SUPPORTING INFORMATION

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Experimental Section

1. Synthesis of mesoporous carbon nanotubes

MnO_2 nanotube, nano-rod and nano-thorn microsphere precursors were prepared following procedures described in Refs. S1-S3. The hydrophobic treatment of MnO_2 precursors was performed by dipping the precursors in a solution of Hexadecyl-trimethoxysilane ($C_{19}H_{42}O_3Si$) and toluene (volume ratio 1:30) and stirring for 5 h, followed by filtration, removal of the solution by washing with ethanol and drying at 100 ^{o}C in the air for 12 h. A soluble, low molecular weight phenolic resin, synthesized by a reaction of phenol with formaldehyde, was used as a carbon source. The triblock copolymer PEO-PPO-PEO (P123) was used as a structure-directing agent for generating the mesoporous phases.[3] For a typical procedure, 1.3 g of MnO_2 was immersed into 16.0 g of a homogeneous ethanol solution containing 1.0 g of resol (M_W < 500 as measured by GPC) and 0.5 g of triblock copolymer P123. The impregnated composite monoliths were placed in a dish at 25 ^{o}C for 6 h to evaporate ethanol, followed by further heating at 100 ^{o}C for 24 h. The resulting MnO_2/PF/P123 composites were pyrolyzed in nitrogen at 350 ^{o}C for 2 h at a heating rate of 1 ^{o}C/min to remove P123. After that, the temperature was increased at a rate of 5 ^{o}C/min and kept at 900 ^{o}C for 2 h for further carbonation. The obtained MnO_2/carbon composites were treated with an NH_4OHCl solution (1M in HCl) to remove MnO_2 followed by

washing with deionized water and ethanol and drying at 100 $^{\circ}$C in air for 24 h.

## 2. Characterization and measurements

Nitrogen sorption isotherms were measured at 77 K with a Micromeritics Tristar 3000 analyzer (USA). Before measurements, the samples were degassed in vacuum at 200 $^{\circ}$C for at least 6 h. The specific surface areas (S_{BET}) were calculated by the Brunauer–Emmett–Teller (BET) method using adsorption branch in a relative pressure range from 0.04 to 0.2. The total pore volumes (Vt) were taken equal to the adsorbed amount at a P/P_0 of 0.992. The pore sizes (Dp) were derived from the adsorption branches of isotherms using the Barrett–Joyner–Halenda (BJH) model. The scanning electron microscopy (SEM) was conducted on a Philips XL-60 microscope. Transmission electron microscopy (TEM) experiments were conducted on a JEOL 2011 microscope (Japan) operated at 200 kV. Samples for TEM measurements were suspended in ethanol and supported on a holey carbon film on a Cu grid.

3. Electrochemical measurements

Electrodes were prepared by mixing 85 wt.% of carbon material, 10 wt.% of conductive agent (carbon black), and 5 wt.% of poly(tetrafluoroethylene) (PTFE) binder dispersed in isopropanol to form a homogeneous slurry. The slurry was rolled to obtain a film and dried at 80 °C for 10 min to remove the solvent before pressing. Then, the film was pressed (1.2×10^7 Pa) on a metal screen (Al and stainless steel screens were employed as current collectors for positive and negative charge carriers, respectively). The electrodes were cut into disks of Φ = 12 mm in diameter,

vacuum-dried at 100 °C for 24 h, and weighted. A typical mass load was about 5 mg/cm^2. The cell assembly was accomplished in a glove box (model 100G, MBraun, Germany) filled with pure argon. The electrolyte solution was 1.0 M $(C_2H_5)_4NBF_4$ in propylene carbonate (PC) (Honeywell Corp.). Electrochemical measurements were performed in a CR2016 coin-type cell on a Solartron Instrument Model 1287 electrochemical interface controlled by a computer. The capacitance of a carbon material can be estimated from CV curves using an equation $C = 2i/v$, where C is the differential capacitance, i is the current density (its value at 1.5 V is used here for calculations), v is the scan rate multiplied by a factor of two because two carbon electrodes of the capacitor are connected in series.

Results and Discussion
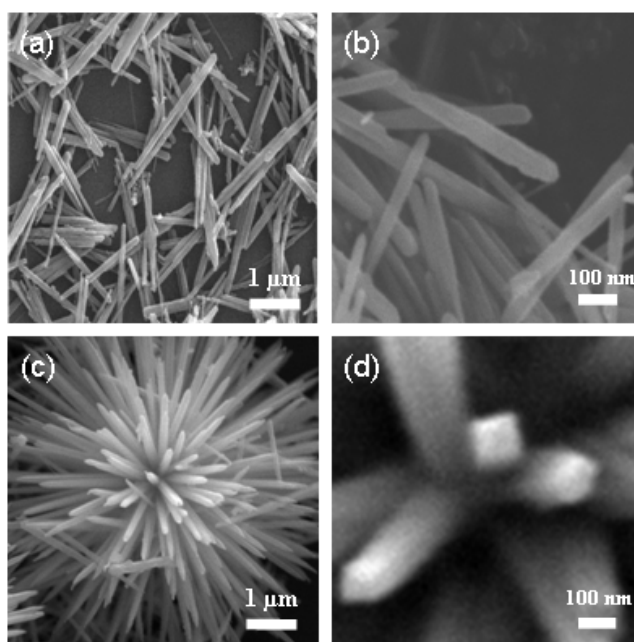
Fig. S1 SEM images of MnO_2 nano-rods ((a) and (b)) and a MnO_2 nano-thorn microsphere ((c) and (d)).

As shown in Fig. S1 ((a) and (b)), all MnO_2 samples analyzed with SEM show a

nano-rod morphology with nano-rod diameters of about 50 nm and lengths ranging

between 2.5 and 4.0 μm. Fig. S1 ((c) and (d)) reveals that, nano-thorn microspheres

are composed of uniform tetragonal nano-rod prisms with square cross-sections. The

nano-rods of each cluster originate from one core, and the length of each individual

nano-rod is about 2 μm. The nano-rods have diameters of about 100 nm.
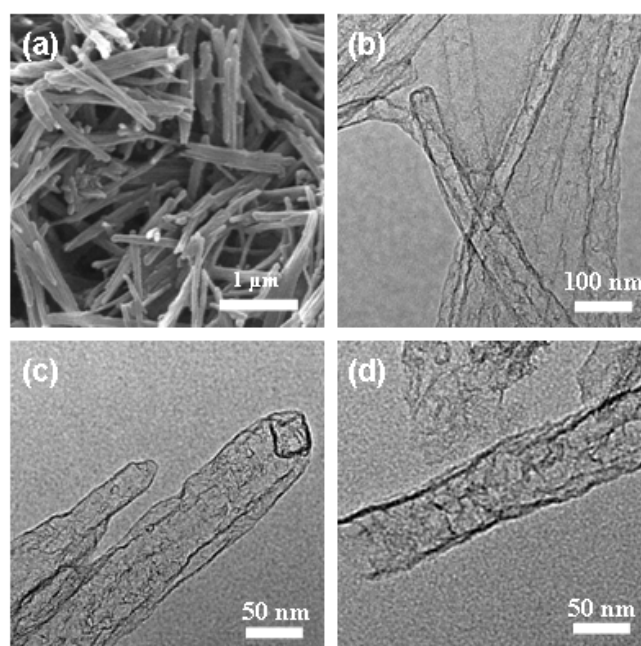

**Fig. S2** SEM and TEM images of MCNTs templated by MnO_2 nano-rods.
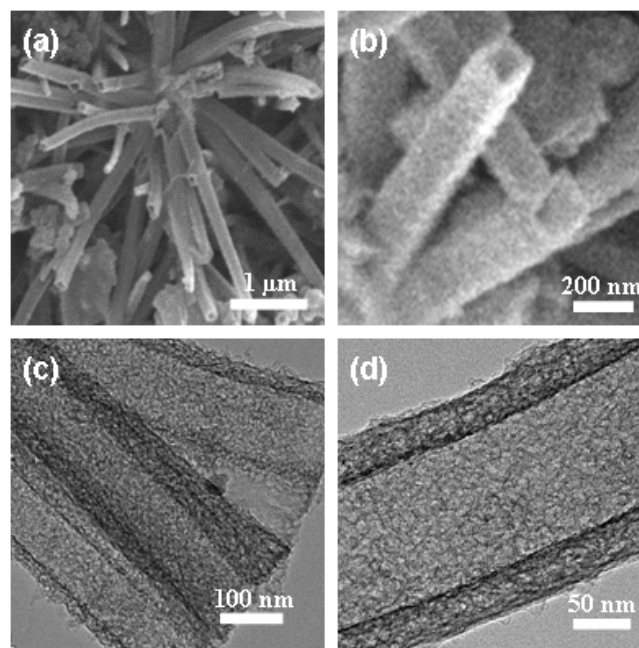
Fig. S3 SEM and TEM images of MCNTMSs templated by MnO_2 nano-thorn microspheres.

Hydrophobic treatment has been successfully used to decorate the surface of MnO_2 precursors without morphology damage. An SEM image of MCNTs after dissolving the MnO_2 template is shown in Fig. S2 (a). The carbon nanotubes have a diameter of approximately 50 nm, which is evident from the typical side-view TEM images in Fig. S2 (e) and (f). This diameter is comparable to the diameter of the templating MnO_2 nano-rods. SEM images of MCNTMS are shown in Fig. S3 (a) and (b). As seen, the nano-thorn microsphere is composed of uniform tetragonal nanotube prisms with square cross-sections. The nanotubes of each cluster have a wall thickness of 40 nm, and the channel in each individual nanotube is about 100 nm in diameter, as is shown in Fig. S3 (c) and (d). However, due to the lack of restrain provided by the template, the mesoporous structure of carbon nanotubes synthesized outside the MnO_2 is disordered.
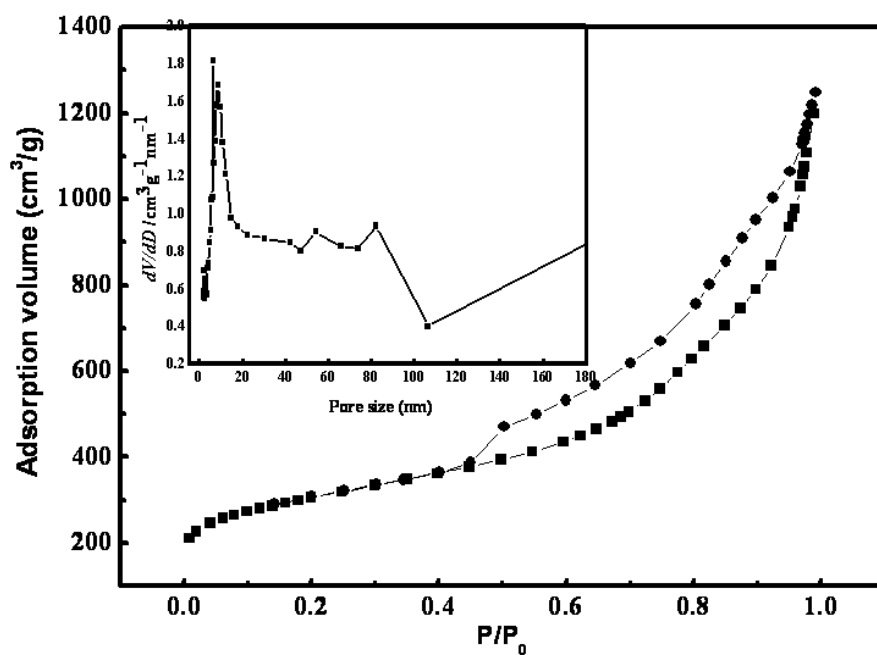
**Fig. S4** N_2 sorption isotherms and pore size distribution for MCNTs templated by MnO_2 nano-rods.
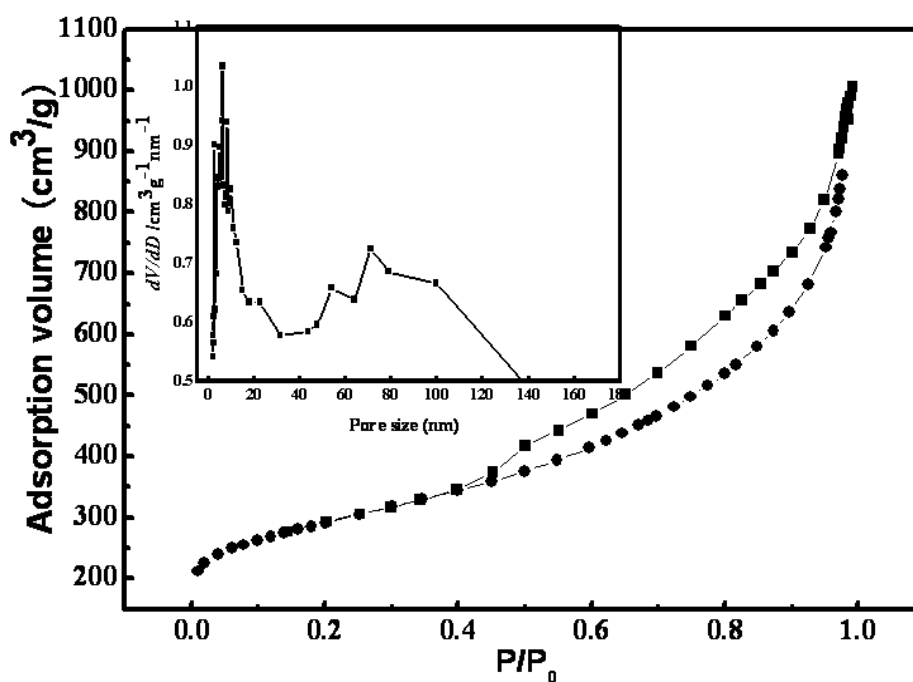
Fig. S5 N_2 sorption isotherms and pore size distribution of MCNTMSs templated by MnO_2 nano-thorn microspheres.

Nitrogen adsorption-desorption isotherms of MCNTs and MCNTMSs show

pronounced hysteresis at high relative pressures of 0.45-0.95, indicating a narrow

mesopore opening, as is evident from Fig. S4 and S5. The BET specific surface area

of MCNTs is 1079 m^2/g, and a total pore volume is about 1.93 cm^3/g. The pore size

calculated from the adsorption branch in Fig. S6 using the BJH model is 9.6 nm (inset

in Fig. S4) corresponding to mesopores on the nanotube walls. The BET specific

surface area of MCNTMSs is 1023 m^2/g, and a total pore volume is about 1.55 cm^3/g.

The pore size calculated from the adsorption branch in Fig. S7 using the BJH model is
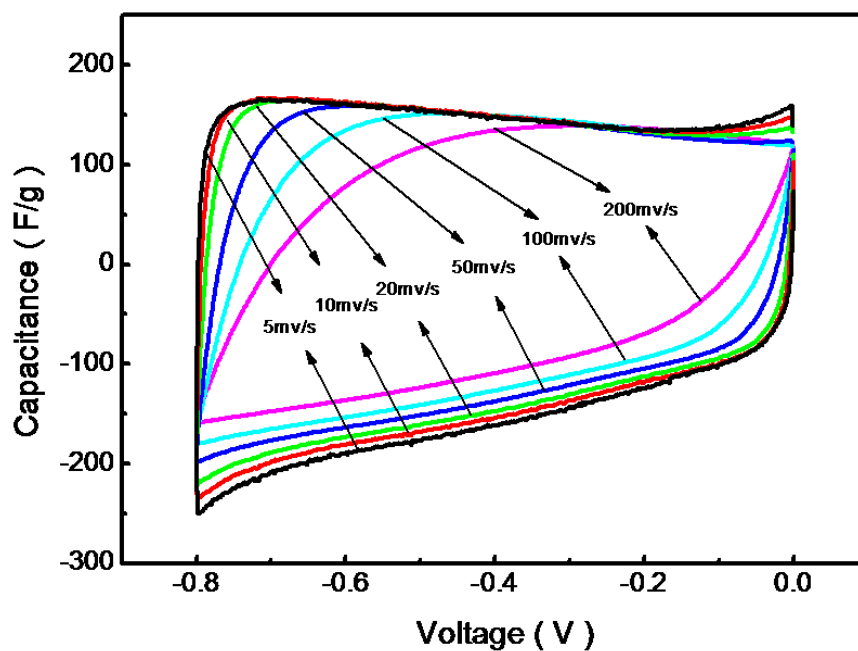
8.5 nm (inset in Fig. S5).
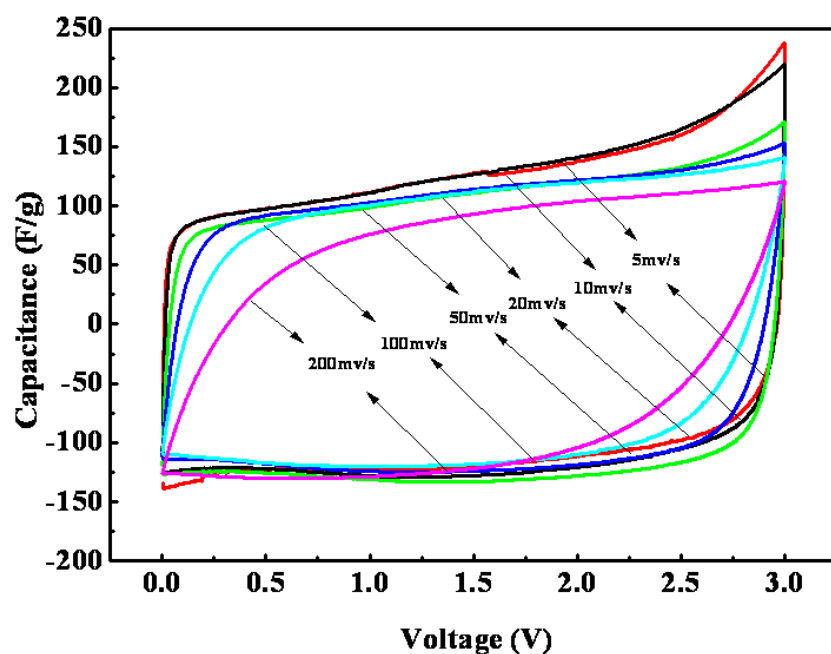
Fig. S6 CV profiles of MCNTs investigated at different scan rates from 5 to 200 mV/s

between 0 and 3 V in a 1 M $(C_2H_5)_4NBF_4$/PC electrolyte using a two-electrode
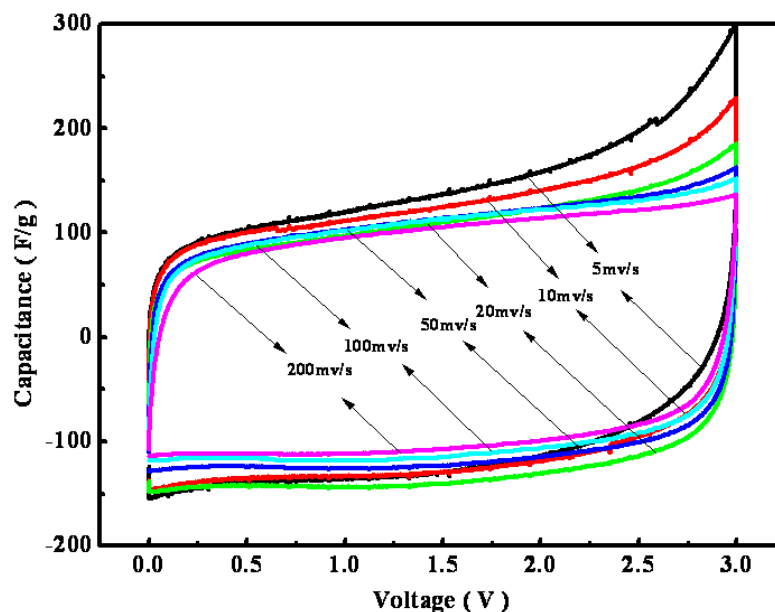
quasi-capacitor.

Fig. S7 CV profiles of MCNTMSs investigated at different scan rates from 5 to 200 mV/s between 0 and 3 V in a 1 M $(C_2H_5)_4NBF_4$/PC electrolyte using a two-electrode quasi-capacitor.

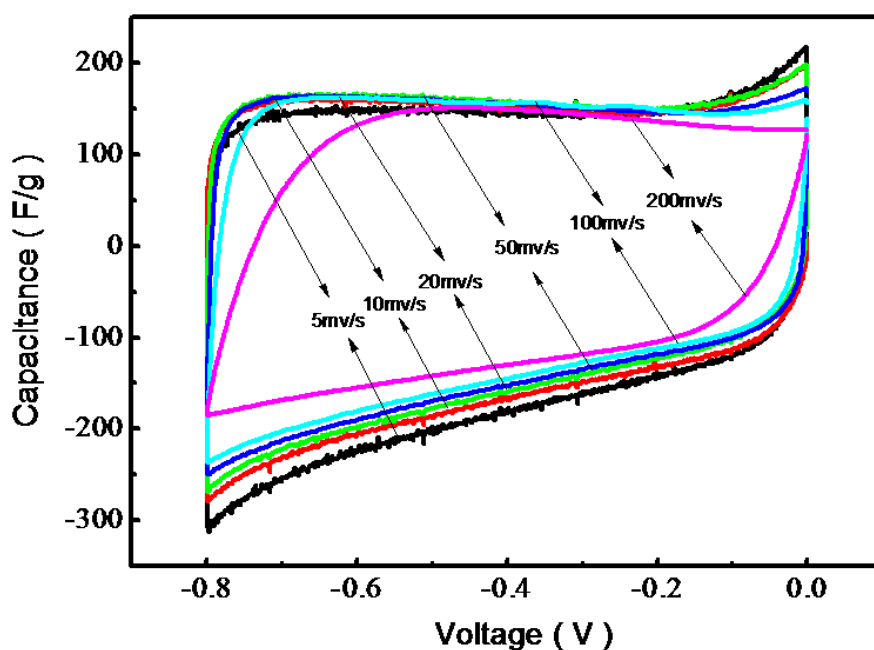CV curves of MCNTs and MCNTMSs are shown in Fig. S6 and S7, respectively. The curves were obtained at different scan rates from 5 to 200 mV/s between 0 and 3 V in a 1 M $(C_2H_5)_4NBF_4$/PC electrolyte using a two-electrode quasi-capacitor. The weight specific capacitance of MCNTs is estimated to be about 124 F/g, and 128 F/g for MCNTMSs. The large channels in the nanotubes reserve enough electrolyte during the charge/discharge process, and therefore, MCNTs and MCNTMSs demonstrate an excellent EDLC performance with a high rate capability.
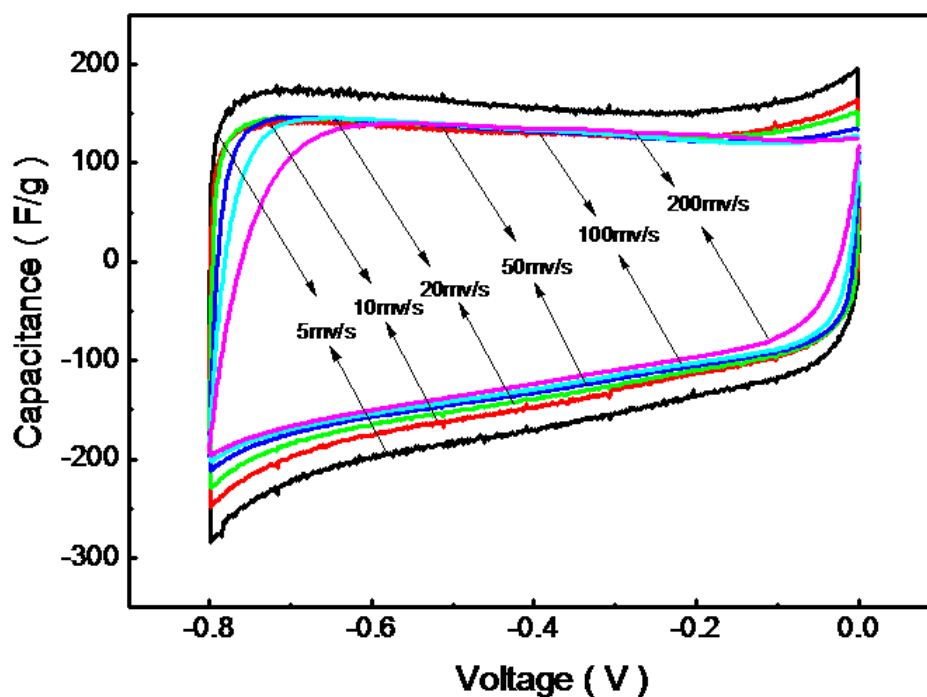
Fig. S8 CV profiles of MCNWNTs investigated at different scan rates from 5 to 200 mV/s between -0.8 and 0 V in a 6 M KOH electrolyte using a three-electrode glass cell in which Pt foil was used as the counter electrode, and a Hg/HgO electrode was used as the reference electrode.

Fig. S9 CV profiles of MCNTs investigated at different scan rates from 5 to 200 mV/s between -0.8 and 0 V in a 6 M KOH electrolyte using a three-electrode glass cell in

which Pt foil was used as the counter electrode, and a Hg/HgO electrode was used as

the reference electrode.

Fig. S10 CV profiles of MCNTMSs investigated at different scan rates from 5 to 200

mV/s between -0.8 and 0 V in a 6 M KOH electrolyte using a three-electrode glass

cell in which Pt foil was used as the counter electrode, and a Hg/HgO electrode was

used as the reference electrode.

CV curves of MCNWNTs，MCNTs and MCNTMSs are shown in Fig. S8-S10,

respectively. The curves were obtained at different scan rates from 5 to 200 mV/s

between -0.8 and 0 V in a 6 M KOH electrolyte using a three-electrode glass cell in

which Pt foil was used as the counter electrode, and a Hg/HgO electrode was used as

the reference electrode. The weight specific capacitance of MCNWNTs is estimated

to be about 155 F/g, 162 F/g for MCNTs and 160 F/g for MCNTMSs.
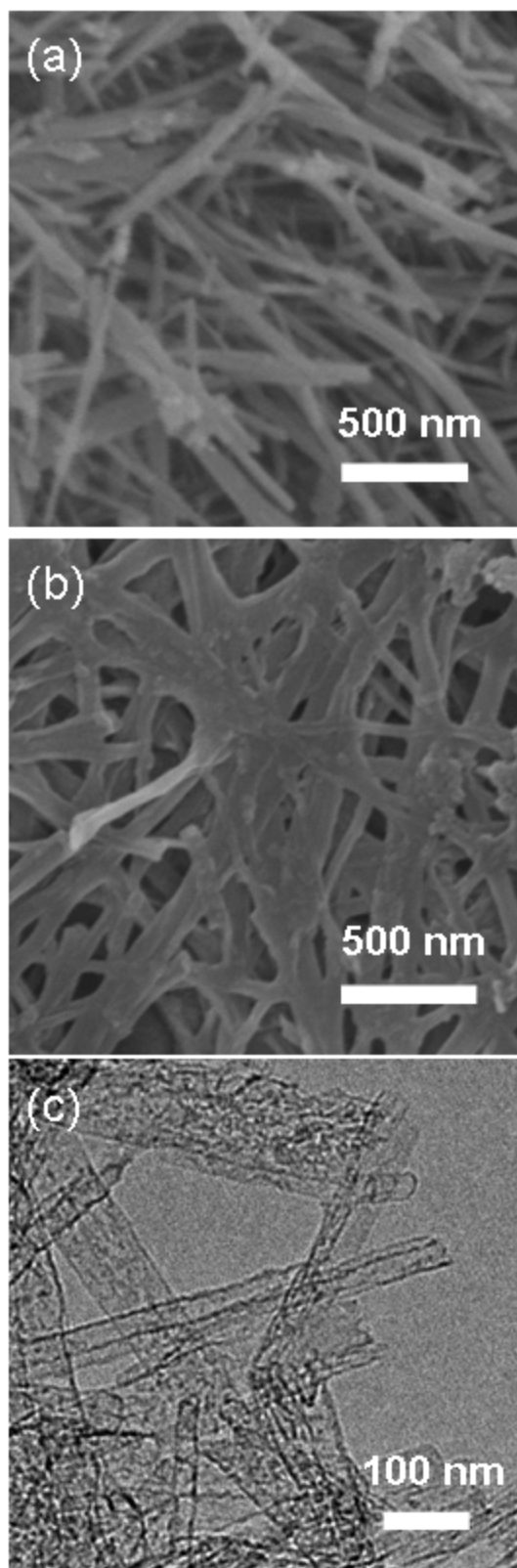
Figure S11 (a) SEM image of MnO_2 nanowires; (b) SEM image of resulting SiO_2 nanotubes; (c) TEM image of resulting SiO_2 nanotubes.

We have prepared nano-sized mesoporous SiO_2 nanotubes using MnO_2

nanowires as templates by this synthesis method as shown in Figure S11. Fig. S11(a)

shows SEM image of MnO_2 nanowires with a diameter of about 50 nm. Fig. S11(b)

and (c) show SEM and TEM images of resulting SiO_2 nanotubes, because of the wall

is so thin that the mesopores on the wall are not very ordered.

References

S1 Lee, J. S.; Joo, S. H.; Ryoo, R. J. Am. Chem. Soc. 2002, 124, 1156-1157.

S2 Wang, X.; Li, Y. D. J. Am. Chem. Soc. 2002, 124, 2880-2881.

S3 Zheng, D. S.; Sun, S. X.; Fan, W. L.; Yu, H. Y.; Fan, C. H.; Cao, G. X.; Yin, Z. L.;

Song, X. Y. J. Phys. Chem. B 2005, 109, 16439-16443.

S4 Chu, P. P.; Wu, H. D.; Polymer 2000, 41, 101-109.