Supplemently Information

A new restriction effect of hard templates for the shrinkage of mesoporous polymer during carbonization

Mingbo Zheng,[a] Guangbin Ji,[a] Yongwen Wang,[a] Jian Cao,[a] Shaoqing Feng,[a] Lei Liao,[b] Qinglai Du,[a] Lifeng Zhang,[a] Zongxin Ling,[a] Jinsong Liu,[a] Ting Yu,[b] Jieming Cao*[a] and Jie Tao[a]

Nanomaterials Research Institute, College of Materials Science and Technology, Nanjing University of Aeronautics and Astronautics, Nanjing 210016, China; Division of Physics and Applied Physics, School of Physical and Mathematical Sciences, Nanyang Technological University, 637371, Singapore

[a] Nanjing University of Aeronautics and Astronautics.
[b] Nanyang Technological University.
*E-mail: jmcao@nuaa.edu.cn

Experimental Details:

Preparation of anodic aluminum oxide (AAO) membrane:

The AAO membranes with average pore diameters of 50, 90, and 200 nm were prepared by ourselves. The aluminium foil (purity 99.5%) was anodized in 0.5 mol/L of oxalic acid solution or 0.36 mol/L of phosphoric acid solution. The AAO membranes with an average pore diameter of 300 nm was purchased from Whatman Ltd.

Preparation of SiO_2 colloidal crystal:

Nearly monodisperse SiO_2 microspheres with an average diameter of 220 nm were synthesized by hydrolyzing tetraethyl orthosilicate (TEOS) and subsequent seed growth polymerization under basic conditions.[1] SiO_2 colloidal crystal was obtained by self-assembling SiO_2 microspheres using a vertical deposition technique. The SiO_2 colloidal crystal was heat-treated at 800 ºC for 3 h. The heat treatment

endows the colloidal crystal with high mechanical strength and forms small necks between neighboring SiO_2 spheres.

Preparation of resol precursor:

The preparation of resol precursor is similar to that reported by Meng. Y et al[2,3]. 2.44 g of phenol was melted at 41 ºC in a rockered flask. 2.6 g of 20 wt % NaOH solution was added to the flask. Then 4.2 g of formalin (37 wt % formaldehyde) was added dropwise at 41 ºC and the reaction mixture was stirred at 70 ºC for 1 h. After cooling to the room temperature, the pH of the mixture was adjusted to 7.0 using 0.6 mol/L of HCl solution. Water was then removed by vacuum evaporation at 43 ºC. The final product was dissolved in 36.0 g of ethanol. 40.0 g of resol–ethanol solution was obtained.

Preparation of Pluronic F127 ($EO_{106}PO_{70}EO_{106}$)–resol mixture solution for AAO template:

1.0 g of Pluronic F127 was dissolved in 20.0 g of ethanol. Then, 20.0 g of resol–ethanol solution was added. After stirring for 10 min, a homogeneous mixture solution was obtained.[2,3]

Preparation of Pluronic F127–resol mixture solution for SiO_2 colloidal crystal template:

1.0 g of Pluronic F127 was dissolved in 20.0 g of ethanol. Then, 10.0 g of resol–ethanol solution was added. After stirring for 10 min, a homogeneous mixture solution was obtained.[2,3]

Preparation of mesoporous–macroporous carbon (MMC) and mesoporous–macroporous polymer (MMP):

The precursor solution was transferred to an evaporating dish. Then, SiO_2 colloidal crystal template was added to the solution. After ethanol evaporated thoroughly at room temperature, the complex of SiO_2–resol–F127 was taken out and heated at 100 ºC for 24 h. Some of the complex were carbonized at 900 ºC in N_2 for 3 h (heating rate: 1 ºC/min). Some of the complex were carbonized at 700 ºC in N_2 for 3

h. The others were heat treated at 350 ºC in N_2 for 3 h. The SiO_2 templates were then etched away with 10% aqueous HF. The corresponding products were MMC-900, MMC-700, and MMP-350, respectively. Furthermore, some of MMP-350 were carbonized at 700 ºC in N_2 for 3 h and the obtained product was MMC-350-700.

Instrumentations:

The morphologies of the mesoporous nanofibers were examined by transmission electron microscopy (FEI TECNAI-20) and scanning electron microscopy (Gemini, LEO1530). The N_2 adsorption–desorption analysis was measured on a Micromeritics ASAP 2010 instrument. The plan-view TEM sample of AAO–MCNF-700 was prepared by dimple grinding followed by ion polishing (Gatan PIPS 691) and characterized by transmission electron microscopy (JEOL JEM-2010FEF). The Raman spectra was carried out with a WITEC CRM200 confocal Raman system.

Table S1. Textural Properties of Mesoporous Materials

sample name	mesopore size [nm]	BET surface area [m^2 g^{-1}]	micropore area [m^2 g^{-1}]	pore volume[a] [cm^3 g^{-1}]	micropore volume[b] [cm^3 g^{-1}]
MCNF-700 (90 nm)	15.2	1154	246	3.44	0.12
MPNF-350 (90 nm)	11.1	783	292	2.04	0.14
MCNF-350-700 (90 nm)	7.3	1308	1032	2.19	0.51
MCNF-700 (50 nm)	14.6	999	290	2.70	0.14
MPNF-350 (50 nm)	9.5	642	113	1.41	0.05
MCNF-350-700 (50 nm)	6.5	907	464	1.28	0.23
MCNF-700 (200 nm)	12.7	1232	343	2.69	0.16
MPNF-350 (200 nm)	10.6	854	270	1.30	0.13
MCNF-350-700 (200 nm)	7.6	1766	1225	1.38	0.60
MCNF-700 (300 nm)	11.4	1300	516	2.35	0.25
MPNF-350 (300 nm)	9.5	696	241	1.05	0.12
FDU-16-350 [3]	6.6	460	230	0.34	
FDU-16-700 [3]	3.8	690	480	0.37	
MMC-900	14.9	1469	409	4.11	0.20
MMC-700	14.8	1243	333	3.49	0.16
MMP-350	11.4	872	216	1.61	0.10
MMC-350-700	8.7	1291	613	1.99	0.30
FDU-15-350	5.6	323	46	0.34	0.02
FDU-15-700	3.2	648	381	0.37	0.19
FDU-15-900	2.9	673	446	0.36	0.22

[a] By using the Barrett-Joyner-Halenda (BJH) model, the pore volume was derived from the adsorption branch of isotherms and estimated from the adsorbed amount at a relative pressure P/P_0 of 0.996.

[b] The micropore volume was calculated by the *V-t* method.

Figure S1-Figure S14

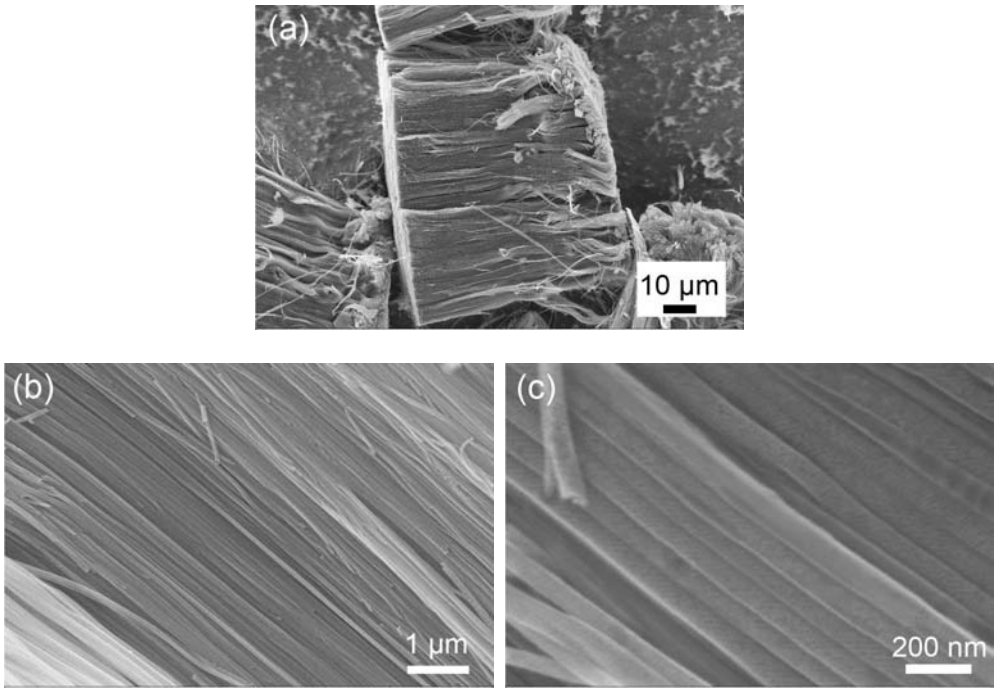

Figure S1. SEM images of MCNF-700 obtained by using AAO with an average pore diameter of 90 nm as template.

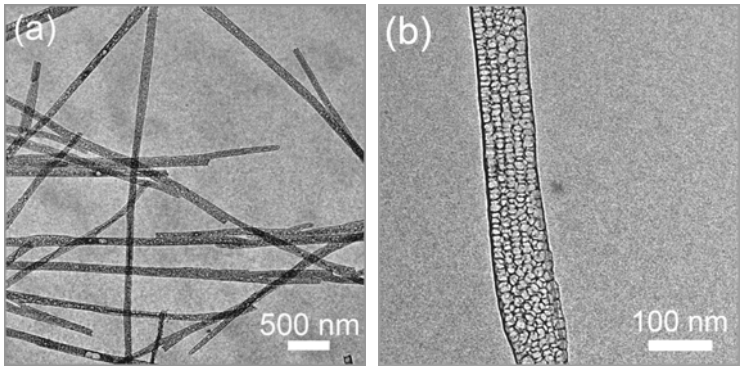

Figure S2. Low-magnification TEM images of MCNF-700 obtained by using AAO with an average pore diameter of 90 nm as template.

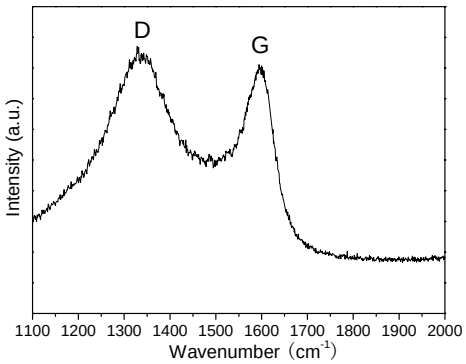

Figure S3. Raman spectra of MCNF-700 obtained by using AAO with an average pore diameter of 90 nm as template. (The Raman spectra of MCNF-700 shows two characteristic vibration modes at about 1340 and 1595 cm^{-1}, respectively. It suggests that MCNF-700 has a low degree of graphitization.)

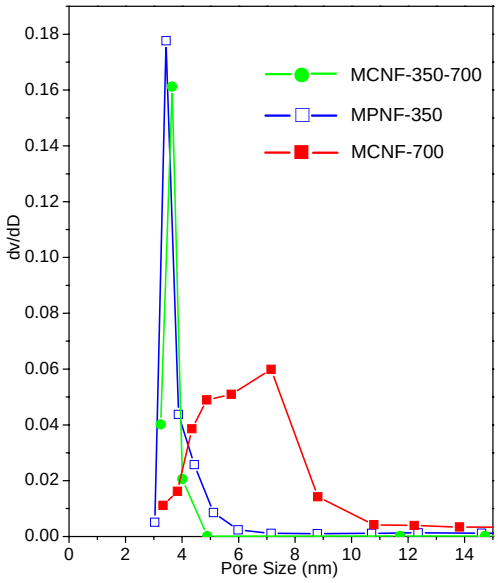

Figure S4. BJH pore size distribution curves from desorption branches for MCNF-700, MPNF-350 and MCNF-350-700 obtained by using AAO with an average pore diameter of 90 nm as template.

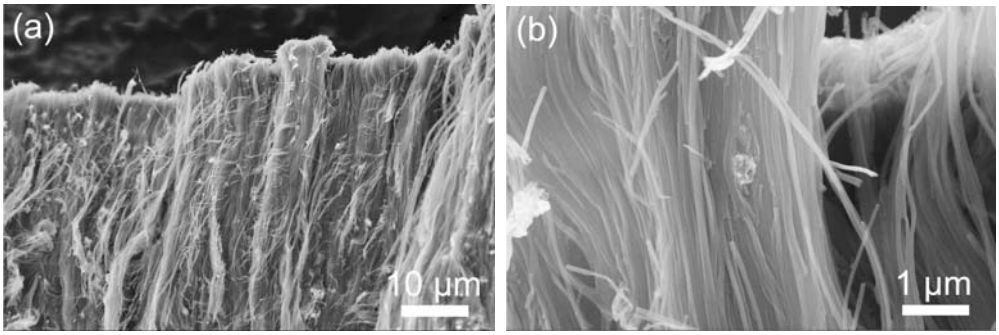

Figure S5. SEM images of MCNF-700 obtained by using AAO with an average pore diameter of 50 nm as template.

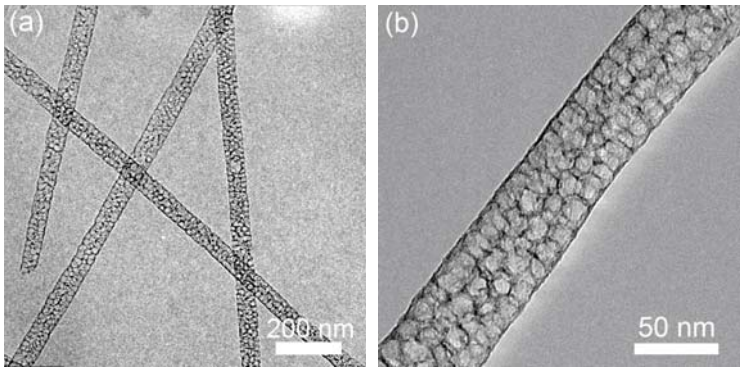

Figure S6. TEM images of MCNF-700 obtained by using AAO with an average pore diameter of 50 nm as template.

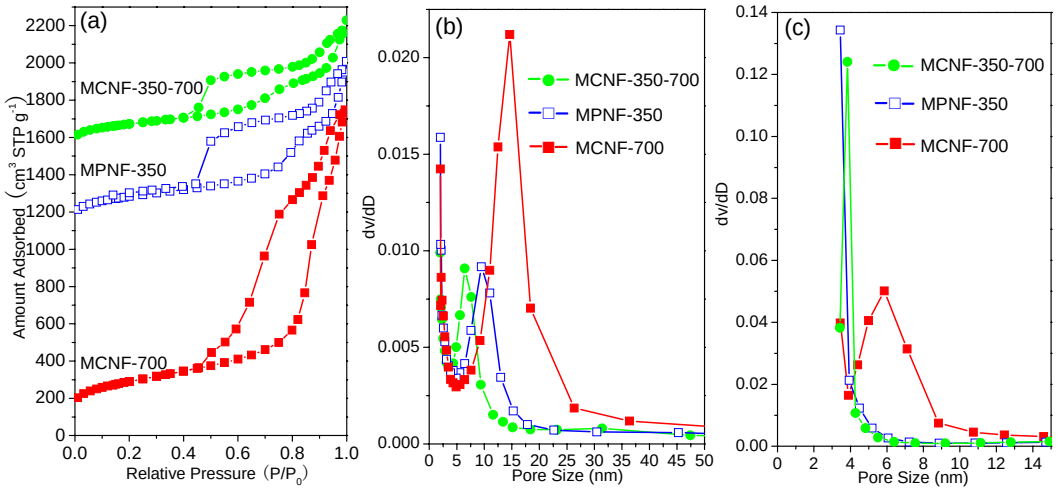

Figure S7. (a) N_2 adsorption–desorption isotherms, (b) BJH pore size distribution curves from adsorption branches, and (c) BJH pore size distribution curves from desorption branches for MCNF-700, MPNF-350, and MCNF-350-700 obtained by using AAO with an average pore diameter of 50 nm as template. The isotherms of MPNF-350 and MCNF-350-700 are offset vertically by 1100 and 1400 cm^3/g, respectively.

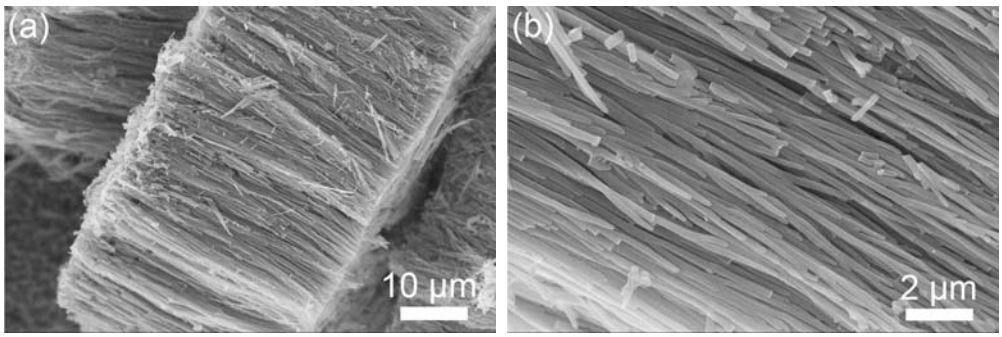

Figure S8. SEM images of MCNF-700 obtained by using AAO with an average pore diameter of 200 nm as template.

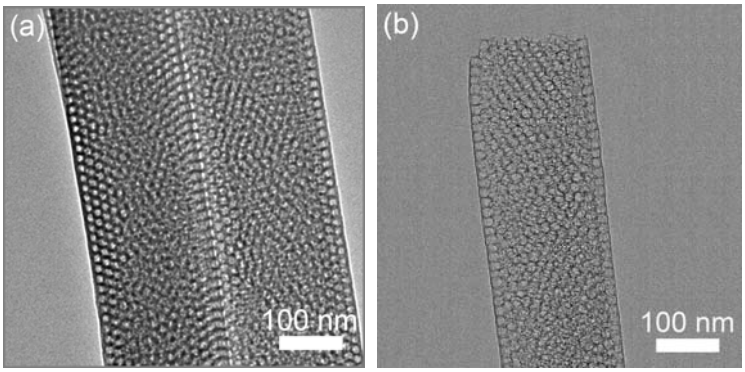

Figure S9. TEM images of MPNF-350 (a) and MCNF-700 (b) obtained by using AAO with an average pore diameter of 200 nm as template.

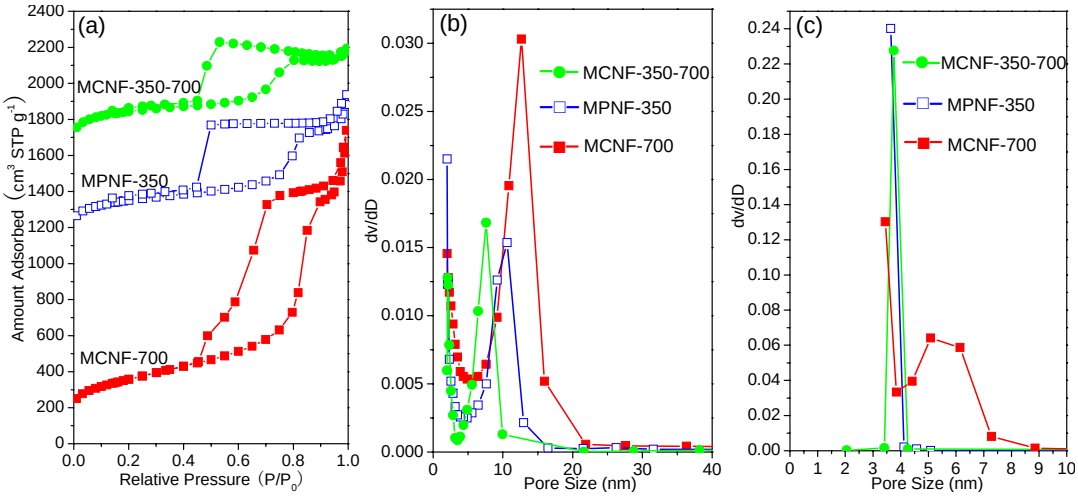

Figure S10. (a) N_2 adsorption–desorption isotherms, (b) BJH pore size distribution curves from adsorption branches, and (c) BJH pore size distribution curves from desorption branches for MCNF-700, MPNF-350, and MCNF-350-700 obtained by using AAO with an average pore diameter of 200 nm as template. The isotherms of MPNF-350 and MCNF-350-700 are offset vertically by 1100 and 1300 cm^3/g, respectively.

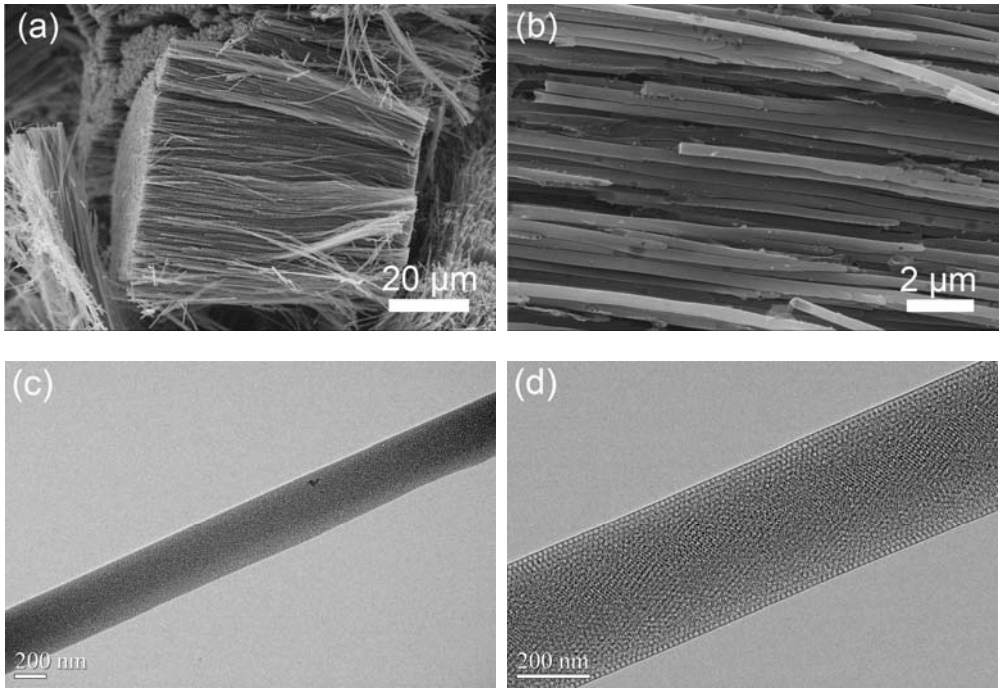

Figure S11. SEM (a,b) and TEM (c,d) images of MCNF-700 obtained by using AAO with an average pore diameter of 300 nm as template.

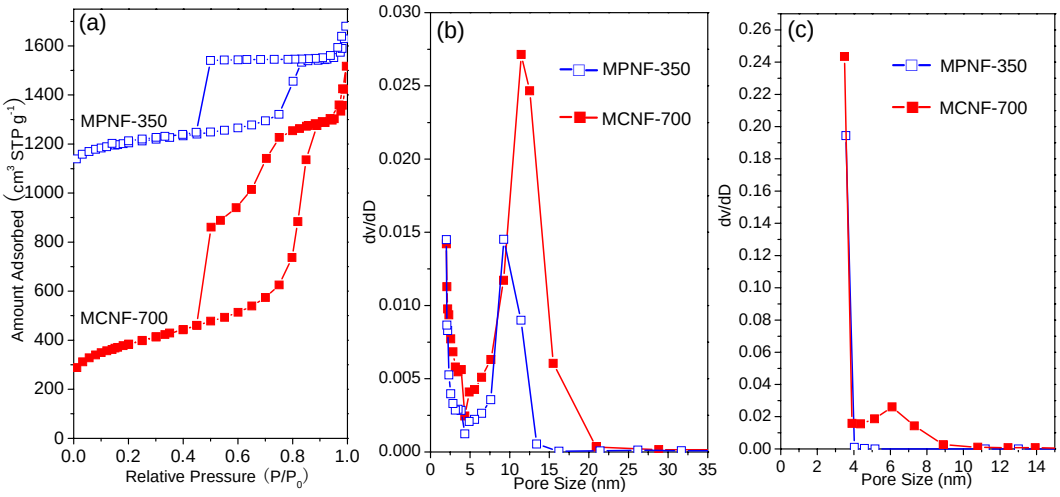

Figure S12. (a) N_2 adsorption–desorption isotherms, (b) BJH pore size distribution curves from adsorption branches, and (c) BJH pore size distribution curves from desorption branches for MCNF-700 and MPNF-350 obtained by using AAO with an average pore diameter of 300 nm as template. The isotherms of MPNF-350 are offset vertically by 1000 cm^3/g. (Figure c indicates that the window of the mesopores was not opened completely, which is due to the restriction effect weakens with increasing the pore diameter of AAO template.)

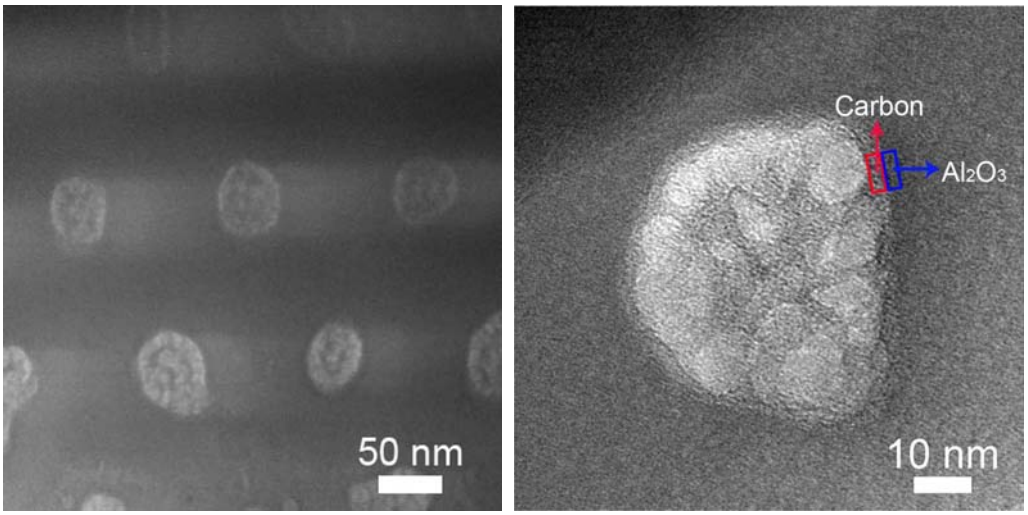

Figure S13. Plan-view TEM images of AAO–MCNF-700 complex obtained by using AAO with an average pore diameter of 50 nm as template. (From the high-magnification TEM image (right), we can see that the surface of the carbon nanofiber connected tightly with the surface of the pore wall of AAO after carbonization at 700 ºC)

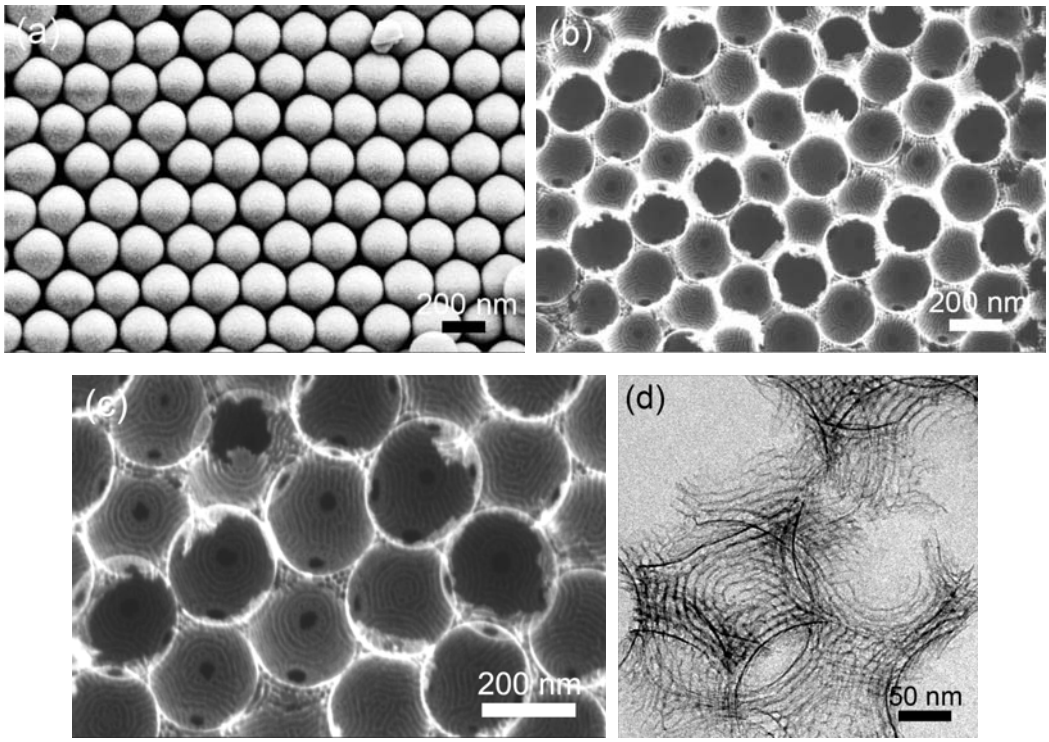

Figure S14. SEM images of SiO_2 colloidal crystal (a) and MMC-700 (b,c), TEM image of MMC-700 (d).

References:

[1] Stöber, W.; Fink, A.; Bohn, E. *J. Colloid Interface Sci.* **1968**, *26*, 62.

[2] Meng, Y.; Gu, D.; Zhang, F.; Shi, Y.; Yang, H.; Tu, B.; Yu, C.; Zhao, D. *Angew. Chem., Int. Ed.* **2005**, *44*, 7053.

[3] Meng, Y.; Gu, D.; Zhang, F.; Shi, Y.; Cheng, L.; Feng, D.; Wu, Z.; Chen, Z.; Wan, Y.; Stein, A.; Zhao, D. *Chem. Mater.* **2006**, *18*, 4447