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In-situ Stöber templating: Facile synthesis of hollow mesoporous carbon spheres from silica-polymer composites for ultra-high level in-cavity adsorption

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SUPPORTING INFORMATION

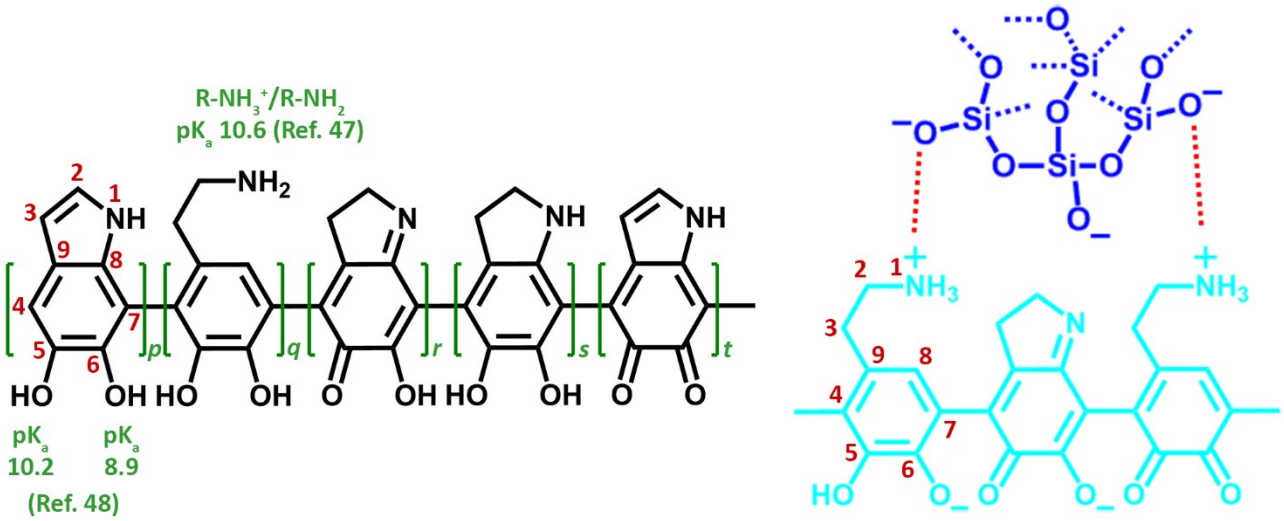


Figure S1: Subunit structures of pristine PDA (a) and PDA-silica composite in solution (b), consistent with contemporary PDA structures [Ref. 33, 46]. Positions numbered according to indole naming convention (red). pK_as of relevant groups given with reference numbers from main text (green).

Table S1: Physical data, TEM measurements and DEHP adsorption performances for HMCS.

	S_{BET}	D_{PORE}	V_{PORE}	V_{MESO}	V_{MICRO}	D_{CAVITY}	D_{SHELL}	D_{TOTAL}	ρ_{SHELL}	V_{TOTAL}	$Q_{max\ DEHP}$	*Reservoir Occupation*
	$m^2 g^{-1}$	nm	$cm^3 g^{-1}$	$cm^3 g^{-1}$	$cm^3 g^{-1}$	nm	nm	nm	$g\ cm^{-3}$	$cm^3 g^{-1}$	mg/g	%
$HMCS_{30\text{-}2.5}$	882	8	1.1	0.97	0.13	262 ±14	15 ±2	298	0.62	4.88	5084	97.9
$HMCS_{30\text{-}5}$	1564	2.5-8	1.55	1.34	0.21	185 ±20	55 ±4	297	0.48	2.67	2971	92.0
$HMCS_{40\text{-}5}$	1475	2.5-6	1.37	1.19	0.18	212 ±8	40 ±2	294	0.53	3.12	3196	99.7
$HMCS_{50\text{-}5}$	1395	2.5	1.23	1.05	0.18	222 ±7	36 ±2	290	0.57	3.21	3435	95.5
$AC_{sci\text{-}carb}$	900	< 2	0.39	0.11	0.27	-	-	-	-	0.39	175	44.0
OMC [38]	1801	2.3	2.0	1.2	0.8	-	-	-	-	2.0	364	17.8

Note: BET surface area (S_{BET}), Mesopore diameter from BJH (adsorption branch) (D_{MESO}), Total pore volume (V_{PORE}), Micropore volume (1.5 nm) from DFT (V_{MICRO}), Mesopore volume (V_{MESO}) calculated from V_{PORE} -$V_{MICRO.}$ Diameter of cavity (D_{CAVITY}) measured from TEM, Thickness of shell (D_{SHELL}) measured from TEM, total particle diameter (D_{TOTAL}) measured from TEM, Density of porous carbon in shell (ρ_{SHELL}) and Total volume of cavity (V_{TOTAL}) calculated from TEM measurements and pore volumes (see SI for calculation), DEHP adsorption capacity ($Q_{max\ DEHP}$) from Langmuir isotherms, and Reservoir occupation based on the volume of DEHP adsorbed (calculated from $Q_{max\ DEHP}$) vs the V_{TOTAL}.

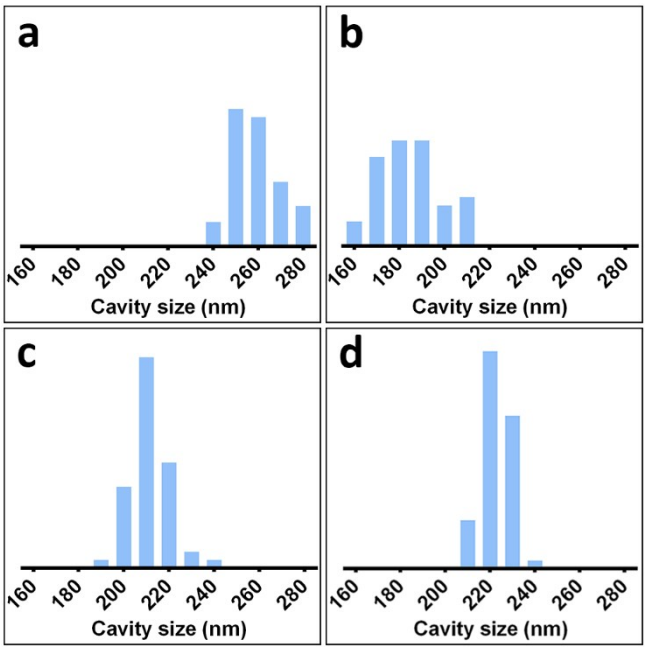


Figure S2: Size distribution histograms showing cavity size measured by TEM of HMCS30-2.5 (a), HMCS30-5 (b), HMCS40-5 (c), HMCS50-5 (d).

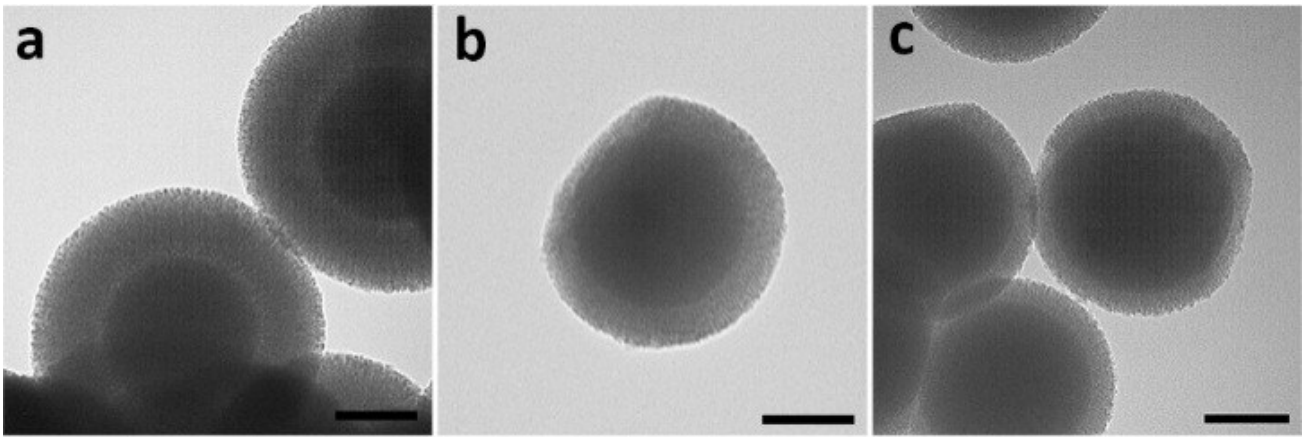


Figure S3: TEM images of silica template structures after calcination, corresponding to $HMCS_{30\text{-}5}$ (a), $HMCS_{40\text{-}5}$ (b), $HMCS_{50\text{-}5}$ (c). Scale bar: 100nm.

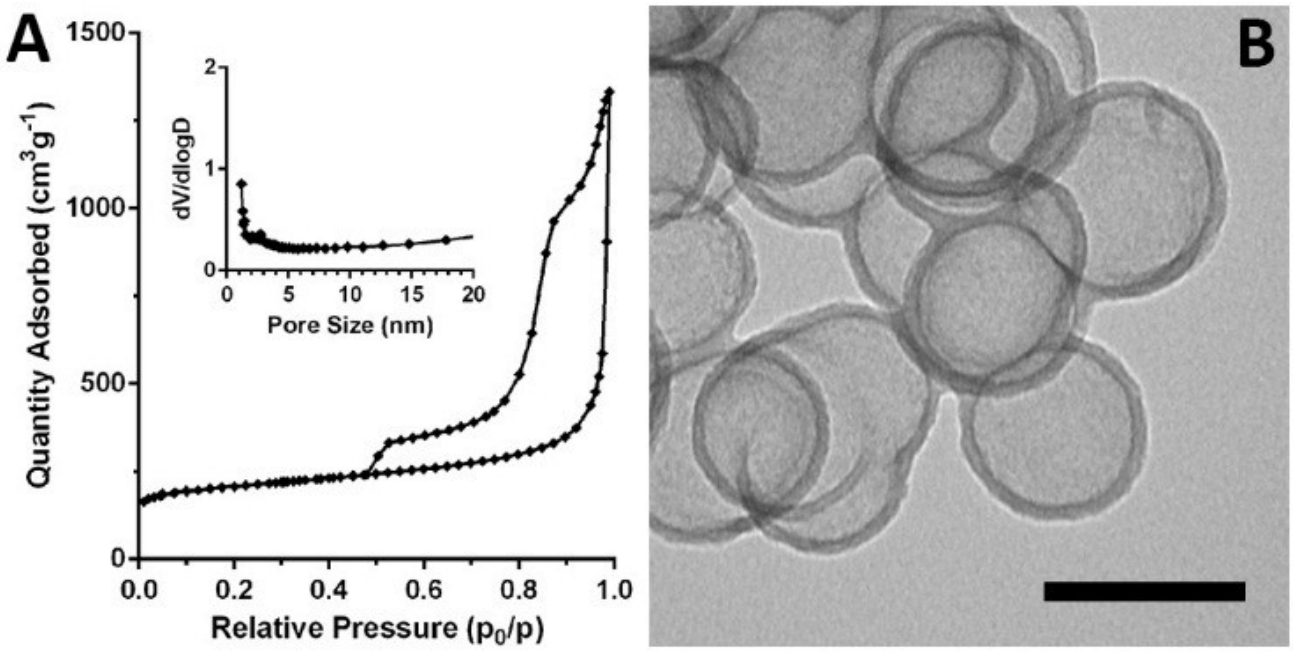


Figure S4: Nitrogen adsorption isotherm (A), BJH PSD (inset of A), and TEM image of HMCS prepared without primary particles with 2.5mg/mL dopamine (B). TEM scale bar: 100 nm.

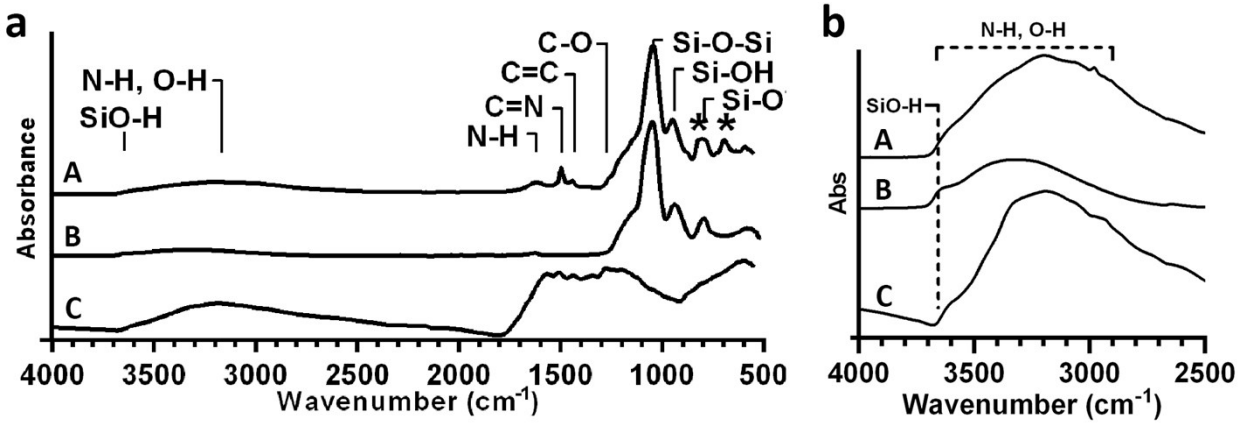


Figure S5. (a) FTIR spectra with anotated peak assignments and (b) expansion of the hig frequency region (4000 cm^{-1} – 2500 cm^{-1}) for the PDA-silica composite (trace A), pristine silica (trace B) and pritine PDA (trace C).

Composite cm^{-1}	Assignment	PDA cm^{-1}	Silica cm^{-1}	Shift cm^{-1}
3610	*v* SiO-H (H-bonded)	-	-	-
3600-2800	*v* O-H, N-H	3600-2800	-	-
1622	*β* N-H (scissoing)	-	-	-
1596	*β* N-H (scissoing, H bonded)	-	-	-
1495	*v* C=N	1507	-	12
1440	*v* C=C	1436	-	-4
1354	*v* C-N-C	1340	-	-14
1277	*v* C-O	1262	-	15
1042	*v* Si-O-Si	-	1047	5
948	*v* Si-OH	-	938	-10
825	*β* N-H (Wag)	-	-	-
793	*v* $Si-O^-$	-	793	0
694	*γ* C-H (out of plane, aromatic)	-	-	-

Figure S6. FTIR absorptions and peak assignments for the PDA-silica composite. Corresponding absorptions and relative shifts from pristine PDA and silica materials are shown. Absorptions and relative shifts from pristine PDA and silica materials are shown.

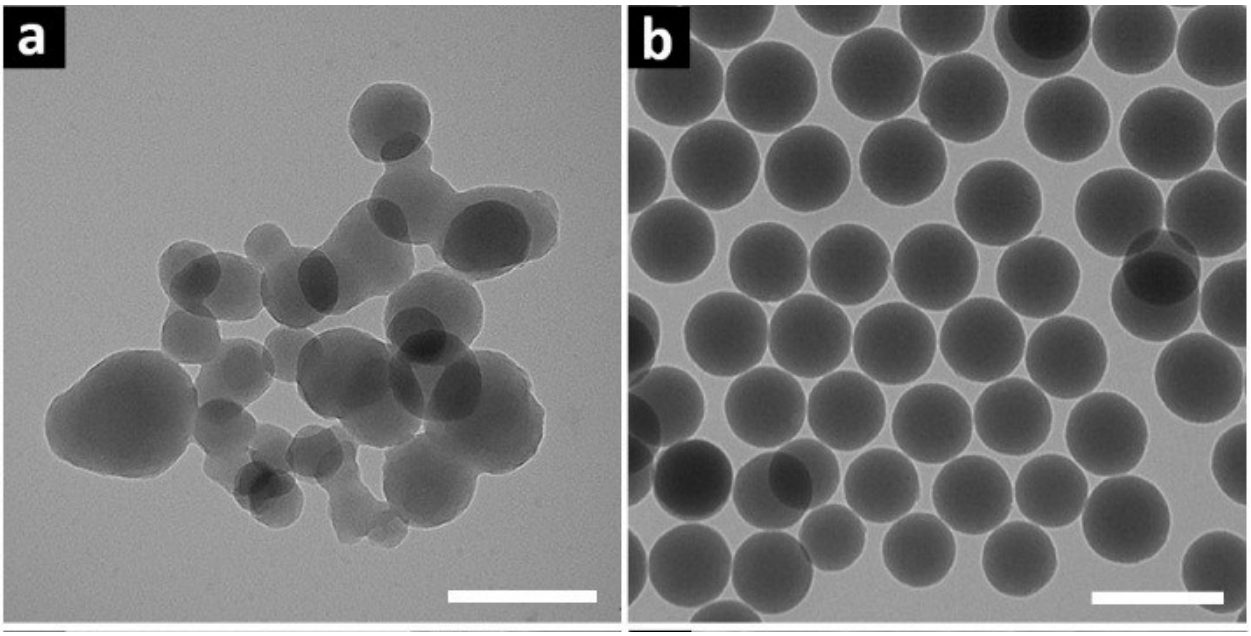


Figure S7. TEM of pristine PDA (a) and pristine silica (b) prepared under the same reaction conditions used in this study using only one precursor.

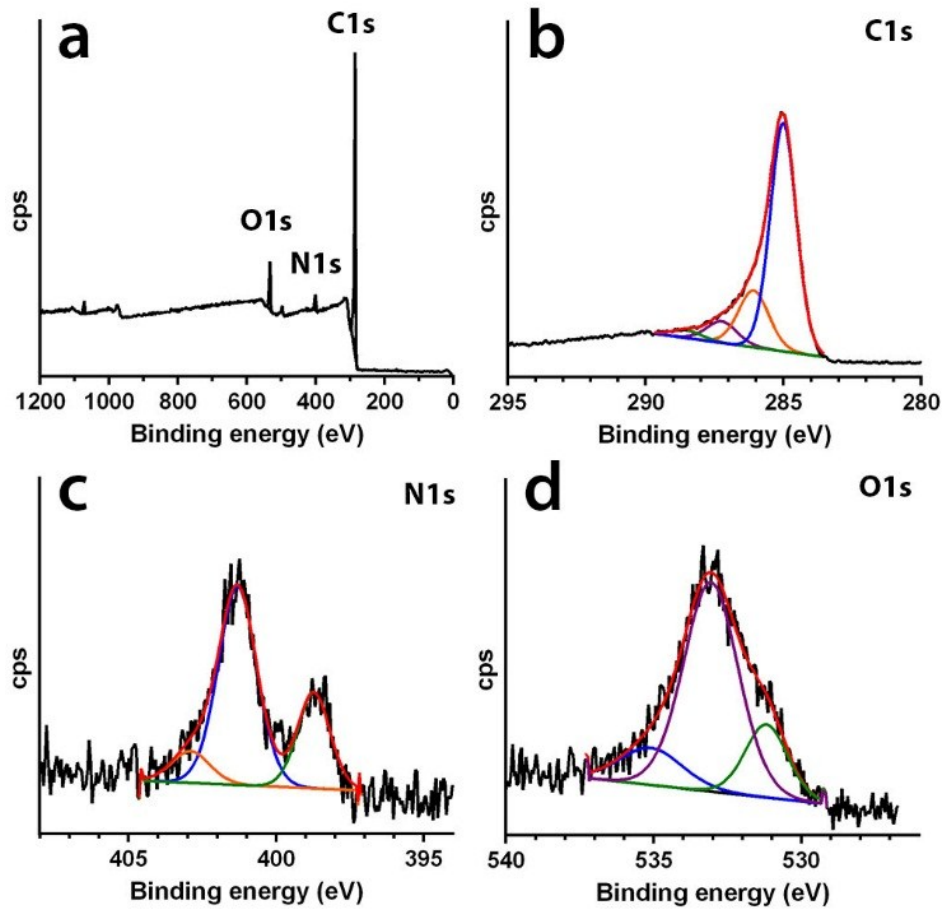
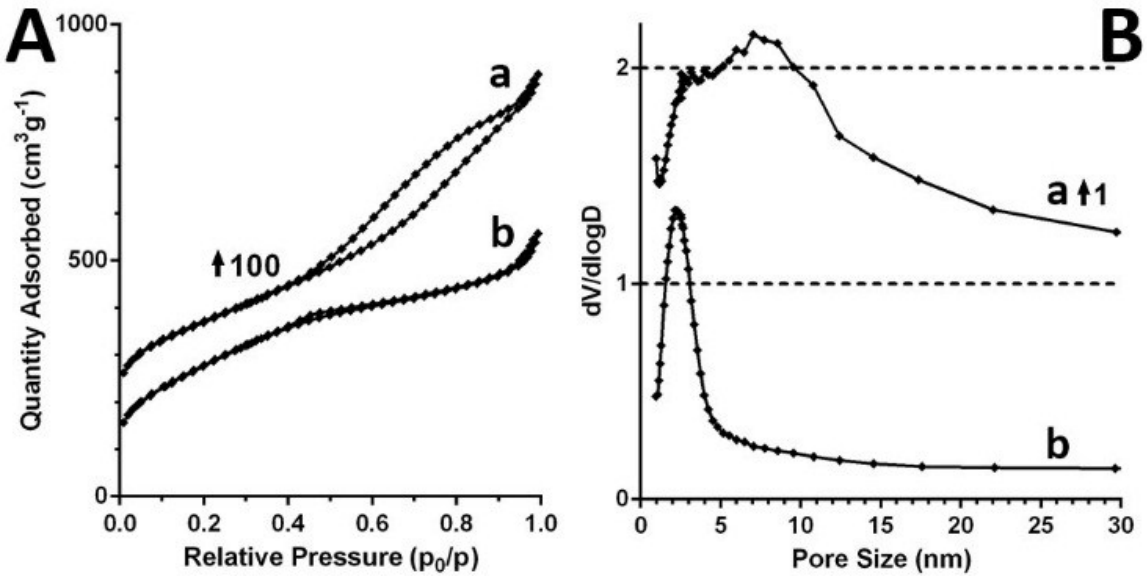


Figure S8. XPS wide scan (a) and high-resolution scans of the C1s (b), N1s (c) and O1s peaks for $HMCS_{5\text{-}30}$ after removal of silica.

XPS analysis confirms the formation of nitrogen-doped-carbon with 3.2 At% nitrogen and 5.5 At% oxygen content in the carbon framework (Fig. S). High resolution scans of the N1s peak reveal the presence of pyridinic, pyrolic and graphitic nitrogen centres. When pristine PDA is carbonised under the same conditions a nitrogen content of 4.2% is maintained. The lower nitrogen content observed in the HNCS materials may result from the association of the amine groups with the silicates during composite assembly. This interaction prevents the normal indole ring closure during PDA polymerisation, resulting in a higher loss of nitrogen from pendant amine groups during pyrolysis.



C	S_{BET} m^2g^{-1}	D_{BJH} nm	V_{Meso} cm^3g^{-1}	V_{Micro} cm^3g^{-1}
$HNCS_{20}$	954	2.5,6	1.12	0.14
$HNCS_{60}$	1007	2.5	0.76	0.15

Figure S9. N_2 adsorption isotherms (A) and BJH pore size distributions (B) for samples prepared by further adjusting addition time of DA to (a) 20 min and (b) 60 min. Table C provides physical characteristics from nitrogen adsorption.

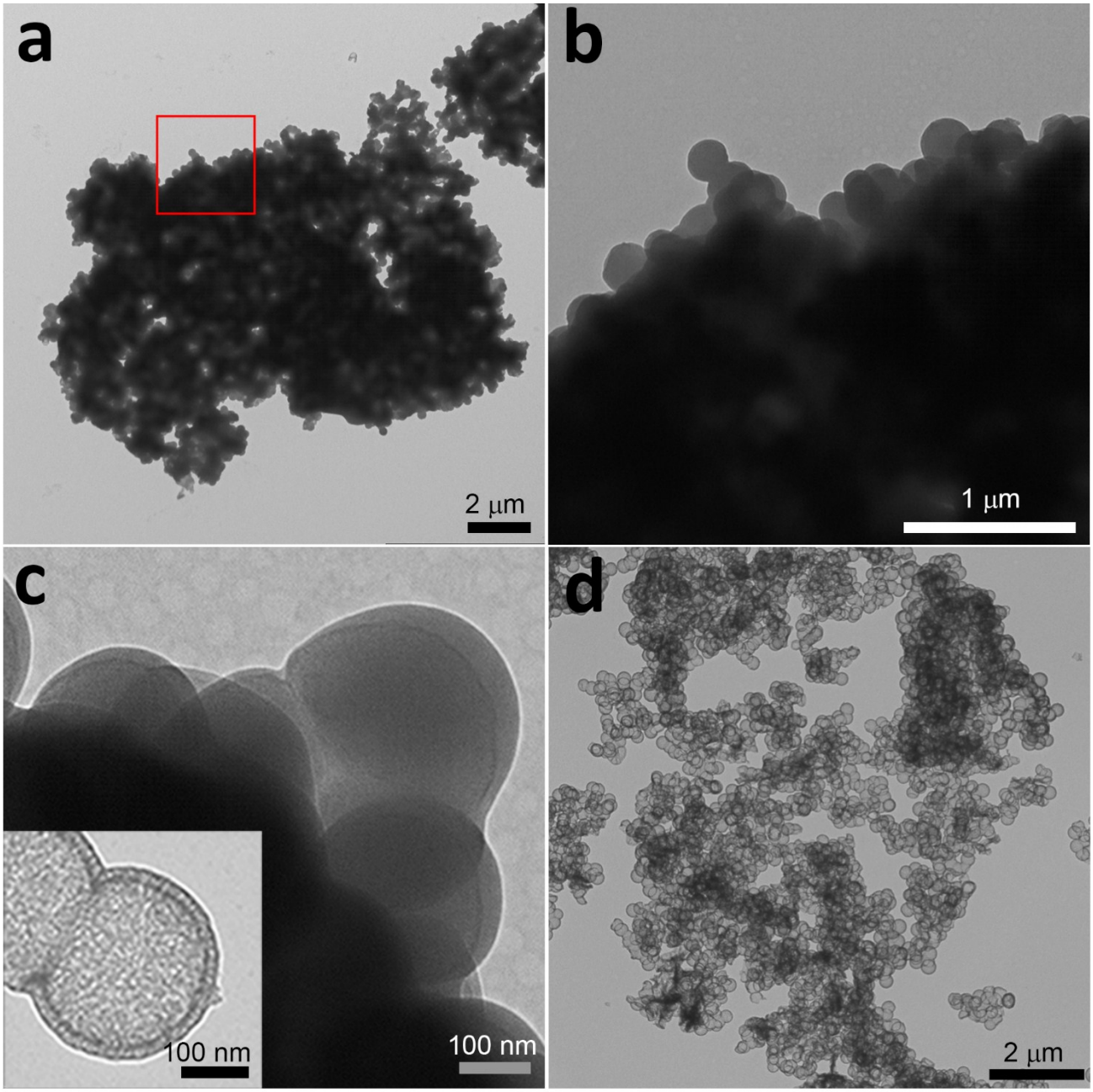
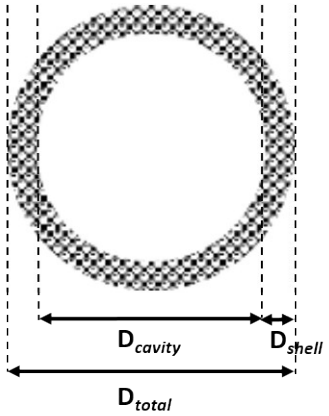


Figure S10. (a) Large area TEM image of HMCS stained with ammonium molybdate with DEHP adsorption; (b) Higher magnification TEM of region indicated by red box in (a); (c) Higher magnification of individual HMCS stained with ammonium molybdate with DEHP adsorption, inset shows HMCS stained with ammonium molybdate without DEHP at the same magnification; (d) Large area TEM of HMCS stained with ammonium molybdate without DEHP adsorption.

Figure S11. Equations used to calculate density of porous carbon shell and total specific void space.



1) $$V_{total} = V_{cavity} + V_{pore}$$
$$= \frac{4\pi r_{cavity}{}^{3}}{M_{of\ 1\ sphere}} + V_{pore}$$

2) $$\rho_{mesoporous\ carbon} = M_{carbon}/V_{mesoporous\ carbon}$$
$$= M_{carbon}/(V_{pore} + V_{carbon})$$
$$= 1/(V_{pore} + \frac{1}{\rho_{carbon}})$$ (assuming 1 g of carbon)

3) $M_{of\ 1\ sphere} = V_{of\ 1\ sphere} \times \rho_{carbon}$

4) $V_{carbon\ in\ 1\ sphere} = (4\pi r_{total}{}^{3} - 4\pi r_{cavity}{}^{3}) \times \rho_{mesoporous\ carbon}/\rho_{carbon}$

V_{total} Total specific volume enclosed by material

$\rho_{mesoporous\ carbon}$ Density of porous shell region, calculated from equation 2

ρ_{carbon} Density of amorphous carbon ~2g/cm^3

V_{cavity} Volume enclosed by cavity of one sphere

V_{pore} Total pore volume measured from nitrogen adsorption (BJH, ads)

$M_{of\ 1\ sphere}$ Approximate mass of one sphere calculated from equation