Supporting Information

PTC MWCNTs/DI-water Switchable composites

Pengcheng Sun[a,b], Yun Huang[b], Jun Yang[b], Guoan Cheng[a], and Ruiting Zheng[a*]

[a]Key Laboratory of Radiation Beam Technology and Materials Modification of Ministry of Education, College of Nuclear Science and Technology, Beijing Normal University, Beijing 100875, P. R. China. Email: rtzheng@bnu.edu.cn
[b]State Key Laboratory of Multi-phase Complex Systems, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China.

Experiment Methods

Raw materials: Short R-MWCNTs (purity:95%) were bought from Chengdu Organic Chemicals Co., Ltd. China. H_2SO_4(95%-98%) and HNO_3(65%-68%) were purchased from Alfa Aesar. Sodium dodecyl benzene sulfonate (SDBS) was bought from Sinopharm Chemical Reagent Beijing Co., Ltd. China. DI-water(5×10^{-6}S/m<EC<5×10^{-5}S/m) was made by the ion filtration instrument.

Prepararion of O-MWCNTs/DI-water composites: Chemical oxidation method was applied for further purification and carboxylation of MWCNTs. H_2SO_4(240ml) and HNO_3(80ml) were mixed to form an oxidative agent, and then reacted with the O-MWCNTs(3.2g) under stirring for 2 hours at room temperature. After the reaction, the reactants were rinsed with self-made de-ionized(DI) water and filtered by a 0.2um microporous membrane (Bei Hua Li Ming membrane separation technology Co., Ltd), repeat the rinsing procedure until the pH value of the solution approach to 7. Then the remaining products were baking on a hotplate at 90°C for 12 hours to get O-MWCNTs. O-MWCNTs were dispersed in the DI-water to create a 0.2％volume fraction of composite under the ultrasonic(100W) for 2 hours.

Preparation of S-MWCNTs/DI-water composites: The R-MWCNTs and SDBS with the mass ratio of 1:2(3.15g: 6.3g) were mixed in a beaker with DI-water(150ml). The beaker was put into a ultrasonic cleaner bath to create a 1％volume fraction of S-MWCNTs/DI-water composite under the ultrasonic(100W) for 4 hours. The obtained uniform composite was then dispersed in DI-water and further ultrasonication was performed for 30 mins to obtain 0.2, 0.4, 0.6, and 0.8％ composites.

Microstructure characterization: The morphologies of R-MWCNTs were observed by scanning electron microscope (S-4800, HITACHI). The microstructures of R-MWCNTs, O-MWCNT and S-MWCNT are examined using a transmission electron microscopy(H600, HITACHI) at room temperature. The functionalization of the SDBS is further characterized by Fourier transform IR (FTIR) spectrum. The evolution of the clusters and percolating structures of the S-MWCNTs in DI-water was observed by a microscope (Axio Imager A2m,Carl Zeiss) with the help of a LED backlight.

Sample temperature regulation and measurement: The measured cell was put in a thermostatic bath (Thermo Scientific HAAKE) and its temperature maintained between -15-15ºC. A thermocouple (E-type) was placed in the central of the sample, as the temperature was read using a data acquisition board (National Instrument PCI 6221) and Labview software.

Electrical conductivity measurement: The electrical resistance of composite was measured by pouring CNTs gels into a self-made conductivity cell that has two dipping parallel vertical copper electrodes ~2.99 cm apart and with an area of ~0.68 cm^2. The resistances of the composites varied from 2KΩ–6.4MΩ. The parasitic resistance of the conductivity cell is ~0.5Ω, which is far below the sample resistance. The resistance is measured by a four point method (Keithley 2612A multimeter). The EC of the composites is given by the equation $\sigma = k/R$, where R is the measured resistance and $k = 4.4\ cm^{-1}$ is the cell constant. We estimate that the uncertainty in the EC measurement is ~1.4%.

Thermal conductivity measurement: The transient hot-wire method was used to measure the TC of the S-MWCNTs/DI-water composites. A 25um diameter Pt wire with a 3um thick Isonel insulating adhesion layer was fully immersed in the samples. The wire was subjected to a current pulse. The current was 80 mA, and the power on time was 2s for one pulse, there were 10 pulses in one measurement, the interval time between two consecutive

pulses was 3 minutes, and the thermal penetration length in the sample was about 200 um. The resulting temperature rise was determined as a function of time by monitoring changes in the electrical resistance of the wire. By analyzing the temporal temperature profile using solutions to the heat conduction equation, we determined the TC of each sample.

Other information: During the freezing of water, the MWNTs are pushed to the gain boundary by the growth of columnar-like ice crystals, generating the transport networks inside of the composites (Figure S1). The black lines represent MWCNTs, whereas the gray area represents columnar ice crystals, in which lots of air bubbles can be observed.

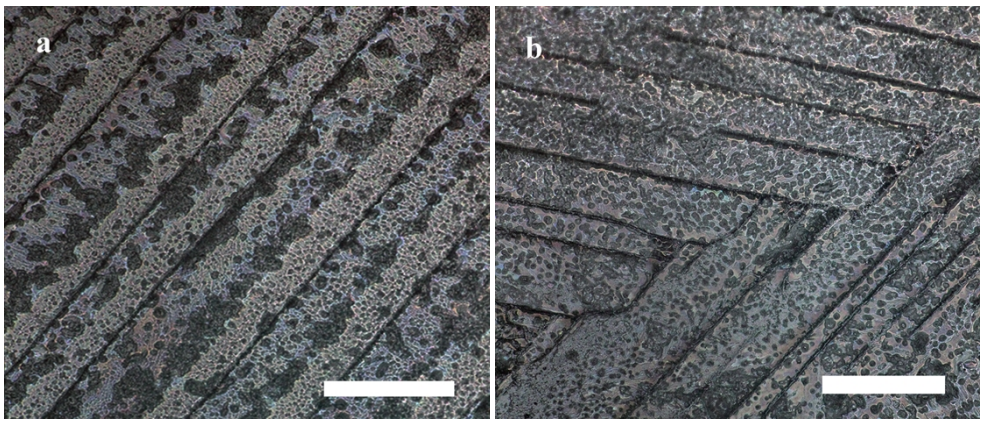

Figure S1. Optical microscope images of the frozen MWCNTs/DI-water composites. (a) O-MWCNTs/DI-water. (b) S-MWCNTs/DI-water. Scale bar is 200 μ m