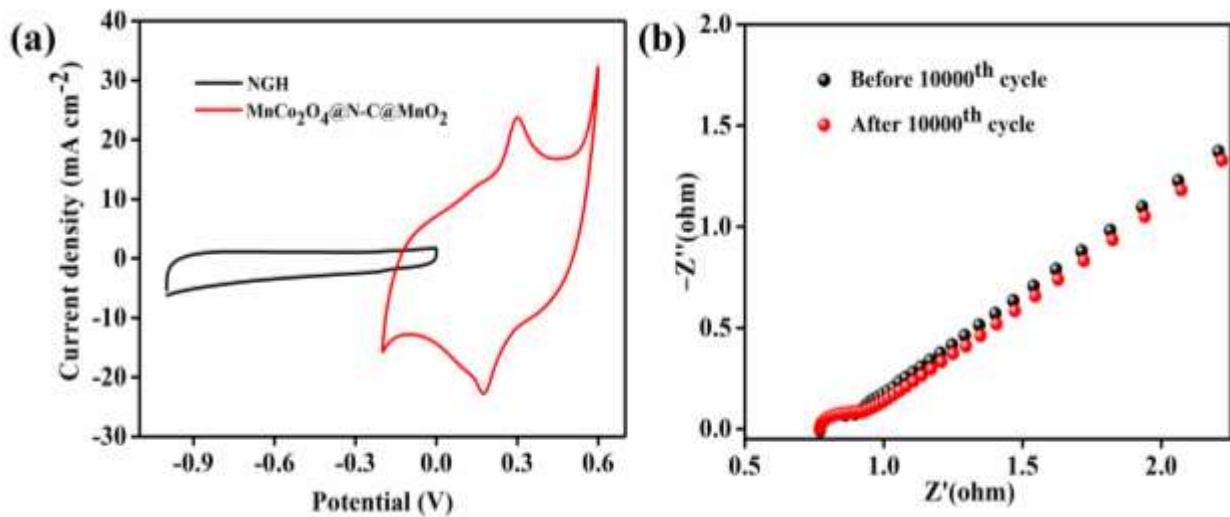
**Figure S10.** (a) The schematic representation of ideal EIS plot (b) The EIS Nyquist plot of MnCo<sub>2</sub>O<sub>4</sub>@N-C@MnO<sub>2</sub> electrode before and after 10,000 cycles.



**Figure S11.** The digital photograph of the final fabricated asymmetric device setup.



**Figure S12.** (a) Photograph of the N–doped graphene hydrogel(NGH) (b) FE-SEM image of the NGH (c) Electrochemical performance of the NGH.



**Figure S13.** (a)  $\text{MnCo}_2\text{O}_4@\text{N-C}@{\text{MnO}_2}$  and NGH measured the CV at scan rate 10  $\text{mV s}^{-1}$  (b) EIS Nyquist plot  $\text{MnCo}_2\text{O}_4@\text{N-C}@{\text{MnO}_2}/\text{NGH}$  device before and after 10,000 cycles.

**Table S1. Comparison of electrochemical performance of  $\text{MnCo}_2\text{O}_4@\text{N-C}@{\text{MnO}}_2$  electrode with recently reported core@shell electrode material.**

| Electrode material  | Areal capacitance/capacity<br>[F cm <sup>-2</sup> /mA h cm <sup>-2</sup> ] | Specific capacitance/capacity<br>[F g <sup>-1</sup> /mA h g <sup>-1</sup> ] | Current density       | Electrolyte                     | Stability (cycles) | Reference |
|---|--|---|-----------------------|---------------------------------|--------------------|-----------|
| $\text{CoO}@\text{MnO}_2$   | –  | 1,835 F g <sup>-1</sup>   | 1 A g <sup>-1</sup>   | 6 M KOH                         | 97.7%<br>(10,000)  | [1]       |
| $\text{Co}_3\text{O}_4@\text{MnO}_2$                              | –  | 1,693 F g <sup>-1</sup>   | 1 A g <sup>-1</sup>   | 1 M LiOH                        | 89.8%<br>(10,000)  | [2]       |
| $\alpha\text{-MnO}_2$<br>NWs@ $\delta\text{-MnO}_2$<br>core-shell | –  | 231 F g <sup>-1</sup>   | 1 A g <sup>-1</sup>   | 6 M KOH                         | 98.1%<br>(10,000)  | [3]       |
| Cobalt-doped $\text{MnO}_2$<br>yolk–shell                         | –  | 350 F g <sup>-1</sup>   | 0.1 A g <sup>-1</sup> | 1 M<br>$\text{Na}_2\text{SO}_4$ | 90%<br>(1,000)     | [4]       |
| $\text{TiO}_2@\text{MnO}_2@\text{C}$                              | –  | 488 F g <sup>-1</sup>   | 1 A g <sup>-1</sup>   | 1 M<br>$\text{Na}_2\text{SO}_4$ | 97.4%<br>(10,000)  | [5]       |
| $\text{MnCo}_2\text{O}_4 @\text{Ni(OH)}_2$                        | –  | 2,154 F g <sup>-1</sup>   | 5 Ag <sup>-1</sup>    | 2 M KOH                         | 90%<br>(2,500)     | [6]       |
| $\text{NiCo}_2\text{O}_4@\text{MnO}_2$                            | 5.3 F cm <sup>-2</sup>   | –   | 1 mA cm <sup>-2</sup> | 6 M KOH                         | 90.1%<br>(5,000)   | [7]       |
| $\text{MnNiCoO}_4@\text{MnO}_2$                                   | –  | 1,931 F g <sup>-1</sup>   | 0.8 A g <sup>-1</sup> | 6 M KOH                         | 91.2%<br>(6,000)   | [8]       |
| $\text{MnO}_2/\text{carbon}$                                      | –  | 628 F g <sup>-1</sup>   | 1 A g <sup>-1</sup>   | 3 M KOH                         | 98.5%              | [9]       |

|  |                         |                           |                         |                                     |               |      |
|--|-------------------------|---------------------------|-------------------------|-------------------------------------|---------------|------|
|  |                         |                           |                         |                                     | (2,000)       |      |
| MnO <sub>2</sub> nanoflake/CNT                                   | –                       | 370 F g <sup>-1</sup>     | 0.5 A g <sup>-1</sup>   | 1 M Na <sub>2</sub> SO <sub>4</sub> | 100% (4,000)  | [10] |
| CC@ZnCo <sub>2</sub> O <sub>4</sub> @MnO <sub>2</sub>            | 3.6 F cm <sup>-2</sup>  | –                         | 2 mA cm <sup>-2</sup>   | 2 M KOH                             | 95.5% (5,000) | [11] |
| MnCo <sub>2</sub> O <sub>4</sub> @MnO <sub>2</sub>               | –                       | 858 F g <sup>-1</sup>     | 1 A g <sup>-1</sup>     | 3 M KOH                             | 88% (5,000)   | [12] |
| MnCo <sub>2</sub> O <sub>4</sub> Nanowire@MnO <sub>2</sub>       | –                       | 2,262 F g <sup>-1</sup>   | 1 Ag <sup>-1</sup>      | 6 M KOH                             | 87.1% (5,000) | [13] |
| MnCo <sub>2</sub> O <sub>4</sub> @CoMoO <sub>4</sub>             | –                       | 2,115.4 F g <sup>-1</sup> | 1.1 A g <sup>-1</sup>   | 1 M KOH                             | 119% (5,000)  | [14] |
| MnCo <sub>2</sub> O <sub>4</sub> @Ni <sub>3</sub> S <sub>2</sub> | –                       | 2807 F g <sup>-1</sup>    | 3 A g <sup>-1</sup>     | 6 M KOH                             | 92% (5,000)   | [15] |
| MnCo <sub>2</sub> O <sub>4</sub> @MnMoO <sub>4</sub> CSNs        | –                       | 885 C g <sup>-1</sup>     | 3 A g <sup>-1</sup>     | 6 M KOH                             | 95% (5,000)   | [16] |
| MNA-MnCo <sub>2</sub> O <sub>4.5</sub>                           | –                       | 517.9 C g <sup>-1</sup>   | 3.6 A g <sup>-1</sup>   | 3 M KOH                             | 98.3% (1,000) | [17] |
| Co <sub>3</sub> O <sub>4</sub> @MnCo <sub>2</sub> O <sub>4</sub> | –                       | 736.5 F g <sup>-1</sup>   | 1 mA cm <sup>-2</sup>   | 3 M KOH                             | 76.9% (3,000) | [18] |
| porous MnCo <sub>2</sub> O <sub>4</sub> nanorod                  | –                       | 845.6 F g <sup>-1</sup>   | 1 A g <sup>-1</sup>     | 2 M KOH                             | 90.2% (2,000) | [19] |
| CoO@MnO <sub>2</sub>   | 3.03 F cm <sup>-2</sup> | 1515 F g <sup>-1</sup>    | 2.0 mA cm <sup>-2</sup> | 6 M KOH                             | –             | [20] |

|  |  |                               |  |                                     |                         |                  |
|--|--|-------------------------------|--|-------------------------------------|-------------------------|------------------|
| porous C/MnO <sub>2</sub>                                    | –  | 392 F g <sup>-1</sup>         | 0.5 A g <sup>-1</sup>                          | 1 M Na <sub>2</sub> SO <sub>4</sub> | –                       | [21]             |
| CuO@C@MnO <sub>2</sub>                                       | –  | 650 F g <sup>-1</sup>         | 0.4 Ag <sup>-1</sup>                           | 1 M Na <sub>2</sub> SO <sub>4</sub> | 97.2% (2,000)           | [22]             |
| CoMoO <sub>4</sub> @C@MnO <sub>2</sub>                       | –  | 1,824 F g <sup>-1</sup>       | 3 A g <sup>-1</sup>                            | 3 M KOH                             | 82% (5,000)             | [23]             |
| NiCo <sub>2</sub> O <sub>4</sub> @MnO <sub>2</sub>           | –  | 913.6 F g <sup>-1</sup>       | 0.5 A g <sup>-1</sup>                          | 1 M KOH                             | 87.1% (3,000)           | [24]             |
| NiCo <sub>2</sub> O <sub>4</sub> –MnO <sub>2</sub> /graphene | 5.15 F cm <sup>-2</sup>                                      | 2,577 F g <sup>-1</sup>       | 1 A g <sup>-1</sup> /<br>2 mA cm <sup>-2</sup> | 6 M KOH                             | 94.3% (5,000)           | [25]             |
| MnO <sub>2</sub> /C  | –  | 497 F g <sup>-1</sup>         | 1 A g <sup>-1</sup>                            | 1 M Na <sub>2</sub> SO <sub>4</sub> | 90% (5,000)             | [26]             |
| <b>MnCo<sub>2</sub>O<sub>4</sub>@N-C@MnO<sub>2</sub></b>     | <b>0.75 mA h cm<sup>-2</sup>/<br/>312 mA hg<sup>-1</sup></b> | <b>2,955 F g<sup>-1</sup></b> | <b>3 mA cm<sup>-2</sup></b>                    | <b>3 M KOH</b>                      | <b>89.6%<br/>10,000</b> | <b>This work</b> |

**Table S2. Comparison of MnCo<sub>2</sub>O<sub>4</sub>@N-C@MnO<sub>2</sub>/NGH asymmetric capacitor.**

| Material<br>Cathode//Anode  | Working<br>potential (V) | Energy density<br>(Wh kg <sup>-1</sup> ) | Power density<br>(W kg <sup>-1</sup> ) | Electrolyte                         | Stability<br>(cycles) | References |
|---|--------------------------|--|--|-------------------------------------|-----------------------|------------|
| ZnCo <sub>2</sub> O <sub>4</sub> @MnO <sub>2</sub> //AC               | 1.6                      | 29.4                                     | 628.4                                  | PVA/KOH                             | 95.3%<br>(3,000)      | [27]       |
| MnCo <sub>2</sub> O <sub>4</sub> @CoMoO <sub>4</sub> //AC             | 1.6                      | 37.5                                     | 527.8                                  | 1 M KOH                             | –                     | [14]       |
| MnCo <sub>2</sub> O <sub>4</sub> @CoS//AC                             | 1.6                      | 55.1                                     | 477.3                                  | PVA/KOH                             | 91 %<br>(6,000)       | [28]       |
| MnO <sub>2</sub> /C/MECN  active<br>carbon/Ni-foam                    | 2.0                      | 55.5                                     | 4000                                   | 1 M Na <sub>2</sub> SO <sub>4</sub> | 87.6%<br>(5,000)      | [26]       |
| NiCo <sub>2</sub> O <sub>4</sub> –MnO <sub>2</sub> /GF<br>//CNT/GF    | 1.5                      | 55.1                                     | 187.5                                  | –                                   | 89.4%<br>(2,000)      | [25]       |
| CuO@MnO <sub>2</sub> /MEGO  | 1.8                      | 22.1                                     | 85600                                  | 1 M Na <sub>2</sub> SO <sub>4</sub> | 101.5%<br>(10,000)    | [29]       |
| FeCo <sub>2</sub> O <sub>4</sub> @MnO <sub>2</sub> //AC               | 1.6                      | 22.6                                     | 406.01                                 | 3 M KOH                             | 90.1%<br>(5,000)      | [30]       |
| MnCo <sub>2</sub> O <sub>4</sub> @MnMoO <sub>4</sub> //AC             | 1.6                      | 49.4                                     | 815                                    | 6 M KOH                             | 91%<br>(5,000)        | [31]       |
| MnO <sub>2</sub> @NiCo <sub>2</sub> O <sub>4</sub> //AC               | 1.6                      | 26.6                                     | 800                                    | –                                   | –                     | [32]       |
| MnO <sub>2</sub> /C/Ag//AC  | 1.7                      | 48.3                                     | 851.7                                  | 3 M KOH                             | 98.5%<br>(2,000)      | [33]       |
| MnCo <sub>2</sub> O <sub>4</sub> @Co <sub>3</sub> O <sub>4</sub> //AC | 1.5                      | 31                                       | 208.5                                  | 2 M KOH                             | 101.2%<br>(8,000)     | [34]       |
| rGO-MnCo <sub>2</sub> O <sub>4</sub> //AC                             | 1.5                      | 19                                       | 1551                                   | 3 M LiOH                            | -                     | [35]       |
| NHCSs@MnO <sub>2</sub> //AC   | 1.8                      | 43.9                                     | 408                                    | 1 M Na <sub>2</sub> SO <sub>4</sub> | 81.4%<br>(4,000)      | [36]       |

|  |            |             |              |                |                            |                  |
|--|------------|-------------|--------------|----------------|----------------------------|------------------|
| MnCo <sub>2</sub> O <sub>4</sub> @NF//rGO                | 1.6        | 53.7        | 1600         | 2 M KOH        | 82%<br>(5,000)             | [37]             |
| <b>MnCo<sub>2</sub>O<sub>4</sub>@N-C@MnO<sub>2</sub></b> | <b>1.6</b> | <b>68.2</b> | <b>749.2</b> | <b>PVA/KOH</b> | <b>91.1 %<br/>(10,000)</b> | <b>This work</b> |

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