## Electronic Supplementary Information (ESI)

## for

## Ultra-Small Carbon Nanospheres (< 50 nm) of Uniform Tunable Sizes by a Convenient Catalytic Emulsion Polymerization Strategy: Superior Supercapacitive and Sorption Performances

Vimal K. Tiwari,<sup>a</sup> Zhe Chen,<sup>a</sup> Fan Gao,<sup>b</sup> Zhiyong Gu,<sup>b</sup> Xueliang Sun,<sup>c</sup> and Zhibin Ye<sup>a,\*</sup>

- <sup>a.</sup> Bharti School of Engineering, Laurentian University, Sudbury, Ontario P3E 2C6, Canada
- <sup>b.</sup> Department of Chemical Engineering, University of Massachusetts, Lowell, Massachusetts
   01854, United States
- <sup>c.</sup> Department of Mechanical and Materials Engineering, Western University, London, Ontario
   N6A 5B9, Canada
- \* Corresponding author; Email: zye@laurentian.ca



**Figure S1.** DLS particle size distribution of the polymer nanospheres (PNS11 and PNS21) obtained by the miniemulsion polymerization.



**Figure S2.** SEM images of PNS21 after hydrothermal treatment and CNS21. Scale bar = 100 nm. The PNS21 sample was gold-coated for SEM imaging.



Figure S3. XRD pattern of CNS21.



**Figure S4.** Micropore size distribution curves of A-CNS21 and AC-PDEB determined with NLDFT model.



Figure S5. XPS survey spectra (a) and elemental compositions (b) of A-CNS21 and AC-PDEB.



Figure S6. Raman spectra of PNS21 (after hydrothermal treatment), A-CNS21 and AC-PDEB.



**Figure S7.** GCD curves of A-CNS21 in a two-electrode cell configuration in  $1.0 \text{ M H}_2\text{SO}_4$  at different current densities within (a) 0.1-1 A/g; (b) 10-50 A/g.



**Figure S8.** Electrochemical supercapacitive results of AC-PDEB in a two-electrode cell configuration in 1 M  $H_2SO_4$  aqueous electrolyte: (a) CV curves at different voltage sweep rates; (b) GCD curves at different current densities within (b) 0.1–1 A/g, (c) 1–10 A/g, and (d) 10–100 A/g.

**Table S1.** Summary of supercapacitive performances of representative porous carbon electrodes in a two-electrode symmetrical cell configuration with aqueous electrolyte.

Sample			Reference data			Data from this work with A-CNS21	
		Current density range	Capacitance (F/g) at initial current density	Capacitance retention (%) at final current density	R ef.	Capacitance (F/g) at initial current density	Capacitance retention (%) at final current density
	Polystyrene-based hierarchical porous carbon spheres	5–50 mV/s	185 a	89 a	1	223	93.7
Porous carbon spheres	Mesoporous size controllable carbon microspheres	1–20 A/g	268 a	60.8 <sup>a</sup>	2	255	82.0
	Highly porous carbon spheres	5–100 mV/s	169	83	3	223	89.7
	Nitrogen-dopedcarbonmicrospheresfromorganicframeworks	0.2–20 A/g	282 ª	55 a	4	<b>283</b> (@0.25 A/g)	<b>74</b> (20 A/g)
	Mesoporous carbon nanospheres	10–200 mV/s	185	75	5	223	74.9
	Carbon spheres with microporous structure	5–50 mV/s	~182	70	6	223	93.7
	Hierarchcally porous carbon spheres by hydrothermal method	0.1–10 A/g	170	82	7	305	71.8
	Carbon microspheres	0.1–20 A/g	241	80	8	305	68.5
Hollow carbon	Ultrahigh-surface- area hollow carbon nanospheres	0.5–10 A/g 5–50 mV/s	~185 201	81.8 92.9	9	268 223	81.7 93.7
	Porous nitrogen-doped hollow carbon spheres	0.5–10 A/g	213 <sup>a</sup>	55.6 <sup>a</sup>	10	268	81.7
	Hierarchical porous carbon hollow spheres	0.5–10 A/g	270 <sup>a</sup>	72.8 <sup>a</sup>	11	268	81.7
spheres	Carbon nanocages (CNC700)	0.1–10 A/g	260	68.4	12	305	71.8
	Nitrogen-doped carbon nanocages	1-50 A/g	313	75	13	255	75.3
	Carbon nano-onions	0.75–25 A/g	126.3	71	14	<b>268</b> (at 0.5 A/g)	<b>75</b> (at 30 A/g)
Mesoporous carbons	Porous carbon with small mesopores	0.1–50 A/g	425	~66	15	305	63.0
Carbon aerogels	Magnetite carbon aerogels	5–100 mV/s 0.5–6 A/g	369.2 <sup><i>a</i></sup> 337.2 <sup><i>a</i></sup>	38.5 <sup><i>a</i></sup> 65.9 <sup><i>a</i></sup>	16	<b>223</b> <b>268</b> (at 0.5 A/g)	<b>89.7</b> <b>81.7</b> (at 10 A/g)

	Mesoporous carbon/graphene aerogels	0.5–10 A/g	197 <sup>a</sup>	71.6 <sup>a</sup>	17	268	81.7
Hierarchical ly porous carbons	Hierarchically porous carbons (CNB-3)	0.5–20 A/g	247 <sup>a</sup>	67.6 <sup>a</sup>	18	268	78.0
	3D microporous conducting carbon beehive	0.5–30 A/g	254	55	19	268	75.3
	Porous carbon from metal- organic framework	5–50 mV/s	204	77.9	20	223	93.7
	Nitrogen-doped ordered nanoporous carbons	0.1–10 A/g	~270	47	21	305	71.8
	Hierarchical carbide-derivde carbon foams	1–20 A/g	240	72.9	22	255	82.0
	Microporous carbon nanoplates	0.1–52.5 A/g	264	120	23	305	<b>63.0</b> (at 50 A/g)
	Mesoporous graphene-like carbon sheet	5–200 mV/s	~255 a	~78 ª	24	233	78.0
	3D N-doped graphene-CNT networks	0.5–5 A/g	180	52.8	25	268	85.4
	Porous graphene carbons	1–20 A/g	280	~46	26	255	82.0
Graphene/ CNTs	2D porous carbon nanosheets	1–20 A/g	228	89	27	255	82.0
	Holey graphene frameworks	1–50 A/g	310	82	28	255	75
	Microporous carbon nanosheets	0.5–10 A/g	213 <i>a</i>	75.1 <sup>a</sup>	29	268	81.7
	Functionalized graphene hydrogel	1–20 A/g	441	80	30	255	82.0
	Graphene and CNT foam	5–100 mV/s	270	80	31	223	89.7
	Graphene-based frameworks	5–100 mV/s	175	47	32	223	89.7
	GO/MWCNT composites	5–100 mV/s	251 <i>a</i>	30 <i>a</i>	33	223	89.7
	GO reduced by urea	0.5–30 A/g	255 a	29 <i>a</i>	34	268	75.3
Carbons	Dead leaves derived carbons	0.5–10 A/g	401	64	35	268	81.7
from biomass	Carbonized chicken eggshell membranes with 3D architecture	0.2–20 A/g	297 ª	66 ª	36	<b>283</b> (at 0.25 A/g)	<b>73.9</b> (20 vs. 0.25 A/g)

<sup>*a*</sup> Data obtained in a 3-electrode cell configuration, where the specific capacitance data are often significantly higher than the corresponding ones obtained in a 2-electrode symmetrical cell at the same current density (see Ref. 37).

Sample		To	oluene Methanol		hanol	
		Relative	Adsorption	Relative	Adsorption	Defense
		vapor	capacity	vapor	capacity	Reference
		pressure	(mg/g)	pressure	(mg/g)	
		0.01	159	0.01	21	
		0.05	585	0.05	167	
	A-CNS21	0.1	866	0.1	366	This work
		0.99	967	0.99	937	
		0.01	38	0.01	46	
		0.05	163	0.05	250	
	AC-PDEB	0.1	366	0.1	380	I his work
		0.99	631	0.99	572	
	Ultrahigh-surface-area hollow	0.1	~ 800	0.1	~ 240	9
	carbon nanospheres	0.9	1500	0.9	1230	
	(HCN-900-20H2R)					
	Single-walled carbon nanotubes	0.1	~160			38
	(CVD80)	0.94	456			
Porous		0.1	~130	0.1	~40	39
carbons	Activated grahene aerogel	1	710	1	641	
	Activated carbon	1	640			40
	Hierarchical porous carbon	0.9	243			41
	microfibers					
	Activated carbon fiber cloth	0.1	560 (20°C)			42
		0.9	600 (20°C)			
	Porous aromatic framework	0.1	~800			43
	(PAF-1)	1	1357			
	Porous aromatic framework	0.1	482	0.1	81	44
	(PAF-5)	1	1061	1	933	
	Porous aromatic framework	0.1	~300	0.1	~65	45
	(PAF-11)	1	780	1	654	
Porous	Porous polymeric nanoscale			0.1	~82	46
polymers	networks			0.9	741	
1 5	Mesoporous conjugated	0.1	~200			47
	polycarbazole (CPOP-9)	1	1355			
	Porous conjugated	0.1	~400	0.1	~160	48
	polyporphyrins (CPOP-12)	1	1192	1	766	
	Microporous polymeric	0.08	~360	0.08	~100	49
	microsphere	1	887	1	574	
		0.06	~608			50
MOF	HKUSI-I	0.9	620			
	MIL-101	0.08	~239			51
		0.9	1389			
	PdCl <sub>2</sub> /MIL-101	0.06	660			51
		0.9	1285			
		0.1	510	0.08	25	52
	$[Zn_4O(bdc)(bpz)_2]$ •4DMF•6H <sub>2</sub> O	0.9	~550	0.2	420	
				0.9	~480	
	$[Cu_2(bdc)_2(DMF)]$			0.1	~90	53
	• $H_2O$ •(DMF)(C <sub>2</sub> H <sub>5</sub> OH) <sub>0.5</sub>			0.9	171	

**Table S2.** Summary of adsorption capacities of representative porous materials toward toluene and methanol vapors at 25 °C.

**Table S3.** Summary of  $CO_2$  adsorption capacity (at 0 °C and 1 bar) of most representative porous carbons.

	CO <sub>2</sub> adso		
Sample	Adsorption capacity (wt%)	CO <sub>2</sub> /N <sub>2</sub> selectivity (mol/mol)	Reference
A-CNS21	26	11	This work
AC-PDEB	28	11	This work
Carbon microspheres	15.8		8
Monodisperse carbon spheres	19.2		54
Highly microporous carbon spheres	29		55
Activated carbon molecular sieves from petroleum pitch (VR-5-M)	38	2.8	56
Activated carbon molecular sieves from petroleum pitch (VR-93-M)	24	14	56
Phenolic resin-based activated carbon spheres (CS*-P-A)	39		57
Carbide derived carbon	31		58
Purified SWCNTs	22		59
Activated carbon	16		60
Activated carbon fibres	14		61
Activated carbon	12		62
Activated carbon	11		59
Nitrogen enriched porous carbon spheres	27		63

**Table S4.** Summary of  $H_2$  adsorption capacity (at 77 K and 1 bar) of most representative porous carbons.

Sample	H <sub>2</sub> adsorption capcity (wt%)	Reference
A-CNS21	2.5	This work
AC-PDEB	2.4	This work
Activated carbon	2.49	64
Biomass waste-derived microporous carbons	2.55	65
MOF-derived hierarchically porous carbons	3.25	66
Activated carbon (AC Norit 990293)	2.1	67
TiC carbide-derived carbon	3.0	68
Single-walled carbon nanotubes	0.924	69
Multi-walled carbon nanotubes	ca. 0.2	68
Superactivated carbide-derived carbons	2.7	70
MOF-derived nanoporous carbon (C1000)	2.77	71
Carbon hollow spheres	1.1–1.5	72

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