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Supporting Information:

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

Parama Chakraborty Banerjee<sup>a,b, e</sup>, Derrek E. Lobo<sup>a,d,e</sup>, Tim Williams<sup>b</sup>, Mahdokht Shaibani<sup>a</sup>, Matthew R. Hill<sup>c,b</sup>, Mainak Majumder<sup>a,f</sup>\*

<sup>a</sup>Nanoscale Science and Engineering Laboratory (NSEL), Department of Mechanical and Aerospace Engineering, Monash University, Clayton, VIC 3800, Australia
 <sup>b</sup>Department of Chemical Engineering, Monash University, Clayton, VIC 3800, Australia
 <sup>c</sup>Monash Centre for Electron Microscopy, Monash University, Clayton, VIC 3800, Australiad
 <sup>d</sup>CSIRO, Clayton, VIC 3168, Australia
 E-mail: mainak.majumder@monash.edu
 <sup>e</sup>Authors with similar contribution
 <sup>f</sup>ARC Research Hub for Graphene Enabled Industry Transformation, Monash University, Clayton, Victoria, Australia

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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  $Ar/H_2$  gas (250 sccm). Once the temperature had stabilised, the sample was placed in the furnace and the  $Ar/H_2$  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  $Ar/H_2$  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  $Ar/H_2$  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  $Ar/H_2$  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  $1/\rho$ .



Figure S2 Schematic of the conductivity measurement setup. Material was compressed between two conducting electrodes in a tube with inner diameter of 3 mm

### **S3** Parametric calculations

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

$$C = \frac{\int i.\,dt}{mV}$$

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],

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

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

Sample	Peak position (cm-1)		Peak an	Peak amplitude		FWHM		ID/IG	La (nm)
	D	G	D	G	D	G	r2		
0.5% Ni CNF	1324.7	1581.9	478.3	386.3	197.2	82	0.973	1.24	3.553645
1% Ni CNF	1326.8	1583.6	1342.5	1251.8	257.6	77.3	0.989	1.07	4.102988
5% Ni CNF	1326.2	1583.3	615.3	466.7	200.9	84.9	0.981	1.32	3.337422
10% Ni CNF	1324.3	1582.9	688.7	489.2	142.3	79.7	0.979	1.41	3.125362
30% Ni CNF	1322.9	1582	885.6	632.2	136.6	77.4	0.982	1.4	3.140914

Table S1 Parameters extracted from the peak fitting of the Raman spectra

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<sub>2</sub>SO<sub>4</sub>



**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 Na<sub>2</sub>SO<sub>4</sub>



**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

Electrode	Synthesis	Precursor	*Surface	*Capacitance	*Energy	*Power	Pseudo-	Refs
material	temperature		area		density	density	capacitance	
			$(m^{2}/g)$		(Wh/kg)	(W/kg)	contribution	

NT.	(5000	MOL 5	1.501	100 5/			) T	[2]
Nanoporous carbon	650°C	MOF-5	1521	100 F/g	_	_	None	[3]
N <sub>2</sub> doped	950°C	ZIF-8 and	934	285.8 F/g			Positive	[4]
porous		sucrose		-	_	_		
carbon		composite						
Nanoporous	530°C	MOF-5	2872	258 F/g	_	_	None	[5]
carbon		and						
		furfuryl						
		alcohol						
		composite						
Nanoporous carbon	800°C	ZIF-67	943	238 F/g	19.6	700	None	[6]
N2 doped nanoporous carbon	800°C	ZIF-8	1523	251 F/g	10.86	225	Positive	
N2 doped porous carbon	950°C	IRMOF-3	1221	239 F/g	_	-	Positive	[7]
N2 doped porous carbon	800°C	ZIF-8	798	160.8 F/g	_	_	Positive	[8]
Nanoporous carbon	900°C	Bimetallic MOF composed of ZIF-8 and ZIF-67	890	95 F/cm <sup>3</sup>	_	_	None	[9]
Carbon nanorods	1000°C	MOF-74	1559	164 F/g	-	_	None	[10]

Graphene	First step:	MOF-74	1492	198 F/g	_	_	None	[10]
nanoribbons	1000°C	derived						
	Second step:	carbon						
	800°C	nanorods						

**Table S3** Surface area and electrochemical properties of various CNF supercapacitors (\* correspond to maximum values reported for those parameters)

Electrode material	Synthesis temperature	Precursor	*Surface area (m²/g)	*Capacitance	*Energy density (Wh/kg)	*Power density (W/kg)	Pseudo- capacita nce contribu tion	Refs
CNF	First step:	PVP/PAN	531	221 F/g	—	_	None	[11]
	300°C	blend						
	Second step:	nanofibers						
	500°C							
	Third step:							
	970°C							
	Fourth step:							
	850°C							
CNF	470°C	Alumina coated (1 nm) Ni foam	_	1.2 F/cm <sup>2</sup>	_	_	None	[12]
Poly- aniline coated CNF	600°C	Iron powder	_	264 F/g	_	_	Positive	[13]
KOH activated CNF	750°C	Novolac type phenolic resin and a high density	1520	255 F/g	_	-	Positive	[14]

		polyethylene						
		pyrolyzing						
		polymer in a						
		ratio of 3:7						
CNF	750°C	Finely	—	14 F/g	—	—	None	[15]
		dispersed Fe-						
		Ni alloy						
		catalyst						
Maga	000°C	Dhanal	1424	152 E/a			None	[14]
Meso-	900 C		1424	132 F/g	_	_	None	[10]
porous		formaldenyde						
CNF		resol						
		infiltrated						
		anodic						
		alumina oxide						
	10000			142 5/			D :::	[17]
CNF and	1000°C	Polyacrylonitri	—	142 F/g	—	—	Positive	[[/]
$MnO_2$		le (PAN)						
composite								
CNF	800°C	PAN	1160	133 F/σ			None	[18]
	000 C	1 / 11 1	1100	155 178	_	_	THONG	[10]

#### 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  $\pm$  10 mV. The principal redox reactions at Ni in presence of alkaline electrolytes are as follows [19],

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

(ii) Concurrent conversion of  $\alpha - Ni(OH)_2$  to  $\beta - Ni(OH)_2$  and oxidation of metallic Ni to  $\beta - Ni(OH)_2$  at 0.73 V < E < 1.53 V (vs Ag/AgCl in KCl)

$$\alpha - Ni(OH)_2 \rightarrow \beta - Ni(OH)_2 \dots \dots (2)$$
  
$$Ni^o + 2OH^- \rightarrow \beta - Ni(OH)_2 + 2e^- \dots (3)$$

(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)

$$\beta - Ni(OH)_2 + OH^- \rightarrow \beta - NiOOH + H_2O + e^- \dots (4)$$

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

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)

$$\beta - NiOOH + H_2O + e^- \rightarrow \beta - Ni(OH)_2 + OH^- \dots \dots (6)$$

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

$$H_2 0 + e^- \rightarrow \frac{1}{2} H_2 + 0 H^- \dots (7)$$

(vii) In case of metallic Ni being cycled at 0.03 V  $\leq E \leq 0.73$  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  $\leq E \leq 0.35$  V (vs Ag/AgCl in KCl)

$$\alpha - Ni(OH)_2 + 2e^- \rightarrow Ni^o + 2OH^- \dots (8)$$

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 < E  $\leq$  0.73 V (vs Ag/AgCl in KCl) were indeed  $\alpha - Ni(OH)_2$  and  $Ni^o$  respectively.

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