

# Fluorination of “brick and mortar” soft-templated graphitic ordered mesoporous carbons for high power lithium-ion battery

Pasquale F. Fulvio,<sup>a</sup> Gabriel M. Veith,<sup>b</sup> Jamie L. Adcock,<sup>c</sup> Suree S. Brown,<sup>c</sup> Richard T. Mayes,<sup>a</sup> Xiqing Wang,<sup>‡a</sup> Shannon M. Mahurin,<sup>a</sup> Bingkun Guo,<sup>a</sup> Xiao-Guang Sun,<sup>a</sup> Alex A. Puzos,<sup>d</sup> Christopher M. Rouleau,<sup>d</sup> David B. Geohegan,<sup>d</sup> and Sheng Dai<sup>\*,a,c</sup>

<sup>a</sup> Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831. Fax: ++1- 865-576-5235; Tel: ++1-865-576-7307; E-mail: [dais@ornl.gov](mailto:dais@ornl.gov)

<sup>b</sup> Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831

<sup>c</sup> Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996

<sup>d</sup> Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831

<sup>‡</sup> Present Address: Nanotek Instruments, Inc., Dayton, Ohio 45404

## Synthesis

Mesoporous carbon samples were prepared by the self-assembly of resorcinol (Sigma-Aldrich, 99%) and formaldehyde (Sigma-Aldrich, 37 wt %) in the presence of triblock copolymer Pluronic F127 (EO<sub>106</sub>-PO<sub>70</sub>-EO<sub>106</sub>, BASF) purchased from Sigma-Aldrich according to previously reported recipe.[9] In a typical synthesis, approximately 1.1g of resorcinol and 1.1g of Pluronic F127 were dissolved in 4.5ml of ethanol, 3.4 ml of water and 1.1ml of concentrated HCl (37 wt%). To this, 1.3ml of formaldehyde solution (37 wt%) was added and the system stirred until phase separation was observed. The carbon black (CB, Sigma Aldrich, acetylene, <200nm), multi-walled carbon nanotube (MWNT, Sigma), single-walled carbon nanohorn<sup>1</sup> (SWNH) and graphene platelets (XG Sciences, 25 μm) composites were prepared by substituting the resorcinol by weight %, (10-25wt %) and the amount of formaldehyde adjusted proportionally to the amount of resorcinol used. After stirring for an additional 30min, the suspensions were centrifuged at 9500rpm for 5min and the aqueous phases discarded. The isolated polymer-rich phases were quickly re-dispersed using minimal amounts of ethanol with strong stirring followed by casting on Petri dishes. Thin films were cured at room temperature for 6 hours (and reference resorcinol/formaldehyde-F127 film overnight) and at 150°C for 24h. The phenolic resin-triblock copolymer nanocomposites were finally carbonized at 400°C for 2h (1°C/min heating rate) and 850°C for 2h in flowing nitrogen and using 2°C/min as heating rate. Composites were labeled as CB- *x*, MWNT-*x*, SWNH-*x* and GnP-*x*, respectively, where *x* stands for the initial wt. % of graphitic nanostructures added with respect to resorcinol in the synthesis gels.

## Fluorination

Samples were dried in the sealed FBR reactors at 150 to 160 °C (60 V) for almost 2 hours under He flow (46 sccm), when fluorine was admitted at 3.2 sccm (~7% F<sub>2</sub>/He), at the initial temperature of 150 °C overnight. The temperature was increased in a stepwise manner, first up to 210 °C at 20 °C/h and kept for 12 h, and finally up to 250 °C, where it was kept for another 12h and the He flow was reduced to 12 sccm. The He flow was further reduced to 6 sccm for the final 4 h. The F<sub>2</sub> flow was then stopped, heat was turned off and the helium reduced to 4 sccm and the reactor allowed to flush and to cool slowly for 24 to 72h.

## Characterization

For TEM characterization, carbon powders were dispersed in ethanol using ultrasonic bath. The final suspensions were transferred to lacy carbon coated 200-mesh copper TEM grids and dried in ambient air prior to electron microscopy analysis. Specimens were then characterized using a Hitachi HD-2000 operating in STEM mode using a secondary electron (SE) and/or bright-field STEM detector operating at 200 kV.

X-ray photoelectron spectroscopy (XPS) data were collected using a PHI 3056 spectrometer with an Al anode source operated at 15kV and an applied power of 350 W. Samples were manually pressed between two pieces of indium foil; the piece of In foil with the sample on it was then mounted to the sample holder with a piece of carbon tape (Nisshin E.M. Co. LTD). Adventitious carbon was used to calibrate the binding energy shifts of the sample (C1s = 284.8 eV). High resolution data was collected at pass energy of 5.85 eV with 0.05 eV step sizes and a minimum of 100 scans to improve the signal to noise ratio; lower resolution survey scans were collected at pass energy of 93.5 eV with 0.5 eV step sizes and a minimum of 25 scans. Peak assignments were made according to previously reported graphite intercalation compounds (GIC).<sup>2</sup>

Nitrogen adsorption isotherms were measured at -196°C using TriStar 3000 volumetric adsorption analyzer manufactured by Micromeritics Instrument Corp. (Norcross, GA). Before adsorption measurements the carbon powders were degassed in flowing nitrogen from one to two hours at 200°C. The specific surface area of the samples was calculated using the Brunauer-Emmett-Teller (BET) method within the relative pressure range of 0.05 to 0.20.<sup>3</sup> Pore size distributions were calculated using

the BJH algorithm for cylindrical pores according to the KJS method calibrated for pores up to  $10 \text{ nm}^4$  and statistical film thickness for a reference carbon adsorbent<sup>5</sup> also used for the  $\alpha_s$ -plot analysis.<sup>6</sup>

Coin cells (CR2032) were assembled to test the electrochemical performance of the various carbon fluoride materials. The cathode was prepared by spreading a slurry of active material (75 wt%), carbon black (10 wt%), and polyvinylidene fluoride (PVDF, 15 wt%) in N-methyl-2-pyrrolidone (NMP) onto Al foil. The active material loading was  $1\text{-}2 \text{ mg cm}^2$ . The electrodes were dried in a vacuum over at  $120^\circ\text{C}$  overnight before transferring into an Argon-filled glovebox (VAC OMNI-LAB). The anode is a lithium metal disc, and the separator is Cegard 2034. The C-rate calculation was based on the theoretical capacity. The electrolyte is 1.0M LiPF<sub>6</sub> in ethylene carbonate/dimethyl carbonate/diethylene carbonate (EC/DMC/DEC, 1:1:1 vol%). The coin cells were discharged on an Arbin BT2000 instrument at room temperature by applying a constant current with a cutoff voltage of 1.5V. The discharge rate ranging from 0.05 to 5C was used.

**Table S 1** - Calculated parameters from the nitrogen adsorption analysis at  $-196^\circ\text{C}$  for ordered mesoporous carbon nanocomposites with graphene nanoplatelets (GnP25-*x*), multi-walled carbon nanotubes (MWNT-*x*) and single-walled carbon nanohorns (SWNH-*x*), fluorinated mesoporous carbon nanocomposites with graphene nanoplatelets (GnP-*x*/F), multi-walled carbon nanotubes (MWNT-*x*/F) and single-walled carbon nanohorns (SWNH-*x*/F); *x* corresponds to the weight percent of the nanomaterials added to resorcinol, 10 and 25 wt.%. Calculated parameters for bulk carbon black, graphene, carbon nanotubes and nanohorns are provided for comparison.<sup>‡</sup>

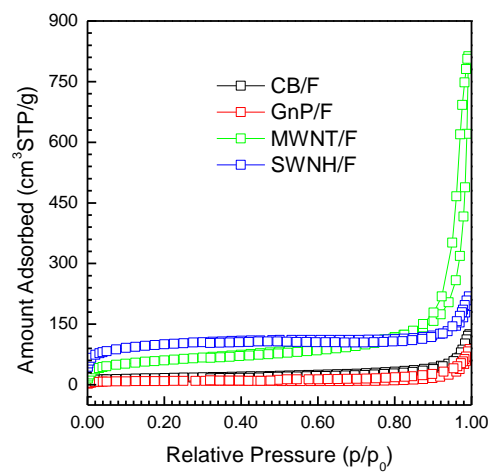
<i>Sample</i>	<sup>a</sup> <i>V</i> <sub>SP</sub> (cm <sup>3</sup> /g)	<sup>b</sup> <i>V</i> <sub>mi</sub> (cm <sup>3</sup> /g)	<sup>c</sup> <i>S</i> <sub>mi</sub> (m <sup>2</sup> /g)	<sup>d</sup> <i>S</i> <sub>BET</sub> (m <sup>2</sup> /g)	<sup>e</sup> <i>w</i> <sub>KJS</sub> (nm)	<sup>f</sup> <i>SG</i>
<b>CB</b>	0.08*	0.03	70	103	-	
<b>CB-10</b>	0.62	0.19	407	704	7.0	
<b>CB-25</b>	0.64	0.12	285	556	8.2	
<b>CB/F</b>	0.07*	0.01 <sup>†</sup>	20	59	-	CF <sub>0.322</sub>
<b>CB-10/F</b>	0.38	0.05	118	344	7.6	CF <sub>0.805</sub>
<b>CB-25/F</b>	0.34	0.07	152	330	7.9	CF <sub>0.703</sub>
<b>GnP</b>	0.08*	0.03 <sup>†</sup>	42	112	1.5	
<b>GnP-10</b>	0.70	0.14	307	671	8.2	
<b>GnP-25</b>	0.46	0.07	164	427	8.8	
<b>GnP/F</b>	0.03*	0.01 <sup>†</sup>	26	32	1.7	CF <sub>0.293</sub>
<b>GnP-10/F</b>	0.39	0.05	115	329	8.7	CF <sub>0.745</sub>
<b>GnP-25/F</b>	0.35	0.04	103	302	9.0	CF <sub>0.772</sub>
<b>MWNT</b>	0.42*	0.01 <sup>†</sup>	30	296	-	
<b>MWNT-10</b>	0.69	0.13	289	561	7.8	
<b>MWNT-25</b>	0.73	0.05	118	389	10.9	
<b>MWNT/F</b>	0.27*	0.03 <sup>†</sup>	62	217	-	CF <sub>0.686</sub>
<b>MWNT-10/F</b>	0.46	0.05	112	327	8.4	CF <sub>0.896</sub>
<b>MWNT-25/F</b>	0.42	0.05	117	295	10.9	CF <sub>0.770</sub>
<b>SWNH</b>	0.06*	0.03	72	88	1.4	
<b>SWNH-10</b>	0.57	0.16	348	591	7.9	
<b>SWNH-25</b>	0.58	0.09	190	420	9.3	
<b>SWNH/F</b>	0.20*	0.13	285	346	1.6	CF <sub>0.269</sub>
<b>SWNH-10/F</b>	0.36	0.06	127	322	8.1	CF <sub>1.045</sub>
<b>SWNH-25/F</b>	0.34	0.06	138	308	9.1	CF <sub>0.708</sub>

<sup>‡</sup>*a* – single point pore volume from adsorption isotherms at  $p/p_0 \sim 0.98$  ( $*p/p_0 \sim 0.92$ ); *b* and *c* – micropore volume and micropore surface area calculated in the *t*-plot range of 0.5-0.60 (<sup>†</sup>0.40-0.50), respectively, using the Carbon Black STSA equation; *d* – specific surface area calculated using the BET equation in the relative pressure range of 0.05-0.20; *e* – pore width calculated according to the improved KJS method (M. Jaroniec and L. A. Solovyov, *Langmuir* 2006, 22, 6757) using statistical film thickness for nonporous reference carbon material (J. Choma, J. Gorka and M. Jaroniec, *Microporous and Mesoporous Materials* 2008, 112, 573); *f* – compound stoichiometry from gravimetric analysis.

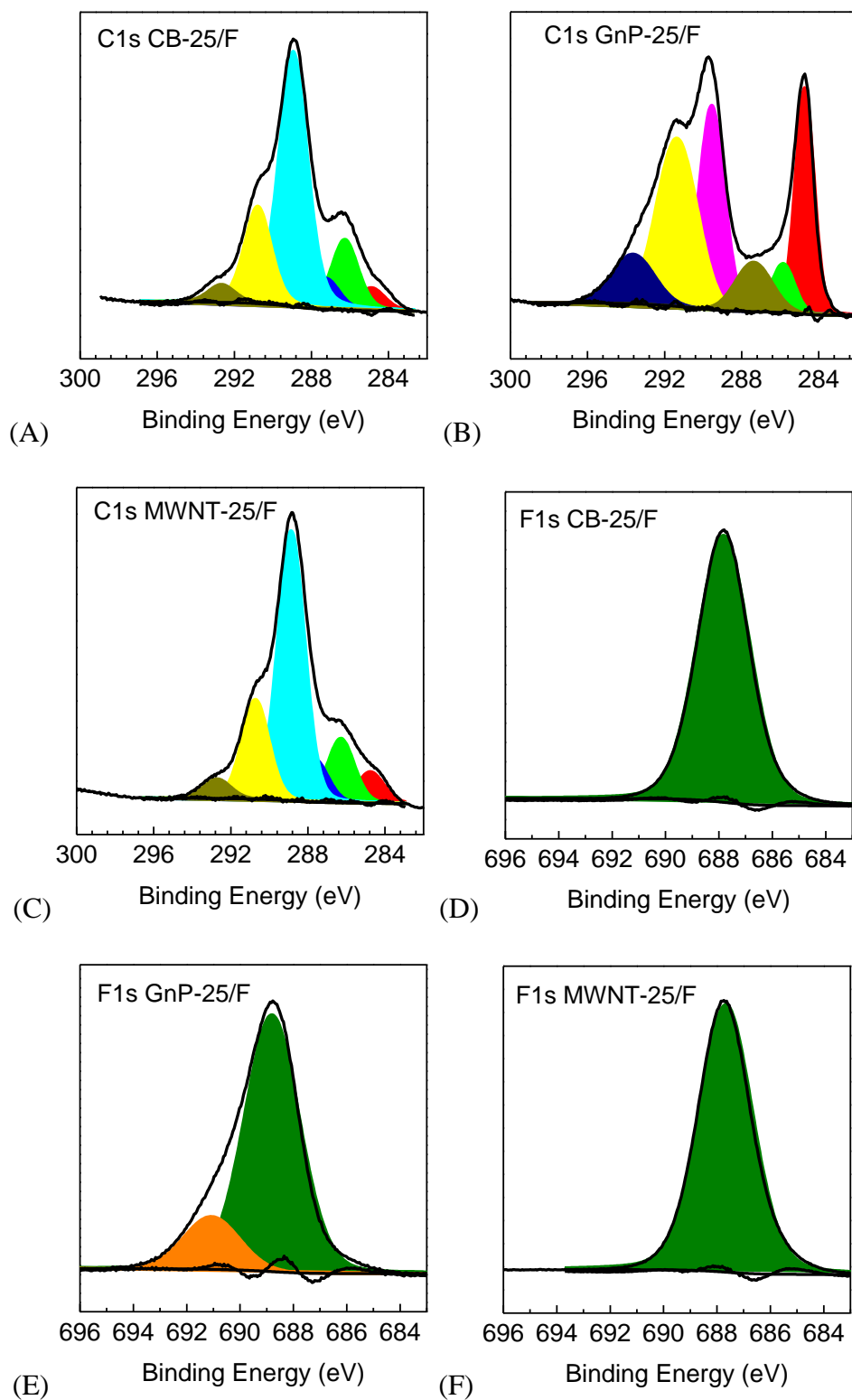
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**Table S 2** - XPS assignments (*Carbon* 2004, 42, 3243-3249) and concentrations for the various fluorinated mesoporous carbon nanocomposites.

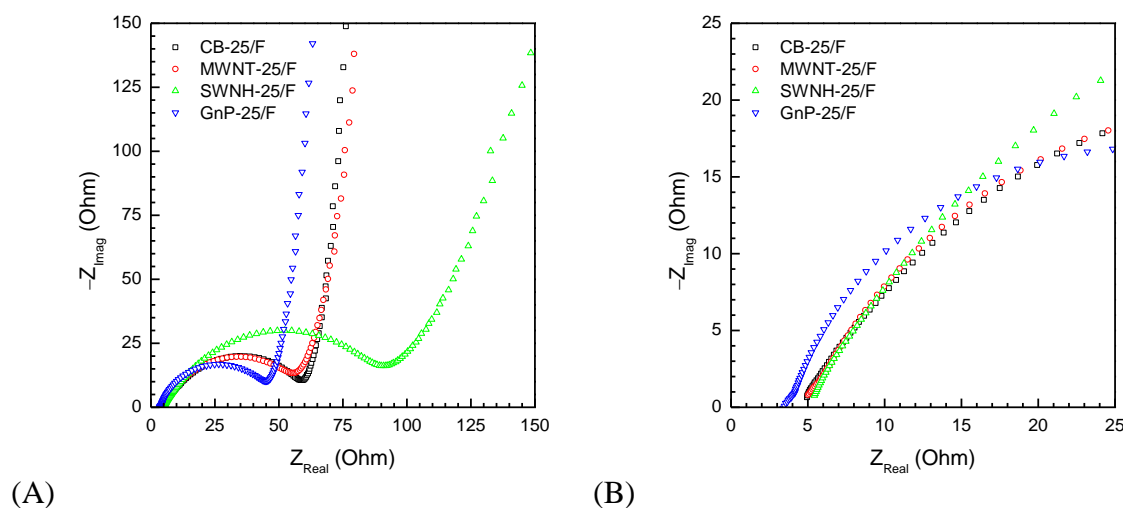
Sample	C-C,C-H	C(C) <sub>2</sub> (CF)	C-C(CF) <sub>3</sub>	FC(C) <sub>3</sub>	FC(CF) <sub>3</sub>	F <sub>2</sub> C(CF) <sub>2</sub>	F <sub>2</sub> C(CF <sub>2</sub> ) <sub>2</sub>	-CF <sub>3</sub>	CF <sub>4</sub>	ionic	Semi-ionic	Covalent	C-F-O
MWNT/F	284.83	286.58	287.93	289.13		290.94	292.76				687.95		43.5-56.5
%	3.5	8.1	5.1	55.6		23.7	4.0				100		
MWNT-10/F	284.7	286.20		289.06	290.31		292.55				688.36		52.5 – 47.5
%	16.0	16.6		35.9	25.7		5.8				100		
MWNT-25/F	284.75	286.28	287.65	288.86		290.71	292.70				687.70		42.8 – 57.2
%	6.0	12.2	8.2	51.0		18.8	3.7				100		
SWNH/F	284.7	286.10		288.49	290.67					684.97	687.37		52.6 – 47.4
%	19.8	16.3		58.4	5.5					8.1	91.9		
SWNH-10/F	284.90		287.05	288.84		291.09				685.97			42.0 – 58.0
%	10.9		57.0	30.6		1.5				100			
SWNH-25/F	284.81	286.61		288.74	290.57		292.79	294.74	296.42	685.66	688.83	691.39	42.6 – 57.4
%	30.7	7.5		6.0	7.5		37.5	9.6	1.2	7.5	16.3	76.2	
GnP/F	284.76	285.83	287.64		289.39	291.53		293.55			688.60		70.0 – 28.3 – 1.6
%	46.8	14.0	6.0		19.8	10.3		3.1			100		
GnP-10/F	284.84	286.39	287.91		289.75		292.03	294.02	296.06		688.89	691.42	56.7 – 43.3
%	15.0	9.4	9.7		25.7		25.3	12.0	2.8		35.0	65.0	
GnP-25/F	284.75	285.88	287.40		289.57	291.39		293.66			688.82	691.09	68.5 – 31.5
%	20.7	5.4	8.3		25.0	31.1		9.5			83.6	16.4	
CB/F	284.82	286.64		289.04		290.99				685.85	688.05		86.7 – 13.3
%	52.4	10.9		31.6		5.0				9.0	91.0		
CB-10/F	284.88	286.58		288.34	289.30	290.98	292.77				687.97		48.0-52.0
%	3.3	10.4		16.5	42.6	22.7	4.6				100		
CB-25/F	284.8	286.22	287.20	288.90		290.74	292.62				687.83		47.8 – 52.2
%	4.6	13.9	6.1	52.7		19.1	3.5				100		



**Fig. S 1** – Nitrogen -196 °C isotherm (A), and corresponding PSD (B) for the OMC-R sample, and isotherms for fluorinated graphitic “bricks” (C).



**Fig. S 2** – C1s (A-C) and F1s (D-F) XPS spectra of CB-25/F (A, D), GnP-25/F (B, E) and MWNT (C, F).



**Fig. S 3** – Electrical impedance spectra (EIS) for selected fluorinated cathode materials (A) and magnification of the high frequency range of the same curve (B). The semi-circles in (A) originate from the electrolyte reaction with lithium before discharge, whereas for battery cells prepared in a similar manner, the lower impedance is the result of the electronic resistivity of the active cathode material.

### References S:

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