# Supporting Information

# Heterogeneous Growth of UiO-66-NH<sub>2</sub> on Oxidized Single-walled Carbon Nanotubes to Form "Beads-on-a-String" Composites

Zidao Zeng,<sup>†</sup> Dan C. Sorescu,<sup>‡,§</sup> David L. White,<sup>†</sup> Sean I. Hwang,<sup>†</sup> Wenting Shao, <sup>†</sup> Xiaoyun He, <sup>†</sup> Zachary M. Schulte,<sup>†</sup> Nathaniel L. Rosi,<sup>†,§</sup> and Alexander Star<sup>\*, †, ||</sup>

<sup>†</sup>Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260, United States

<sup>\*</sup>National Energy Technology Laboratory, United States Department of Energy, Pittsburgh, Pennsylvania 15236, United States

<sup>§</sup>Department of Chemical and Petroleum Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania 15261, United States

Department of Bioengineering, University of Pittsburgh, Pittsburgh, Pennsylvania 15261, United States

\*Corresponding author. Email: astar@pitt.edu

# **Table of Contents**

Materials section	S-3
Experimental section	S-3
Table S1. Volumes of chemical solutions used for different syntheses.	S-3
Computational details	S-4
Characterization section	S-4
Figure S1. TEM image and PXRD of Material 1 and UiO-66-NH <sub>2</sub>	S-6
Figure S2. Computational adsorption heat of MOF precursor (ATA) on SWCNT surfaces	S-7
Figure S3. Computational adsorption heat of MOF precursor (Zr cluster) on SWCNT surfaces	S-7
Figure S4. TEM images of Materials 6 and 7	S-8
Figure S5. TEM image and PXRD of Material 8	S-8
Figure S6. Raman spectra of ox-SWCNT, ox-SWCNT/Zr and material 5	S-9
Figure S7. XPS spectra of ox-SWCNT, ox-SWCNT/Zr and Zr oxide-cluster	S-10
Table S2. Peak-fitted peak positions of XPS.	S-10
Figure S8. Time dependent TEM of material 5	S-11
Figure S9. I-V curves of drop cast ox-SWCNT and material 5	S-12
Figure S10. PXRD pattern of material 5 and material 5 after 5 days in water	S-12
Figure S11. Responses of UiO-66-NH <sub>2</sub> /SWCNT and ox-SWCNT toward DMMP vapor	S-12
References	S-13

# Materials section

Zirconium(IV) propoxide solution (70 wt. % in 1-propanol) (Sigma-Aldrich), 2-aminoterephthalic acid (Alfa Aesar), N,N-dimethylformamide (Fisher Scientific), glacial acetic acid (Macron Fine Chemicals) and Ethanol (Decon Labs) were purchased and used without further purification.

### **Experimental section**

# One-pot synthesis (Materials 1, 2, 5 and 8) (volumes of chemicals in Table S1)

In a 20-mL scintillation vial, to a certain amount of 0.5 g/L ox-SWCNT suspension in DMF, corresponding amount of DMF was added. The vial was sonicated in a bath sonicator during the dilution of the ox-SWCNT suspension. Glacial acetic acid was added to the resulting ox-SWCNT suspension if used. Then corresponding amount of ATA stock solution and Zr oxide-cluster solution were added to the vial. Reaction was left on stirring for 20 hours. The material was separated by centrifugation and was washed twice with DMF and ethanol subsequently. Materials were stored in ethanol at room temperature.

# Syringe pump synthesis (Materials 3, 4, 6 and 7) (Volumes of chemicals in Table S1)

In a 20 mL scintillation vial, to a certain amount of 0.5 g/L ox-SWCNT suspension in DMF, corresponding amount of DMF was added. The vial was sonicated in a bath sonicator during the dilution of the ox-SWCNT suspension. Then glacial acetic acid was added to the vial if used, followed by the corresponding precursor solution. A new mixture of DMF and the other precursor solution was loaded into a syringe. The syringe pump was set to a rate of 0.75 mL/hour. The pumping procedure was finished in 4 hours. The vial content was left on stirring for 20 hours from the beginning of pumping. The material was separated by centrifugation and was washed twice with DMF and ethanol subsequently. Materials were stored in ethanol at room temperature.

Vial					Syringe			
	Ox-SWCNT	DMF	Zr oxide-	ATA	Glacial	DMF	Zr oxide-	ATA
	suspension	(mL)	cluster stock	stock	acetic acid	(mL)	cluster stock	stock
	(µL)		(mL)	(mL)	(mL)		(mL)	(mL)
UiO-66-NH <sub>2</sub>	-	0.6	11	2.4	-	-	-	-
Material 1	316	0.284	11	2.4	-	-	-	-
Material 2	316	12.344	1.1	0.24	-	-	-	-
Material 3	316	9.584	1.1	-	-	2.76	-	0.24
Material 4	316	10.444	-	0.24	-	1.9	1.1	-
Material 5	316	11.944	1.1	0.24	0.4	-	-	-
Material 6	316	9.184	1.1	-	0.4	2.76	-	0.24
Material 7	316	10.044	-	0.24	0.4	1.9	1.1	-
Material 8	316	11.86	1.1	0.24	0.8	-	-	-

Table S1. Volumes of chemical solutions used for different syntheses.

#### **Computational details**

The adsorption properties of Zr<sub>6</sub>O<sub>4</sub>(OH<sub>4</sub>)(CH<sub>3</sub>COO)<sub>12</sub> cluster (Zr(CL)) and of 2,2-aminoterephthalic acid (ATA) molecule on the sidewalls of SWCNT have been investigated using plane-wave DFT calculations in conjunction to 3D periodic boundary conditions as implemented in Vienna Ab Initio Simulation Package (VASP) code.<sup>S1,S2</sup> The Perdew-Burke-Ernzerhof (PBE)<sup>S3</sup> functional has been used to describe the exchange and correlation together with Grimme-D3 method<sup>S4</sup> with Becke-Jonson damping<sup>S5</sup> to describe the van der Waals interactions. The electron-ion interaction has been described using projector augmented wave (PAW) formalism of Blöchl<sup>S6</sup> in the implementation of Kresse and Joubert.<sup>S7</sup> The effect of solvent on the energetic properties has been analyzed using Poisson-Boltzmann implicit solvent model developed by Hennig *et al.*<sup>S8,S9</sup> This has been done for the case of DMF solvent modeled as a continuum with a relative dielectric constant  $\varepsilon = 38.25$  and following the settings of Steinmann et.al. S10 Optimizations in gas phase have been done using a cutoff energy of 400 eV which was increased to 600 eV in the case of solvent calculations. The CNT model used in calculations consists of a (14,0) CNT with seven repeating units and a surface C-C defect functionalized with two COOH and two O species. This nanotube was oriented along Oy axis and was separated along Ox and Oz axes by vacuum widths of 28.0 and 28.8 Å, respectively, leading to supercell with  $28.0 \times 29.1763 \times 40.0$  Å<sup>3</sup> dimensions. These large supercell dimensions are necessary in order ensure a vacuum width of at least 16.9 Å in x and z directions once the Zr(CL) and the three ATA molecules are adsorbed on SWCNT surface. Given the large size of the supercell considered a single  $\Gamma$  point was used in selection of the k-point grid.

### **Characterization section**

*Transmission Electron Microscopy (TEM).* The TEM instrument used was FEI Morgagni. TEM sample was prepared by drop-casting 7  $\mu$ L of diluted sample suspension on TEM sample grids (carbon film, 400 mesh copper grid; Electron Microscopy Science). HRTEM was done with JEOL 2001F transmission electron microscope. The accelerating voltage used was 200 keV.

*Powder X-ray Diffraction (PXRD).* PXRD was conducted with Bruker D8 XRD system equipped with LynxEye detector. Samples were prepared by drop-casting on glass slides.  $2\theta$  angles between 5° and 50° were measured at 0.02° interval with a rate of 0.2 seconds/point. The X-ray source was Cu K $\alpha$  held at 40 kV and 40  $\mu$ A with a 0.2 mm aperture slit width.

*Raman Spectroscopy.* Raman spectra were collected with an XplorA Raman AFM-TERS system with a 785 nm laser (100 mW) operating at 10% power at 1 s exposure time. Spectra curves were averaged over 25 accumulations. All peak positions were calibrated with Si peak at 520.7 cm<sup>-1</sup> from substrate.

*X-ray photoelectron spectroscopy (XPS).* XPS was performed on a Thermo ESCALAB 250 Xi XPS using monochromated Al K $\alpha$  X-rays as the source.

*Gas adsorption studies.* N<sub>2</sub> adsorption isotherms were collected on a Micromeritics 3-Flex gas adsorption analyzer. Approximately 50 mg of sample was added into a pre-weighed sample analysis tube. The samples were degassed at 150 °C under vacuum for 18 hours. A liquid N<sub>2</sub> bath was used for the N<sub>2</sub> adsorption experiments at 77 K. 3-Flex Share software program was used to determine the Brunauer-Emmet-Teller surface area.

*I/V curve and field-effect transistor (FET) electrical measurement set up.* A prefabricated  $2 \times 2$  mm SiO<sub>2</sub> chip with 4 interdigitated gold electrodes was used to collect I-V curves of Materials **5** and ox-SWCNT. Material **5** and ox-SWCNTs were deposited on the electrodes using dielectrophoresis (DEP). A Keithley 3390 Arbitrary Waveform Generator was used to generate a sine wave (10 V<sub>pp</sub>, 10 MHz). 5  $\mu$ L of sample suspension (material **5** in DMF and ox-SWCNT in water) was drop-cast on the device and the sine wave was applied to the electrodes for 2 min. The deposited devices were washed with water and then annealed at 200 °C for 1 hour to remove any solvent residue. The source meter used for I/V curves was Keithley 2400 and LabView software was used for collecting data.

*Conductivity measurement set up.* ox-SWCNT and UiO-66-NH<sub>2</sub>/ox-SWCNT were drop cast from stock solutions onto a 2 x 2 mm SiO<sub>2</sub> chip with 4 interdigitated gold electrodes. Multiple drops were drop cast until a thick layer of material coved the entire chip. Electrode area is  $3.25 \times 10^{-7}$  cm<sup>2</sup> and length of the electrode is  $7 \times 10^{-4}$  cm. I-V curves were collected with Keithley 2602 and LabView software.





**Figure S1**. A) TEM image of Material **1**, SWCNT are highlighted with blue boxes. B) TEM image of UiO-66-NH<sub>2</sub> MOF. C) PXRD pattern of simulated bulk UiO-66-NH<sub>2</sub> (black), Material **1** (blue) and UiO-66-NH<sub>2</sub> (red).



**Figure S2**. DFT calculated adsorption configurations and corresponding binding energies (in kcal/mol units) of ATA molecule on the side wall of (14,0) CNT. Panel a) corresponds to adsorption on an undefective CNT while panels b-d represent the case when adsorption takes place near a Stone-Wales defect functionalized with two O and two COOH groups. The color scheme used: C (gray), O (red), N (blue) and H (white).



**Figure S3**. DFT calculated adsorption configurations and corresponding binding energies (in kcal/mol units) of Zr(CL) ( $Zr_6O_4(OH_4)(CH_3COO)_{12}$ ) cluster on a (14,0) CNT. Panels a-d illustrate different configurations on an undefective CNT while panels e-f represent the case when adsorption takes place near a Stone-Wales defect functionalized with two O and two COOH groups. The inset figures in the top set of panels represent alternate side views along the nanotube axis. The binding of Zr(CL) when an additional ATA molecule is co-adsorbed on the side toward functionalized defect (g) respectively on the opposite side relative to the defect is indicated in panel (h). The color scheme used: C (gray), O (red), N (blue), H (white), Zr (green).



Figure S4. A) TEM image of Material 6. B) TEM image of Material 7.



Figure S5. A) TEM image of material 8. B) PXRD pattern of material 8.



**Figure S6**. a) Raman spectra of ox-SWCNT, ox-SWCNT/Zr and UiO-66-NH<sub>2</sub>/ox-SWCNT (material **5**) with additional Si peak from the substrate. b) Zoomed in Raman spectra of the RBM peak.



**Figure S7**. XPS C 1s spectra of ox-SWCNT (a), ox-SWCNT/Zr (c) and Zr oxide-cluster (e). XPS Zr 3d spectra of ox-SWCNT (b), ox-SWCNT/Zr (d) and Zr oxide-cluster (f).

Sample name	C-C	C=O	Zr 3d <sub>5/2</sub>	Zr 3d <sub>3/2</sub>
ox-SWCNT	284.70	288.07	N/A	N/A
ox-SWCNT/Zr	284.70	286.77	182.09	184.48
Zr oxide-cluster	284.70	288.44	181.95	184.27



**Figure S8**. Time dependent TEM of material **5** at 1 hr (a), 3 hr (b), 6 hr (c), 8 hr (d) and 12 hr (e). Scale bars are 200 nm.



Figure S9. I-V curve of drop cast ox-SWCNT (a) and UiO-66-NH<sub>2</sub>/ox-SWCNT (material 5) (b).



Figure S10. PXRD pattern of material 5 and material 5 after being stored 5 days in water.



Figure S11. Sensing response of ox-SWCNT (gray) and UiO-66-NH<sub>2</sub>/SWCNT (red) toward DMMP vapor.

#### References

- S1. Kresse, G.; Furthmüller, J. Efficiency of Ab-Initio Total Energy Calculations for Metals and Semiconductors Using a Plane-Wave Basis Set. *Comput. Mater. Sci.* **1996**, *6*, 15-50.
- S2. Kresse, G.; Furthmüller, J. Efficient Iterative Schemes for Ab Initio Total-Energy Calculations Using a Plane-Wave Basis Set. *Phys. Rev. B* 1996, 54, 11169-11186.
- S3. Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865-3868.
- S4. Grimme, S. Semiempirical GGA-type Density Functional Constructed with a Long-Range Dispersion Correction. J. Comput. Chem. 2006, 27, 1787-1799.
- S5. Grimme, S.; Ehrlich, S.; Goerigk, L. Effect of the Damping Function in Dispersion Corrected Density Functional Theory. J. Comp. Chem. 2011, 32, 1456-1465.
- S6. Blöchl, P.E. Projector Augmented-Wave Method. Phys. Rev. B 1994, 50, 17953.
- S7. Kresse, G.; Joubert, D. From Ultrasoft Pseudopotentials to the Projector Augmented-Wave Method. *Phys. Rev. B* **1999**, *59*, 1758.
- S8. Fishman, M.; Zhuang, H. L.; Mathew, K.; Dirschka, W.; Hennig, R. G. Accuracy of Exchange-Correlation Functionals and Effect of Solvation on the Surface Energy of Copper. *Phys. Rev. B* 2013, 87, 245402.
- S9. Mathew, K.; Sundararaman, R.; Letchworth-Weaver, K.; Arias, T. A.; Hennig, R. G. Implicit Solvation Model for Density-Functional Study of Nanocrystal Surfaces and Reaction Pathways. J. Chem. Phys. 2014, 140, 084106.
- S10. Steinmann, S. N.; Michel, C.; Schwiedernoch, R.; Sautet, P. Impacts of Electrode Potentials and Solvents on the Electroreduction of CO<sub>2</sub>: a Comparison of Theoretical Approaches. *Phys. Chem. Chem. Phys.* 2015, 17, 13949-13963.
- S11. Mathew K.; Chaitanya Kolluru, V. S.; Mula S.; Steinmann, S. N.; Hennig, R. G. Implicit Selfconsistent Electrolyte Model in Plane-Wave Density Functional Theory. J. Chem. Phys. 2019, 151, 234101.