Supporting Information:

**Graphitic Carbon Nanofiber Growth from Catalytic-Metal Organic Frameworks & their Electrochemical Double Layer Properties**

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S1. CVD setup

CVD was carried out in a tube furnace, with the sample being placed in a quartz boat. The furnace was heated to 650 °C under a flow of Ar/H₂ gas (250 sccm). Once the temperature had stabilised, the sample was placed in the furnace and the Ar/H₂ gas (250 sccm) was allowed to run for a further 20 minutes. Subsequently, ethylene gas was also flowed into the furnace (100 sccm) along with the Ar/H₂ gas (250 sccm) for a total of 40 minutes. Upon completion of this step the ethylene gas was stopped and the furnace was turned off. The sample was allowed to cool under the flow of the Ar/H₂ gas (250 sccm) back to the ambient temperature within the sealed tube. The tube was only opened and the sample removed once it was at ambient temperature (approximately 25 °C). The line diagram of the flow into the CVD system is shown in Figure S1.

Figure S1 The line diagram of the flow into the CVD system. The Ar/H₂ and ethylene flow into the furnace were controlled by the mass flow controllers (MFC) at 250 and 100 sccm respectively

S2. Electrical conductivity measurements

Conductivity was measured by pressing a small amount of CNF between two electrodes (Figure S2). Compression (P) amounting to 2.76 MPA was applied for each test. The total length of the electrodes was measured with and without the material present to obtain the length of material added (L). An Agilent B2902A source measuring unit (SMU) with Agilent Quick IV software was used. The current was measured as the electrode potential was swept from -0.05 V to +0.05 V. The scan rate used in the measurements was 0.022 V/s with a measurement taken every 0.0001 V. The conductivity was calculated using the following formulae [1],

\[
\rho = \frac{R \times A}{L}
\]

Where, \( \rho \) is the resistivity, \( R \) is the electrical resistance, \( A \) is the cross sectional area and \( L \) is the length of material. \( A \) was a constant, the area of the 3 mm inner diameter of the rubber tube. \( L \) was measured for each test with Vernier calipers. The conductivity of the material is simply \( 1/\rho \).
S3 Parametric calculations

The average specific capacitance ($C$) was calculated from CV curves using the following formulae[1, 2]:

$$C = \frac{\int i \cdot dt}{mV}$$

Here, $i$ is the oxidation or reduction current (in mA), $dt$ is the time differential, $m$ is the mass of the active material in the electrode and $V$ indicates the voltage range of one sweep segment.

Energy density ($E$) was derived from the CV plots using the following equation [1, 2],

$$E = \frac{1}{2} CV^2$$

The power density ($P$) was evaluated using the following equation [1, 2],

$$P = \frac{E}{\Delta t}$$

Here, $\Delta t$ represents the time required for a single sweep segment in the CV plot.

S4 Morphological characterization and Energy dispersive X-ray spectroscopy (EDS) analysis

Figure S3 Gram-scale Ni doped MOF 5 (a) before and (b) after the CVD process
Figure S4 Ni doped MOF-5 derived carbon structures in (a) presence and (b) in absence of ethylene
Figure S5 Low magnification SEM images of the Ni doped MOF-5 derived CNFs synthesized at various Ni doping concentrations
Figure S6 50% Ni doped MOF-5 derived carbon structure at (a) low and (b) high magnifications. High Ni doping concentration led to the formation of planar graphitic carbon structures instead of well-defined 1D CNFs.

Figure S7 Energy dispersive spectroscopy (EDS) spectrum of 30% Ni CNF
Figure S8 The diameter identification process for the CNF involved taking an SEM image (a) and mapping the grey intensity to plot a cross-sectional profile (b) where we see a sharp change in intensity at the edge of the fibres.
Figure S9 The histograms of the diameters of the Ni doped MOF-5 derived CNFs synthesized at various Ni doping concentrations. The histograms display an increasing spread of diameters especially in comparison to the lower Ni wt% doped samples and a continued increase in the average diameter with increasing Ni wt%
Figure S10  SEM images of (a) Ni doped MOF-5 prior to CVD and (b) CNFs grown at high temperature (900°C) shows large diameter and scattered growth. (c) Low magnification and (d) high magnification SEM images of the CNFs grown at 650°C
Figure S11 Low magnification TEM image of Ni doped MOF-5 derived CNF shows scattered catalyst particles in the CNF structure

S5 Crystallographic characterization

Figure S12 XRD of MOF-5 doped with different concentrations of Ni
S6 Raman spectra analysis

Figure S13 Raman peak fit analysis for 30% Ni doped MOF-5

Figure S14 Raman peak fit analysis for 0.5% Ni CNF

Figure S15 Raman peak fit analysis for 1% Ni CNF
Figure S16 Raman peak fit analysis for 5% Ni CNF

Figure S17 Raman peak fit analysis for 10% Ni CNF

Figure S18 Raman peak fit analysis for 30% Ni CNF
Table S1 Parameters extracted from the peak fitting of the Raman spectra

<table>
<thead>
<tr>
<th>Sample</th>
<th>Peak position (cm⁻¹)</th>
<th>Peak amplitude</th>
<th>FWHM</th>
<th>Curve fit test</th>
<th>ID/IG</th>
<th>La (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>D</td>
<td>G</td>
<td>D</td>
<td>G</td>
<td>D</td>
<td>G</td>
</tr>
<tr>
<td>0.5% Ni CNF</td>
<td>1324.7</td>
<td>1581.9</td>
<td>478.3</td>
<td>386.3</td>
<td>197.2</td>
<td>82</td>
</tr>
<tr>
<td>1% Ni CNF</td>
<td>1326.8</td>
<td>1583.6</td>
<td>1342.5</td>
<td>1251.8</td>
<td>257.6</td>
<td>77.3</td>
</tr>
<tr>
<td>5% Ni CNF</td>
<td>1326.2</td>
<td>1583.3</td>
<td>615.3</td>
<td>466.7</td>
<td>200.9</td>
<td>84.9</td>
</tr>
<tr>
<td>10% Ni CNF</td>
<td>1324.3</td>
<td>1582.9</td>
<td>688.7</td>
<td>489.2</td>
<td>142.3</td>
<td>79.7</td>
</tr>
<tr>
<td>30% Ni CNF</td>
<td>1322.9</td>
<td>1582</td>
<td>885.6</td>
<td>632.2</td>
<td>136.6</td>
<td>77.4</td>
</tr>
</tbody>
</table>

S7 Surface area and pore structure characterization

Figure S19 Nitrogen adsorption isotherm of Ni doped MOF-5 and CNFs synthesized from MOF-5 doped with various concentrations of Ni
S8 Electrical Conductivity of the carbon structures grown at various CVD conditions

Figure S20 Electrical conductivity of the carbon structures grown in presence and in absence of ethylene

S9 Electrochemical Characterization

Figure S21 A comparison of the Nyquist plots of 30% Ni doped MOF-5 before and after CNF synthesis via CVD in presence of 1 M Na$_2$SO$_4$
**Figure S22** A comparison of the Nyquist plots of the CNF electrodes synthesized from MOF-5 precursors doped with various concentrations of Ni in presence of 1 M Na₂SO₄

**Figure S23** Specific capacitance as a function of scan rate in case of the 30% Ni CNF in presence of 1 M KOH
**Figure S24** Diminution of redox current density as a function of scan rate in case of the 30% Ni CNF electrode in presence of 1 M KOH

**S10 Comparison with literature**

In this section a summary of the literature on the synthesis parameters (synthesis temperature and precursor), surface area and electrochemical behaviour of other MOF derived carbons and CNF has been reported. The high surface area of the achieved in case of most of the MOF derived carbons and CNFs are due to removal of catalyst particle by either high temperature processing or by washing the carbon structure with acidic solutions. The tabulated values for the surface area, capacitance, energy and power densities corresponds to the maximum reported in the respective studies.

**Table S2** Surface area and electrochemical properties of various MOF derived carbons (* corresponds to maximum values reported for those parameters) where the catalyst particles were not electrochemically utilised

<table>
<thead>
<tr>
<th>Electrode material</th>
<th>Synthesis temperature</th>
<th>Precursor</th>
<th>*Surface area (m²/g)</th>
<th>*Capacitance</th>
<th>*Energy density (Wh/kg)</th>
<th>*Power density (W/kg)</th>
<th>Pseudo-capacitance contribution</th>
<th>Refs</th>
</tr>
</thead>
</table>

16
<table>
<thead>
<tr>
<th>Material Description</th>
<th>Temperature</th>
<th>Temperature</th>
<th>Capacitance</th>
<th>Specific capacitance</th>
<th>Conductivity</th>
<th>Moisture</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nanoporous carbon</td>
<td>650°C</td>
<td>MOF-5</td>
<td>1521</td>
<td>100 F/g</td>
<td>_</td>
<td>_</td>
<td>None</td>
</tr>
<tr>
<td>N(_2) doped porous carbon</td>
<td>950°C</td>
<td>ZIF-8 and sucrose composite</td>
<td>934</td>
<td>285.8 F/g</td>
<td>_</td>
<td>_</td>
<td>Positive</td>
</tr>
<tr>
<td>Nanoporous carbon</td>
<td>530°C</td>
<td>MOF-5 and furfuryl alcohol composite</td>
<td>2872</td>
<td>258 F/g</td>
<td>_</td>
<td>_</td>
<td>None</td>
</tr>
<tr>
<td>Nanoporous carbon</td>
<td>800°C</td>
<td>ZIF-67</td>
<td>943</td>
<td>238 F/g</td>
<td>19.6</td>
<td>700</td>
<td>None</td>
</tr>
<tr>
<td>N(_2) doped nanoporous carbon</td>
<td>800°C</td>
<td>ZIF-8</td>
<td>1523</td>
<td>251 F/g</td>
<td>10.86</td>
<td>225</td>
<td>Positive</td>
</tr>
<tr>
<td>N(_2) doped porous carbon</td>
<td>950°C</td>
<td>IRMOF-3</td>
<td>1221</td>
<td>239 F/g</td>
<td>_</td>
<td>_</td>
<td>Positive</td>
</tr>
<tr>
<td>N(_2) doped porous carbon</td>
<td>800°C</td>
<td>ZIF-8</td>
<td>798</td>
<td>160.8 F/g</td>
<td>_</td>
<td>_</td>
<td>Positive</td>
</tr>
<tr>
<td>Nanoporous carbon</td>
<td>900°C</td>
<td>Bimetallic MOF composed of ZIF-8 and ZIF-67</td>
<td>890</td>
<td>95 F/cm(^3)</td>
<td>_</td>
<td>_</td>
<td>None</td>
</tr>
<tr>
<td>Carbon nanorods</td>
<td>1000°C</td>
<td>MOF-74</td>
<td>1559</td>
<td>164 F/g</td>
<td>_</td>
<td>_</td>
<td>None</td>
</tr>
</tbody>
</table>
Table S3: Surface area and electrochemical properties of various CNF supercapacitors (* correspond to maximum values reported for those parameters)

<table>
<thead>
<tr>
<th>Electrode material</th>
<th>Synthesis temperature</th>
<th>Precursor</th>
<th>*Surface area (m²/g)</th>
<th>*Capacitance (F/g)</th>
<th>*Energy density (Wh/kg)</th>
<th>*Power density (W/kg)</th>
<th>Pseudo-capacitance contribution</th>
<th>Refs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphene nanoribbons</td>
<td>First step: 1000°C</td>
<td>MOF-74 derived carbon nanorods</td>
<td>1492</td>
<td>198</td>
<td>_</td>
<td>_</td>
<td>None</td>
<td>[10]</td>
</tr>
<tr>
<td></td>
<td>Second step: 800°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MOF-74 derived carbon nanorods</td>
<td>First step: 133°C</td>
<td>PVP/PAN blend nanofibers</td>
<td>531</td>
<td>221</td>
<td>_</td>
<td>_</td>
<td>None</td>
<td>[11]</td>
</tr>
<tr>
<td></td>
<td>Second step: 152°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Third step: 970°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fourth step: 850°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CNF</td>
<td>470°C</td>
<td>Alumina coated (1 nm)</td>
<td>_</td>
<td>1.2</td>
<td>_</td>
<td>_</td>
<td>None</td>
<td>[12]</td>
</tr>
<tr>
<td></td>
<td>Ni foam</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Poly-aniline coated CNF</td>
<td>600°C</td>
<td>Iron powder</td>
<td>_</td>
<td>264</td>
<td>_</td>
<td>_</td>
<td>Positive</td>
<td>[13]</td>
</tr>
<tr>
<td>KOH activated CNF</td>
<td>750°C</td>
<td>Novolac type phenolic resin and a high density</td>
<td>1520</td>
<td>255</td>
<td>_</td>
<td>_</td>
<td>Positive</td>
<td>[14]</td>
</tr>
</tbody>
</table>
polyethylene pyrolyzing polymer in a ratio of 3:7

<table>
<thead>
<tr>
<th>CNF</th>
<th>750°C</th>
<th>Finely dispersed Fe-Ni alloy catalyst</th>
<th>_</th>
<th>14 F/g</th>
<th>_</th>
<th>_</th>
<th>None [15]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Meso-porous CNF</td>
<td>900°C</td>
<td>Phenol-formaldehyde resol infiltrated anodic alumina oxide</td>
<td>1424</td>
<td>152 F/g</td>
<td>_</td>
<td>_</td>
<td>None [16]</td>
</tr>
<tr>
<td>CNF and MnO2 composite</td>
<td>1000°C</td>
<td>Polyacrylonitrile (PAN)</td>
<td>_</td>
<td>142 F/g</td>
<td>_</td>
<td>_</td>
<td>Positive [17]</td>
</tr>
<tr>
<td>CNF</td>
<td>800°C</td>
<td>PAN</td>
<td>1160</td>
<td>133 F/g</td>
<td>_</td>
<td>_</td>
<td>None [18]</td>
</tr>
</tbody>
</table>

**S11 Electrochemistry of Ni in alkaline media**

An extensive study on the various oxidation states of Ni in an alkaline electrolyte (0.5 M KOH) and their corresponding potentials have been reported by Drunen et al [19]. The potential ranges were reported w.r.t standard hydrogen electrode (SHE). Since we have used Ag/AgCl in KCl as our reference electrode, hence we have converted the potentials accordingly. Typically at room temperature the standard electrode potential of Ag/AgCl electrode in KCl against SHE is +0.230 V ± 10 mV. The principal redox reactions at Ni in presence of alkaline electrolytes are as follows [19],

(i) Oxidation of metallic Ni to $\alpha - \text{Ni(OH)}_2$ at $0.43 \text{ V} < E < 0.63 \text{ V}$ (vs Ag/AgCl in KCl)

$$\text{Ni}^0 + 2\text{OH}^- \rightarrow \alpha - \text{Ni(OH)}_2 + 2\text{e}^- \quad \text{.......... (1)}$$

(ii) Concurrent conversion of $\alpha - \text{Ni(OH)}_2$ to $\beta - \text{Ni(OH)}_2$ and oxidation of metallic Ni to $\beta - \text{Ni(OH)}_2$ at $0.73 \text{ V} < E < 1.53 \text{ V}$ (vs Ag/AgCl in KCl)
\[ \alpha - Ni(OH)_2 \rightarrow \beta - Ni(OH)_2 \quad \ldots \ldots \ldots \quad (2) \]

\[ Ni^0 + 2OH^- \rightarrow \beta - Ni(OH)_2 + 2e^- \quad \ldots \ldots \ldots \quad (3) \]

(iii) Increase of the oxidation state of Ni from +2 to +3 through the oxidation of \( \beta - Ni(OH)_2 \) to \( \beta - NiOOH \) at 1.53 V < E < 1.78 V (vs Ag/AgCl in KCl)

\[ \beta - Ni(OH)_2 + OH^- \rightarrow \beta - NiOOH + H_2O + e^- \quad \ldots \ldots \ldots \quad (4) \]

(iv) Oxygen evolution reaction occurs at E ≥ 1.78 V (vs Ag/AgCl in KCl)

\[ 2OH^- \rightarrow \frac{1}{2}O_2 + H_2O + 2e^- \quad \ldots \ldots \ldots \quad (5) \]

A scan reversal at E = 1.78 V generates the following cathodic processes,

(v) Reduction of \( \beta - NiOOH \) to \( \beta - Ni(OH)_2 \) at 1.33 V < E < 1.63 V (vs Ag/AgCl in KCl)

\[ \beta - NiOOH + H_2O + e^- \rightarrow \beta - Ni(OH)_2 + OH^- \quad \ldots \ldots \ldots \quad (6) \]

(vi) Hydrogen evolution reaction occurs at E < 0.03 V (vs Ag/AgCl in KCl)

\[ H_2O + e^- \rightarrow \frac{1}{2}H_2 + OH^- \quad \ldots \ldots \ldots \quad (7) \]

(vii) In case of metallic Ni being cycled at 0.03 V < E ≤ 0.73 V (vs Ag/AgCl in KCl) in addition to the anodic peak corresponding to \( \alpha - Ni(OH)_2 \) formation, there is also a cathodic peak at 0.11 < E ≤ 0.35 V (vs Ag/AgCl in KCl)

\[ \alpha - Ni(OH)_2 + 2e^- \rightarrow Ni^0 + 2OH^- \quad \ldots \ldots \ldots \quad (8) \]
In our earlier study on a Ni doped MOF-5 electrode [1] a comprehensive crystallographic analysis using XRD had further confirmed the oxidation and reduction products within the potential range of \(0.03 \ V \leq E \leq 0.73 \ V\) (vs Ag/AgCl in KCl) were indeed \(\alpha-Ni(OH)_2\) and \(Ni^{\alpha}\) respectively.

References


