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Supporting Information

Nanocasting in Ball Mills - Combining Ultra-Hydrophilicity and Ordered Mesoporosity in Carbon Materials

*En Zhang, Guang-Ping Hao, Mirian Elizabeth Casco, Volodymyr Bon, Sven Grätz, and Lars Borchardt**

I. Experimental Procedures

Synthesis of SiO_2 template

The silica seeds were prepared as reported[1]. Generally, 400 mg of amino acid L-arginine was added in a flask containing 400 mL H_2O under stirring. Then 23.936 g tetraethyl orthosilicate (TEOS) was added dropwise in the flask. The mixture was covered with a plastic stopper and stirred at 70 °C for 24 h using a magnetic stirrer with a stir bar at 1000 rpm. Thereafter, an adequate amount of the seeds suspension was evaporated with a rotary evaporator and the obtained white powder was subsequently calcined in air at 600 °C with a heating rate of 150 K h^{-1} for 5 h.

Reference Material 1: Synthesis of ordered mesoporous carbon: OMC

1 g of silica spheres and 0.5 g sucrose were dispersed in water under ultrasonication for 15min. Afterwards, two droplets of concentrated sulfuric acid were added in the mixture as a dehydrating agent. The mixture was firstly put in an oven at 100 °C for about 6 h and then the temperature was raised to 160 °C for 6 h. The as-prepared precursor was then pyrolyzed within a horizontal furnace at 900 ^{o}C for 2 h with a heating rate of 150 k h^{-1} under argon atmosphere. Thereafter, a leaching process was carried out to remove the silica template using a mixture of 80 mL water, 80 mL Ethanol and 80 mL 40 vol.% hydrofluoric acid for 24 h.

Finally, the materials were washed with excess of ethanol and water before dried at ambient temperature and denoted as C_{meso}.

Reference Material 2: Synthesis of hydrophilic microporous carbon: PCC

This method was already reported elsewhere[3]. In a typical synthesis, 1.5 g triblock copolymer F127 was dissolved in 110mL 0.1 M 4,4'-bipyridine water-ethanol (volume ratio of 1:10) solution, denoted solution A. Then, 5.6 mM $CuCl_2 \cdot 2H_2O$ solution was prepared in a 2 L vessel, denoted solution B. The reaction was carried out by rapid mixing through pouring solution A (100 mL) into solution B (900 mL) under shaking to ensure sufficient mixing. After static settlement for 4 h, the resulting product was collected through centrifugation with a speed of ca. 4200 rpm for 12 min and washed for 3 times. Afterwards, the as-prepared blue precursor was transferred in a tube furnace, which was subsequently heated to 500 °C with a heating rate of 120 °C h^{-1} under argon atmosphere and maintained for 2 h. The final products were obtained after removal of the copper species using 4 M HNO_3 solution for 24h.

Characterization

Scanning electron microscope (SEM) investigations were carried out with a Hitachi SU8020 instrument and a Zeiss DSM 982 Gemini instrument. Transmission electron microscopy (TEM) images were observed in a JEM 1400plus operated at an acceleration voltage of 120 kV. The samples were collected by soaking the TEM copper grid in the already with ethanol well dispersed carbon suspension.

Raman spectra were obtained using a Raman-spectrometer "RM-2000" with 50x object (N_A = 0.75) from the company RENISHAW. The wavelength for the measurement is 532 nm. The small angle X-ray diffraction (SAXS) experiments were performed in transmission mode on a Bruker Nanostar diffractometer with CuKa1 radiation (λ=0.15405 nm) connected to a position sensitive HiStar detector. A certain amount of sample was put in the measure plate with X-ray amorphous scotch tape and placed in the sample chamber, which was evacuated before measurement and the sample was measured for 1000 s. Nitrogen adsorptions are measured volumetrically at 77 K on a BELSORP adsorption with a sample mass of ca. 35 mg. The Brunauer-Emmett-Teller (BET) method was used to calculate the specific surface area based on the adsorption date in the partial pressure of $0.05<P/P_0<0.20$ and the total pore volume was estimated from the adsorbed nitrogen volume at a relative pressure of about 0.95. Micropore volume was calculated from the density functional theory using the cumulative pore volume up to 2nm. The pore size distributions (PSDs) were evaluated by the equilibrium branches of the isotherms based on Quenched Solid Density Functional Theory (QSFDT, nitrogen on carbon slit/cylindrical equilibrim branch kernel). Dynamic light scattering (DLS) was measured at a MALVERN Zetasizer Nanosizer in quartz cuvettes. Prior to the measurement, the sample was filtered through a 0.2 µm PTFE filter. Per sample 3 measurements with 11 runs were conducted in backscattering mode. The attenuator and measurement position was determined automatically. Thermogravimetric analysis (TGA) was performed on a NETZSCH STA 409 PC/PG system using alumina crucibles under argon or air stream with a heating rate of 5 K min^{-1}. Elemental analysis was obtained from a CHNS elemental analyzer (EuroEA Elemental Analyzer). Water physisorption measurements were carried out on a Quantachrome Hydrosorb 1000 at 298.15K.

II. Structural characterization of HOMC and the corresponding precursors

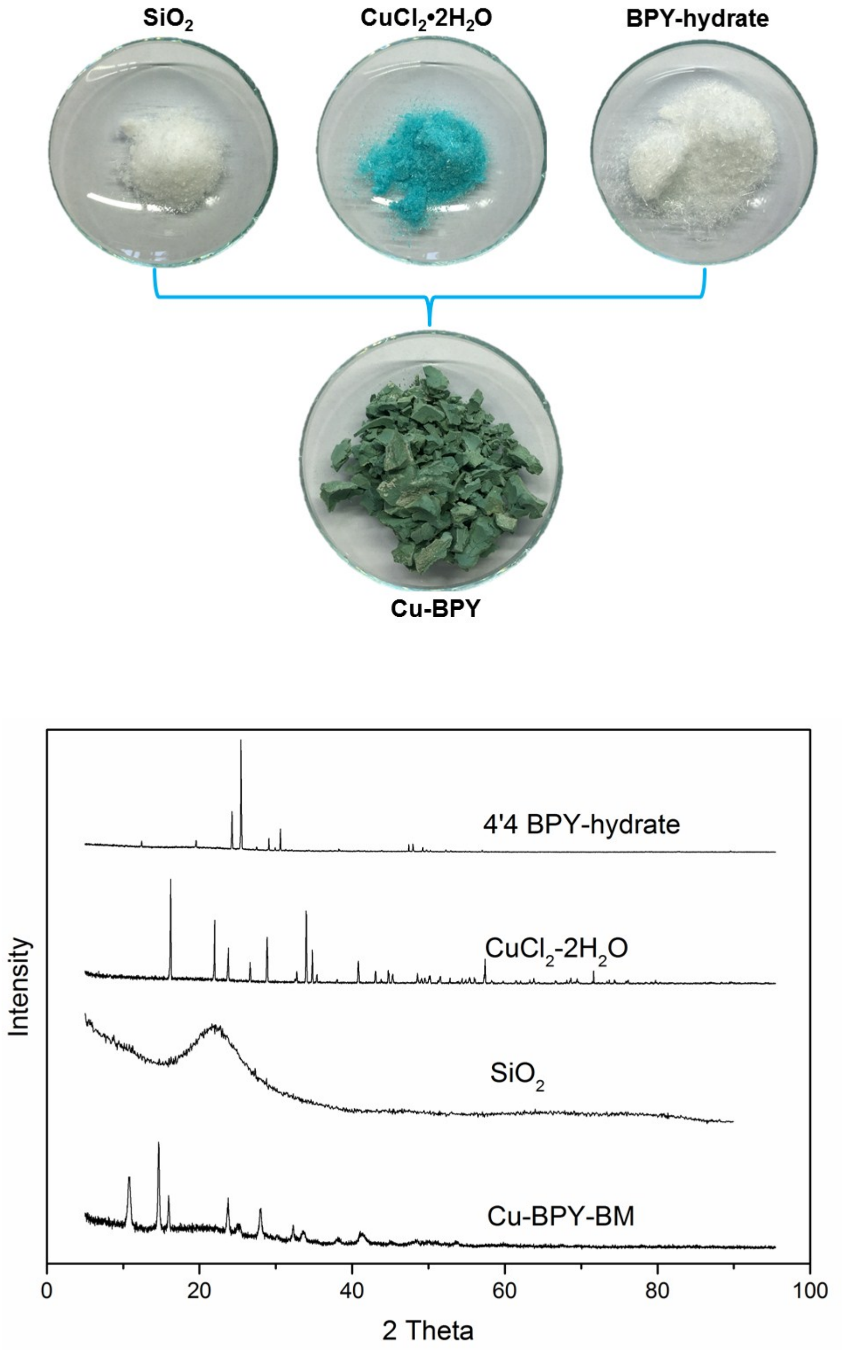


Figure S1 The precursor and the product of the coordination polymer (a) and the corresponding XRD patterns (b). An obvious color change can be observed. From the XRD patterns we can see a phase formed after the ball milling, i.e. the Cu-BPY coordination polymer.

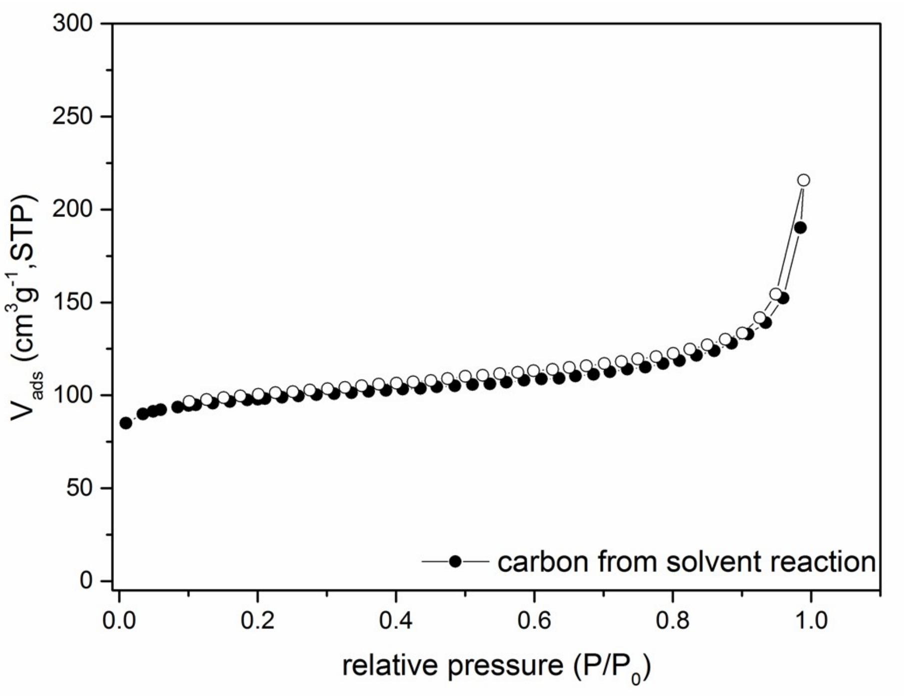


Figure S2 N_2 physisorption at 77K for the carbon material that obtained by a solvent reaction process. In this process, the coordination polymer was obtained by firstly mixing the BPY and silica in DMF and then adding the in DMF dissolved $CuCl_2$, after 0.5h the polymer was collected. The collected polymer underwent the same post-treatment like the HOMC did.

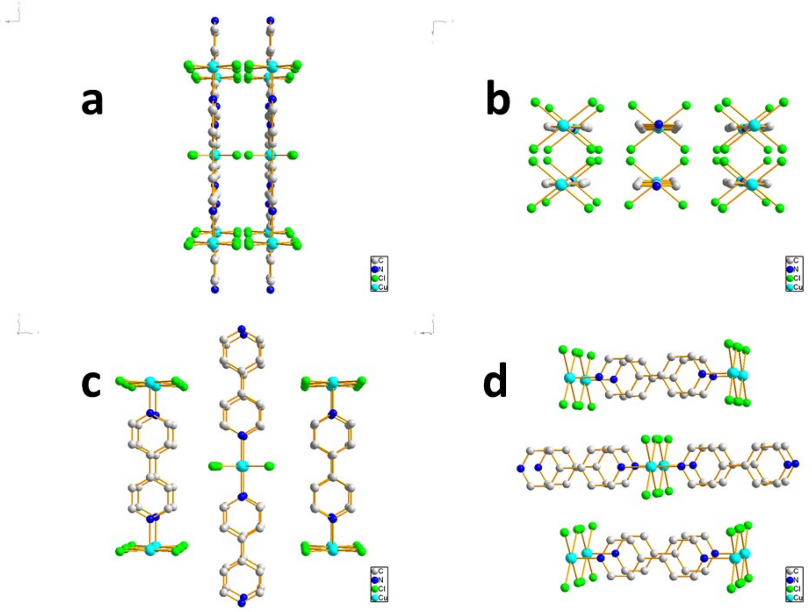


Figure S3. The structure of the Cu-bipyridine polymer viewed along (a) x, (b) y, (c) z and (d) a random orientation for better visualization.

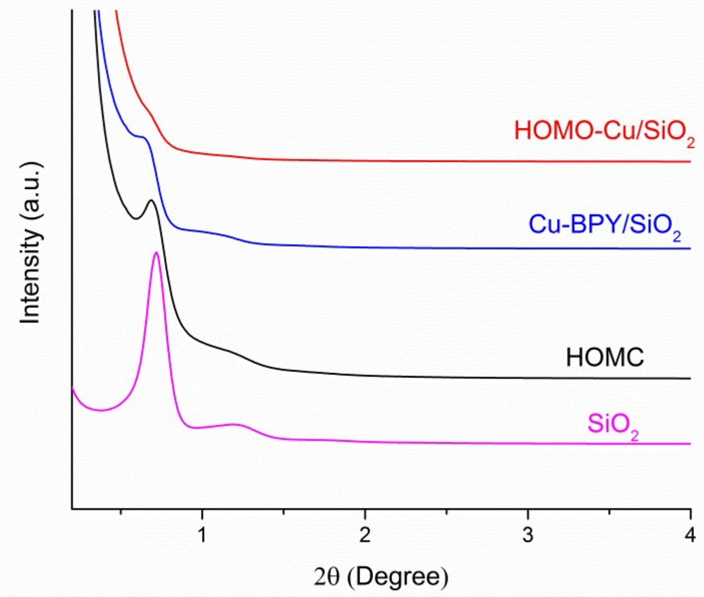


Figure S4. Small Angle X-Ray Scattering of the silica template, hydrophilic ordered mesoporous carbon HOMC, the obtained polymer/silica mixture Cu-BPY/SiO$_2$ and the obtained HOMC-Cu/SiO$_2$ composite after pyrolysis. They show distinguishable but poorly-resolved diffraction peaks, indicating that the inherited ordering from silica template is attenuated by the surrounded coordination polymer or carbon.

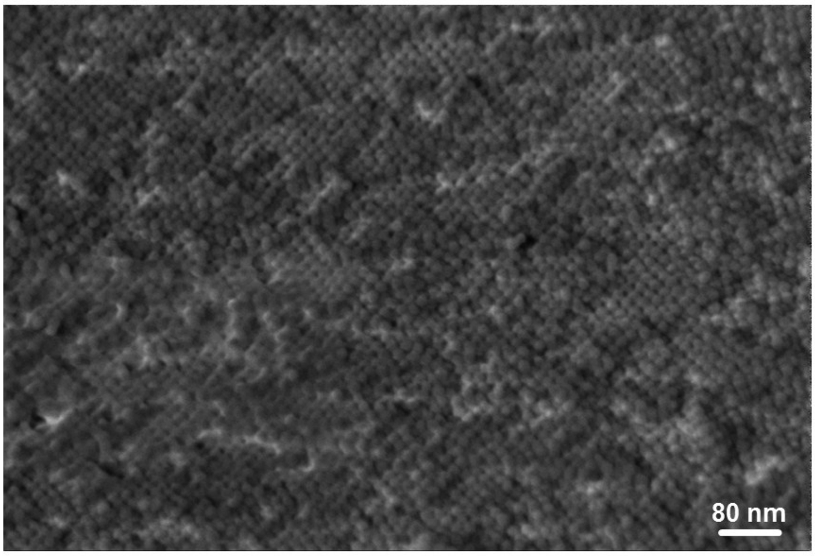


Figure S5. SEM images of silica spheres. Stacking faults can be found randomly in the images.

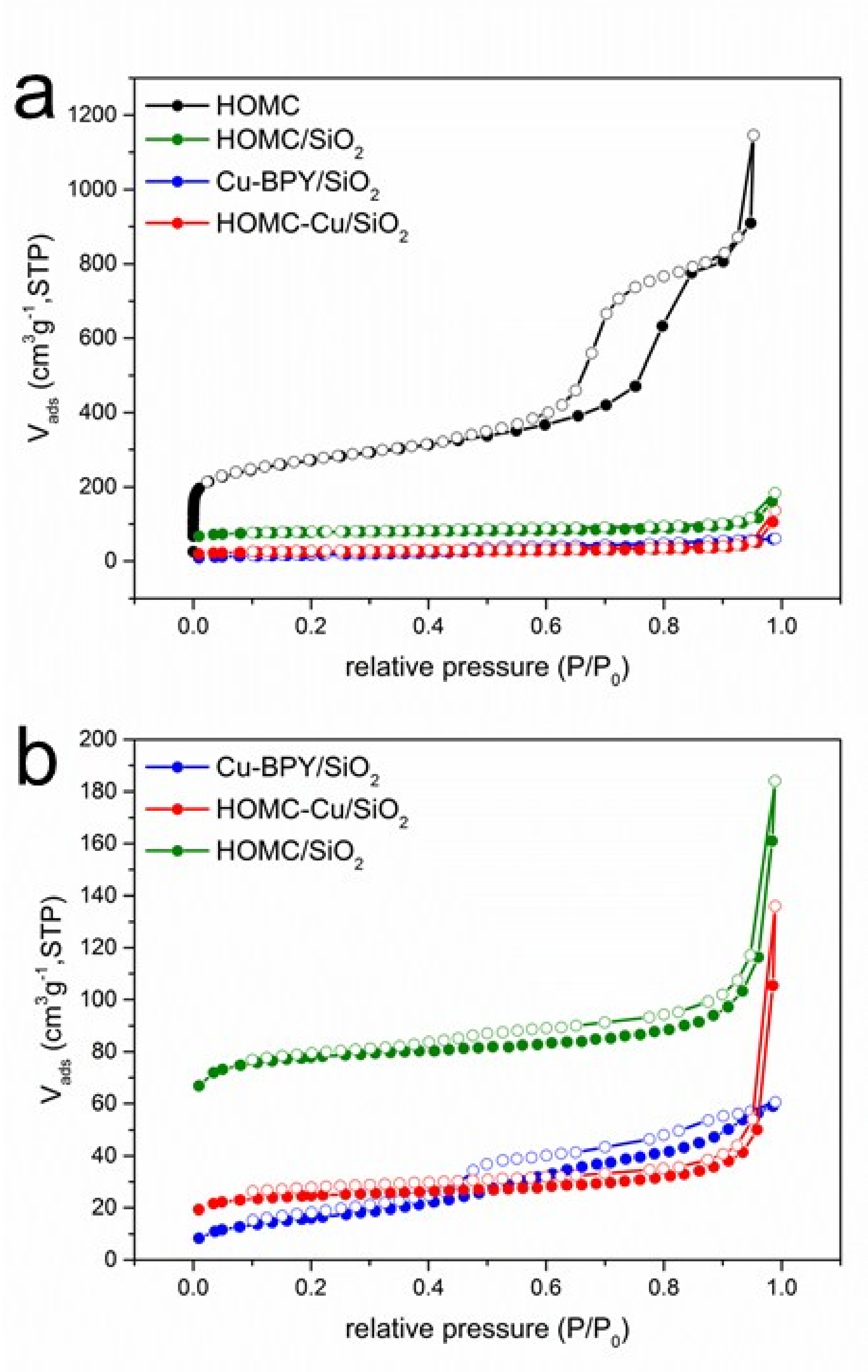
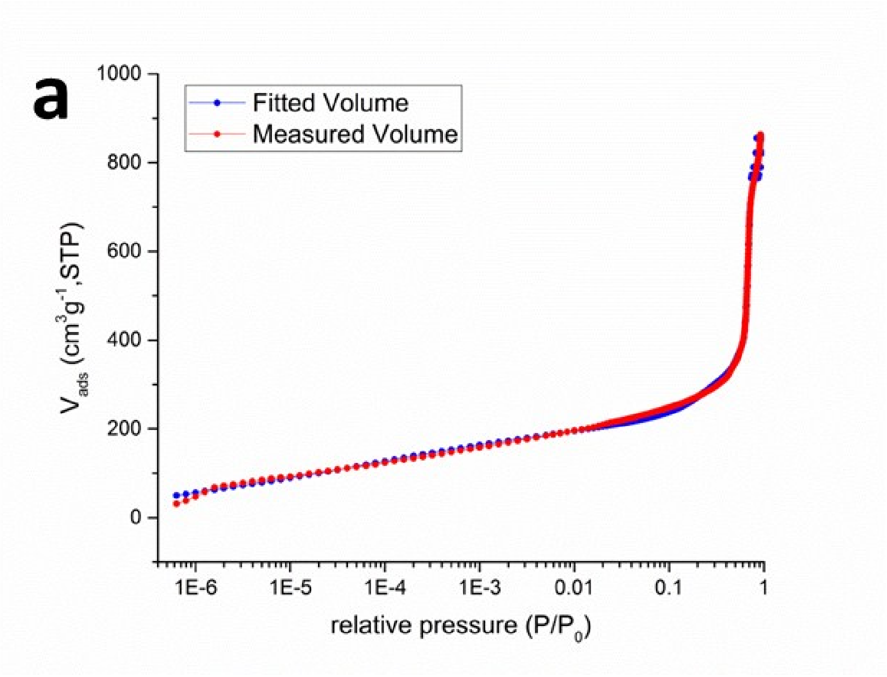


Figure S6. (a) N_2 physisorption of HOMC and (b) the corresponding intermediates along the preparation steps.

As can be seen here, after pyrolysis the pore structure was changed to a micropore network as a Type I isotherm can be observed (Red). After Cu etching, the form of the isotherm changes almost, which means large amount of micropores are generated during the etching process (Green). After removing the silica template, both the micropore and mesopore were evolved.



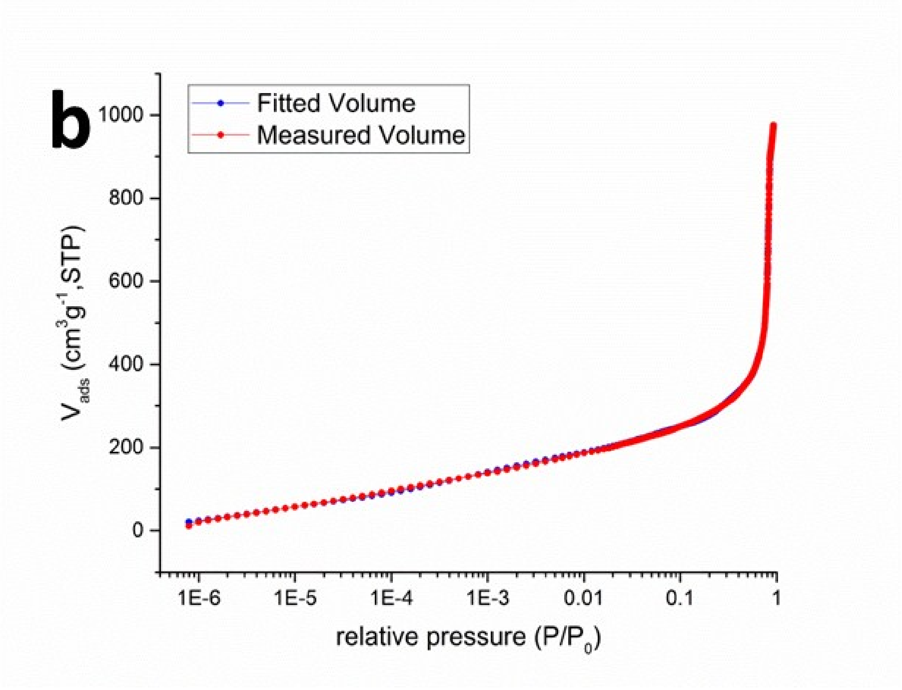


Figure S7 QSDFT fitting of the theoretical isotherm based on the slit/cylindrical adsorption branch kernel and the measured isotherm for N_2 adsorption at 77 K (a) and QSDFT fitting of the theoretical isotherm based on cylindrical adsorption branch kernel and the measured isotherm for Ar adsorption at 87K (b).

It is interesting to find here that compared with the fitting for N_2 adsorption (slit/cylindrical system was chosen), even only cylindrical pore for Ar adsorption fitting was used, it has even a better fitting result, especially the low pressure range, demonstrating the influence of quadrupole effect of N_2.

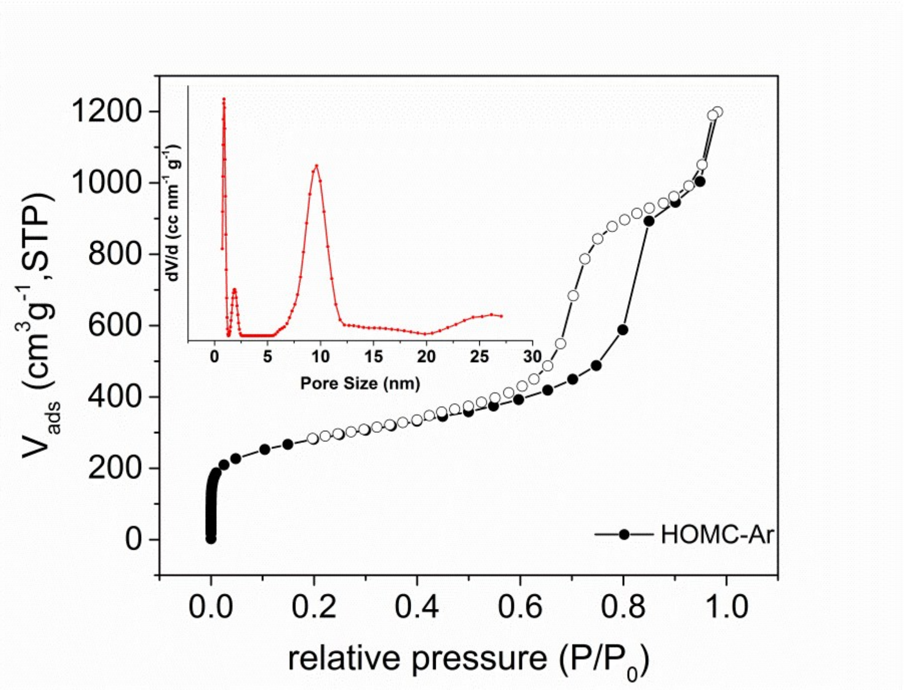


Figure S8 Ar phsisorption isotherm HOMC and the Pore size distribution (inset).

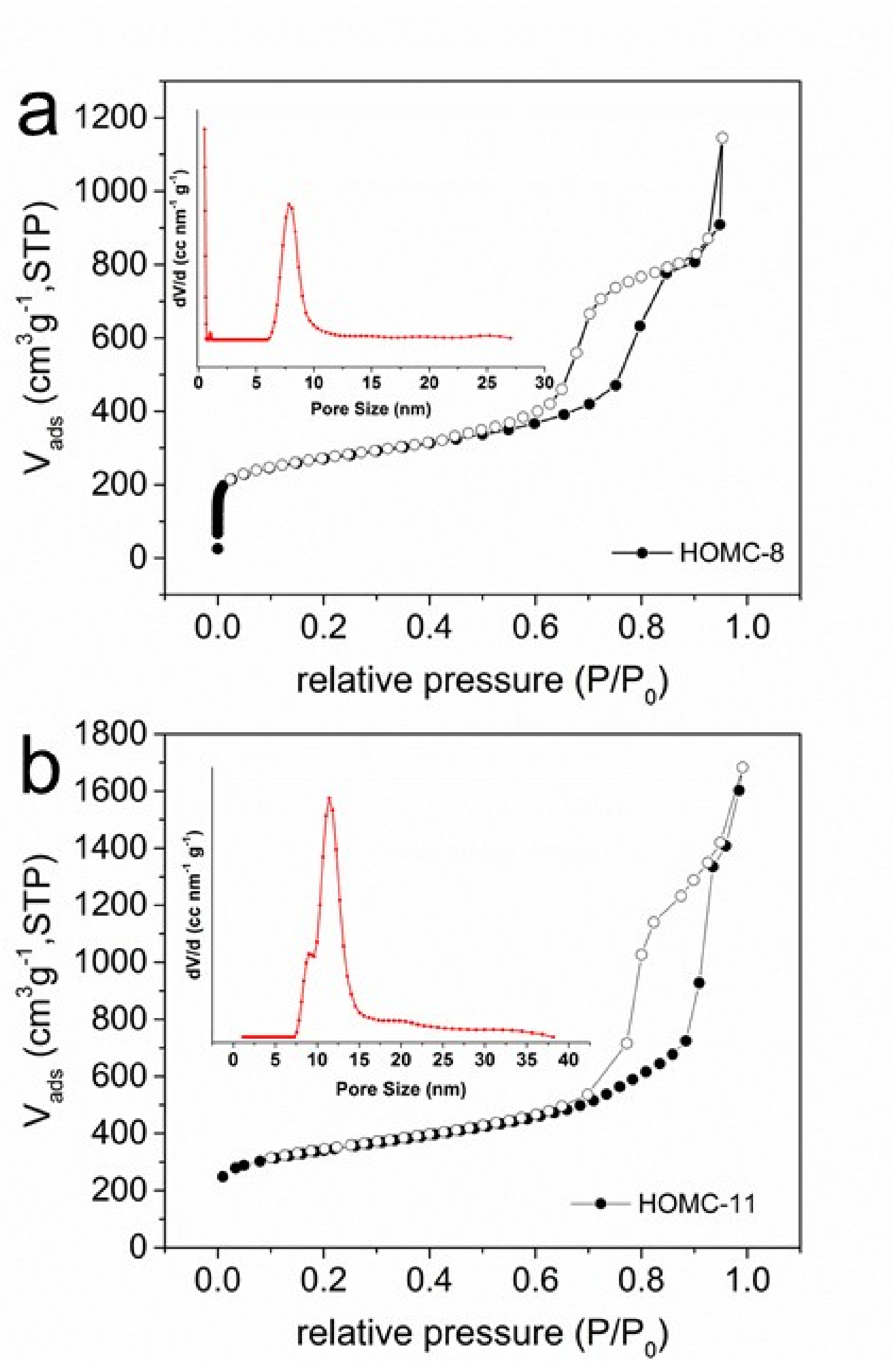


Figure S9. N_2 adsorption isotherm of HOMC (top) and HOMC-11nm (bottom) with larger silica template. Inset: the pore size distribution.

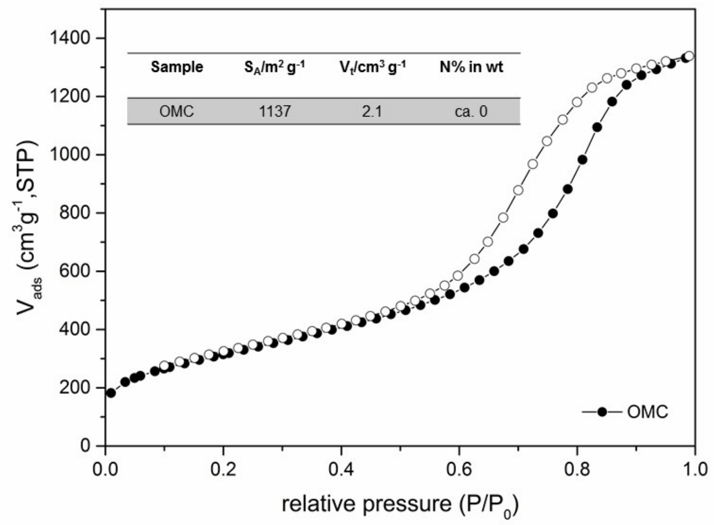


Figure S10. N_2 adsorption isotherm for N-free ordered mesoporous carbon OMC and the pore information (inset).

III. Characterization of the hydrophilicity (dynamic contact angle, water physisorption)

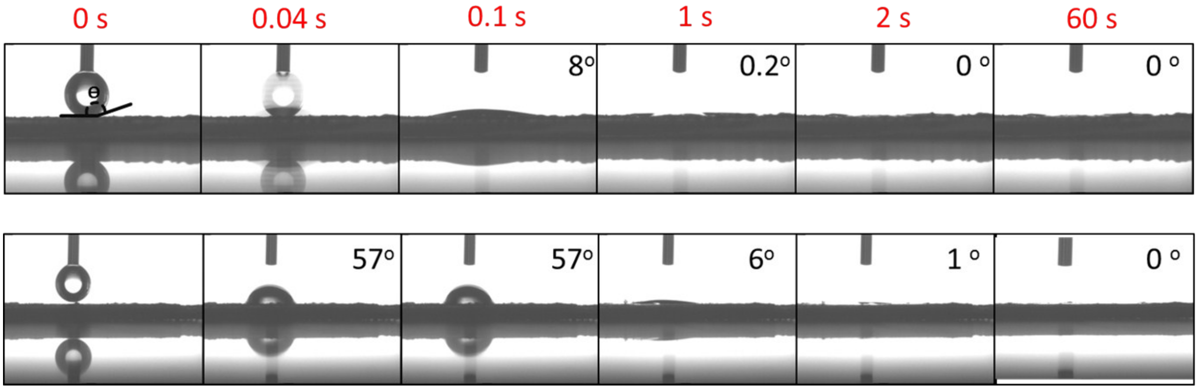


Figure S11. Dynamic contact angle: Comparison between HOMC (top) and PCC (bottom), which has only micropores. Both of the carbon materials have the same carbon and nitrogen precursor.

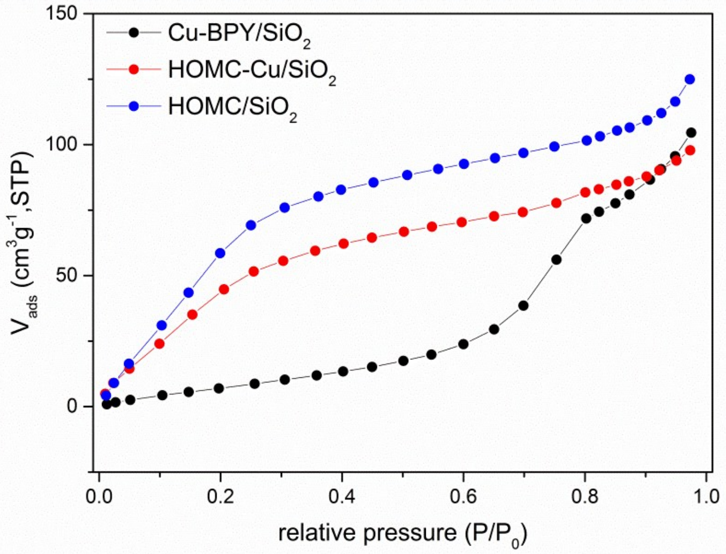


Figure S12. Water adsorption isotherm for the relevant intermediate of HOMC

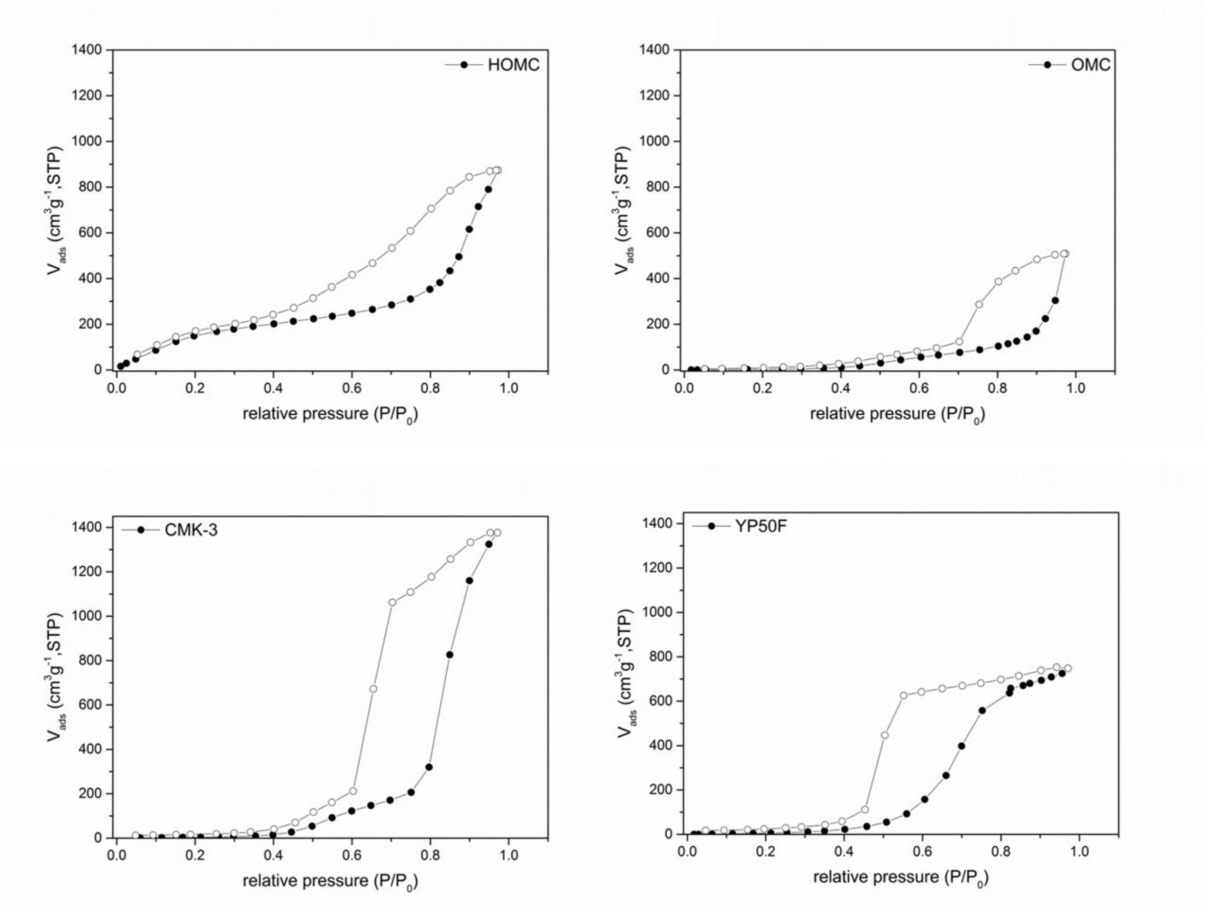


Figure S13. Water adsorption isotherm for the HOMC and the reference materials OMC, CMK-3 and YP50F.

IV. Tabular analysis of HOMC (TableS1-S3)

Table S1. The elemental analysis and henry constant of HOMC

Sample	Measurement	N wt%	C wt%	O wt%	Henry constant*
HOMC	XPS	15.6	74.3	10.1	649
	EA	14.44	62.96	20.03*	
OMC	EA	0.06	87.11	11.99*	10.2

* The O content was calculated from the difference of total amount and (N+C) contents. For a better comparison, the element content in XPS is recalculated to the weight percentage and the H content was not included here. $^{\#}$ Henry constant was calculated from the slope of water physisorption isotherm up to P/P_0=0.1.

Table S2. Fitting details of Raman spectra for HOMC

Curve Name	Centre	Width	Height	% Gaussian	Type	Area	Peak Height	Area	All Area
D2	1170	231.6	1140	44.60	Mixed	3.55E+05	I(D1)/I(G1)=1.5	I(D1)/I(G1)=3.89	
D1	1354	254.9	11345	48.56	Mixed	3.83E+06	I(D2)/I(G2)=0.19	I(D2)/I(G2)=0.3	I(D)/I(G)=1.92
G2	1534	152.7	5913	47.32	Mixed	1.20E+06	I(G2)/I(G1)=0.78	I(G2)/I(G1)=1.22	
G1	1593	98.0	7554	47.59	Mixed	9.84E+05			

Table S3. Comparison between Ar and N_2 physisorption for HOMC

Gas	$S_A$$^{a)}$ $cm^3\ g^{-1}$	$V_{total}$$^{b)}$ $cm^3\ g^{-1}$
Ar	871	1.40
N_2	974	1.29

a) S_A specific surface area calculated by Brunauer-Emmet-Teller applied in the relative pressure range of 0.05-0.2, b) V_{total} is obtained from the cumulative pore volume based on the QSDFT theory.

V. References

[1] R. Watanabe, T. Yokoi, E. Kobayashi, Y. Otsuka, A. Shimojima, T. Okubo, T. Tatsumi, *J. Colloid Interface Sci.* **2011**, *360*, 1–7.

[2] Z. Li, J. Li, J. Liu, Z. Zhao, C. Xia, F. Li, *ChemCatChem* **2014**, *6*, 1333–1339.

[3] G.-P. Hao, G. Mondin, Z. Zheng, T. Biemelt, S. Klosz, R. Schubel, A. Eychmüller, S. Kaskel, *Angew. Chem. Int. Ed.* **2015**, *54*, 1941–1945.

Author Contributions

E.Z. Conceptualization: Equal; Data curation: Lead; Investigation: Lead; Methodology: Equal; Visualization: Lead; Writing – original draft: Equal; Writing – review & editing: Equal

G-P.H. Investigation: Supporting; Writing – original draft: Equal; Writing – review & editing: Equal

ME.C. Data curation: Equal; Investigation: Equal; Resources: Equal; Validation: Equal; Writing – review & editing: Equal

V.B. Data curation: Equal; Investigation: Equal; Visualization: Equal

S.G. Investigation: Equal; Resources: Equal; Writing – review & editing: Equal

L.B. Conceptualization: Lead; Formal analysis: Equal; Funding acquisition: Lead; Methodology: Equal; Project administration: Lead; Resources: Equal; Supervision: Lead; Validation: Equal; Writing – original draft: Equal; Writing – review & editing: Lead.