Room Temperature Electrical and Thermal Switching CNT/Hexadecane Composites

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Temperature regulation of electrical and thermal conductivities of materials has attracted extensive attention because of the diverse applications, such as sensors,[1] smart switches, smart building,[2] thermal energy storage[3] and so on. Electrical conductivity (EC) regulation could be realized by metal-insulator (M-I) transitions which are widely observed in condensed-matter systems, such as: organic films,[4,5] chalcogenides,[6] metal oxides[7–10] and perovskites.[11,12] Most of the M-I materials have relative high transition temperatures, which the lowest transition temperature among M-I materials is 68 °C (VO_2). Although the transition temperature could be decreased by doping,[1] the corresponding process will rise the cost and decrease the temperature coefficient. Furthermore, temperature regulation of thermal conductivity (TC) is much more difficult than EC because of the little variation of TC during the solid-state phase transitions.[13] Materials with EC and TC regulating properties near room temperature have great potential applications in daily life.

Liquid-solid phase transition materials have the properties to regulate thermal conductivities at phase transition temperature, but usually cannot cause a metal-insulator transition. Nanoparticles with high EC and/or TC can be added into liquids to increase the EC and/or TC contrast between the liquid and solid states.[14] In the process of liquid freezing, particles are squeezed towards grain boundaries.[15,16] The internal stress generated during freezing improves the contact among particulates, increasing the EC and/or TC of the composites. When the solid remelts, particles will restore the chaotic distribution, the EC and/or TC of the composites will decrease simultaneously. By combining these effects, novel switch composites with large EC and TC variations in a narrow room temperature range can

be achieved. Base on the above principle, graphite/hexadecane composites with 2 orders of magnitude EC and 3 times of TC variations at 18 °C have been developed.[14] However, the EC contrast of the graphite composites just changes two orders, far less than that of practical PTC thermistors (above four orders). Theoretically, EC contrast could be improved by decrease the volume fraction of graphite flakes,[16] which will makes percolation network broken more easily during phase change. However, the liquid composites will be unstable when the additive is dilute. Furthermore, the graphite flakes tend to stick together under the repeated squeeze of the hexadecane crystal, which is hardly to be re-dispersed because of strong Van der Waals interaction. The switching properties of composites will degrade as well. CNTs have attracted great attention in composites area because of their high electrical and thermal conductivity, remarkable mechanical properties, low density and the unique one-dimensional structures.[17] Using CNTs substitute for graphite flakes may result in lower concentration and higher EC contrast composites. In this communication, we first report the functionalized CNTs/hexadecane switching composites with 5 orders of EC variations and 3 times of TC variations around the phase change point of the hexadecane (18 °C).

Figure 1 is the schematic diagram of the switching process in composites. In order to enhance the EC contrast of the composite, we use functionalized CNTs instead of pure CNTs. By the surface modification with functional groups, the strong Van der Waals interaction among CNTs can be reduced, which makes the CNTs or CNT clusters separate from each other and the composites are almost insulator (Figure 1a). During the freezing of hexadecane, the needle-like hexadecane crystals grow anisotropically (Figure 1b). The strong stress generated by the crystals growth compresses the CNTs contacting with each other and forms a conductive percolation network, the composite turns to be conductor. When the frozen hexadecane remelts, the pressure on the CNTs is released and the CNTs are separated from each other and re-disperse in the liquid again because of the steric effects of functional groups[18] and the liquid convection (Figure 1c). The broken of conductive network results in low EC in composite again, which will cause the large EC contrast ratio of the composite. TC has the similar switching property. The composites will have good reversibility in the subsequent repeat freezing and melting circulation if the CNTs or CNT clusters have good re-dispersion property.

According to the above strategy, we use the short-cut multi-walled carbon nanotubes (MWCNTs) to fabricate the composites, which could avoid serious aggregation during the freezing of hexadecane. To get the functionalized MWCNTs(F-MWCNTs), the common oxidation strategy is followed to introduce carboxylic acid groups on MWCNTs,[19,20] then the functionalized F-MWCNTs are produced by thermal

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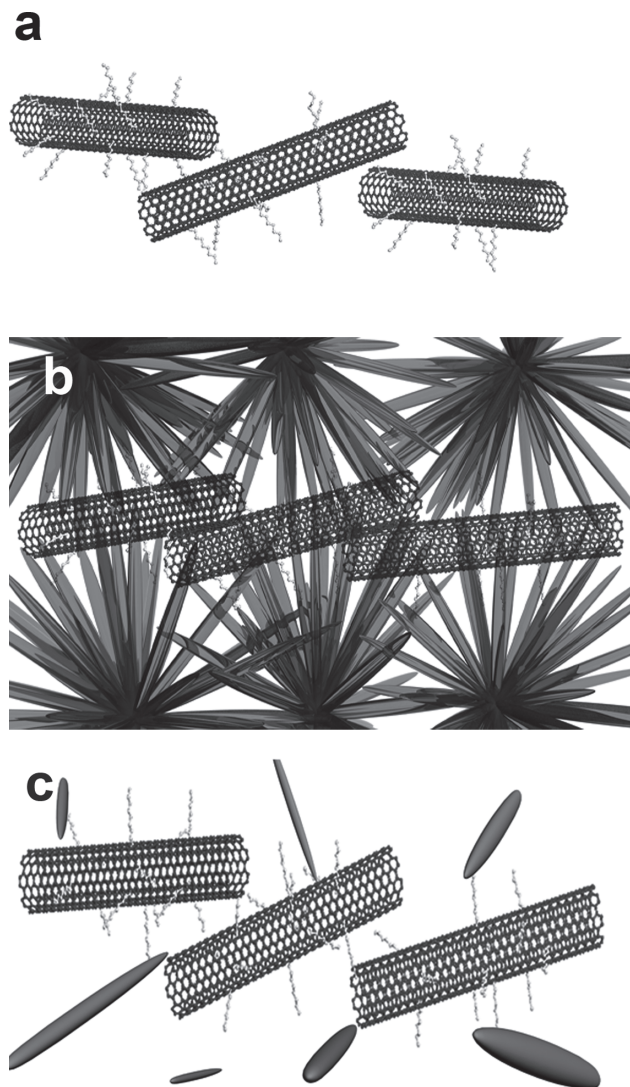MATERIALS
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Figure 1. Schematic diagram of the switching process in composite. a) Original state, CNTs are well dispersed by the help of surface functional groups. b) Frozen state, CNTs are squeezed to the grain boundary and form a conductive network. c) Re-melting state, CNTs are re-dispersed in the liquid, and the conductive network is broken.

mixing of oxidized MWCNTs and octadecylamine (ODA)[21] (See experimental detail in Supporting Information). **Figure 2**a is the SEM image of the original MWCNTs (O-MWCNTs), which are uniformly dispersed on the substrate. The length of the CNTs is about 0.5–1 um and the diameter is about 10–15 nm. Figures 2b and 2c are the high-resolution transmission electron microscopy (HRTEM) images of the O-MWCNT and F-MWNT respectively. It could be observed that the O-MWCNT has the multi-layered structure and smooth surface, and the interlayer distance is about 0.34 nm. Different from the O-MWNT, the HRTEM image of the F-MWCNT shows obvious amorphous substance attached on the surface of MWCNT, which may be caused by the grafting of the long-chain amine groups. The insert photos of Figure 2b and Figure 2c show the 0.2%V/V O-MWNTs and F-MWCNTs dispersed in hexadecane respectively. After one month of standing, obvious sediment could be observed in O-MWNTs suspension, but no sediment is observed in F-MWCNTs suspension, which indicates F-MWCNTs have better stability than O-MWNTs in hexadecane.

The surface structures of F-MWCNTs are further characterized by Fourier transform IR (FTIR) spectrum. Figure 2d shows the IR spectrum of F-MWCNTs, the peaks at 2915 cm^{-1}, 2844 cm^{-1} and 1435 cm^{-1} are confirmed to be C–H stretching modes and bending modes in the alkyl chain respectively, and the peak at 1565 cm^{-1} should come from the C=O stretch mode of carboxyl after be associated with amine via ionic bond.[21] The sharp peaks at 3447 cm^{-1}, 1631 cm^{-1} and 1204 cm^{-1} are probably due to –OH stretching vibration of adsorbed water molecules, C=C stretching mode of the MWCNTs and the C–O stretching modes respectively.[22] The results indicate that the amorphous substance attached on the surface of MWCNT should be the long-chain amine groups.

Figure 3a shows the EC of F-MWCNTs/hexadecane composvites as the function of temperature. In the liquid state, the EC of the composites varies little with temperature. From 18.5 to 17.5 °C, the EC increases several orders. After the hexadecane is completely frozen, the EC stabilizes. The contrast ratio of the EC, which defined as the ratio of EC between the solid and the liquid states near the phase transition, reaches peak (over 5 orders) around the volume fraction of 1.2% (Figure 3e). The corresponding EC changes from 2.03×10^{-7} S m^{-1} (liquid) to 3.34×10^{-2} S m^{-1} (solid).

The peak of EC contrast ratio comes from the different EC variation trend in solid and liquid CNTs composites. At a lower CNTs volume fraction, the EC enhances rapidly in solid composites but slowly in liquid composite with the increases of CNTs volume fraction, so the EC contrast ratio increases as well. The EC is saturated at 1.2%CNTs volume fraction in the solid composite, and it still increases slightly with the increase of CNTs volume fraction in the liquid composite, which cause the EC contrast ratio decrease when the CNTs volume fraction higher than 1.2% (Supporting Information, Figure S3a). The saturated volume fraction (SVF), which is defined as the volume fraction of the EC corresponding to the saturation value, is found in other composite too.[23]

For comparison, the EC of O-MWCNTs/hexadecane composites as the function of temperature is shown in Figure 3b. Different from the situation of F-MWCNTs, EC increases rapidly with the enhancement of CNTs volume fraction in the liquid composite, which cause the decrease of EC contrast ratio at higher volume fraction (Supporting Information, Figure S3b). The biggest contrast ratio is 2 orders at the volume fraction of 0.4%(Figure 3f), the corresponding EC changes from 1.98×10^{-4} S m^{-1}(liquid) to 2.73×10^{-2} S m^{-1}(solid). O-MWCNTs solid composite shows lower EC SVF than F-MWCNTs solid composite in our experiments. The reason could be the better contact among O-MWCNTs in the solid composites.

We believe the functionalization of the MWCNTs plays an important role for the large EC contrast ratio. The stable dispersion of the F-MWCNTs and the steric effect of the insulated functional groups make the composite almost an insulator in the liquid state. The EC of liquid F-MWCNTs composites is orders of magnitude lower than the EC of liquid O-MWCNTs composites (Supporting Information, Figure S4), during the freezing of the hexadecane, the partially grafted F-MWCNTs
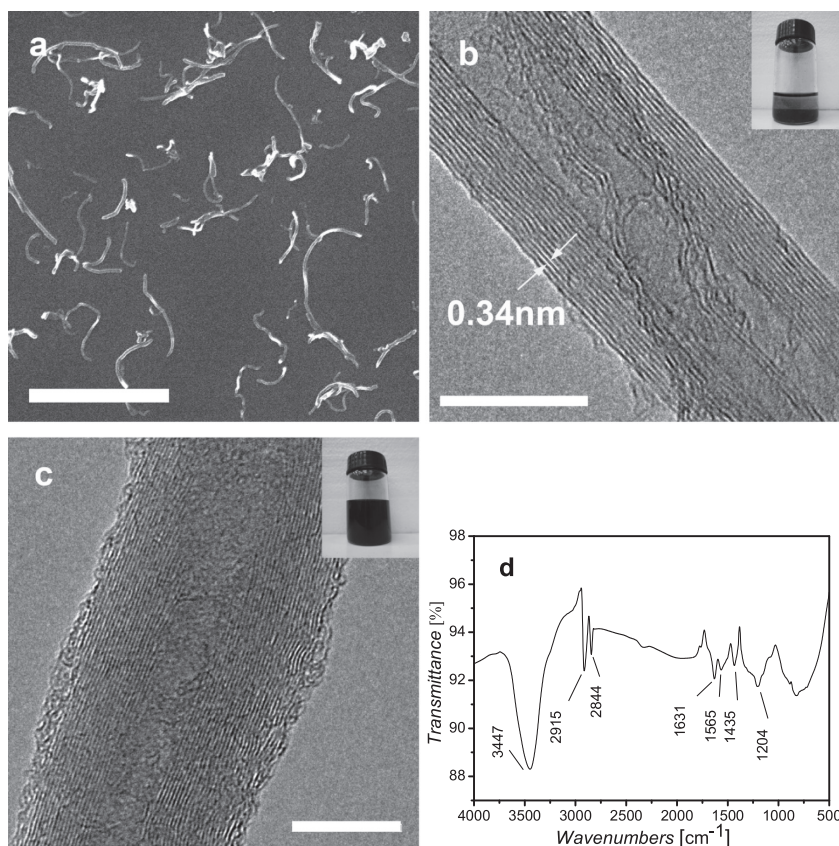
Figure 2. A) SEM image of the O-MWCNTs dispersed on the silicon substrate, the scare bar = 1 um. b) HRTEM image of the O-MWCNT, scare bar = 10 nm, insert photo is the 0.2% V/V O-MWCNTs/hexadecane composites after one month of standing. c) HRTEM image of the F-MWCNT, the scare bar = 10 nm, insert photo is the corresponding 0.2% V/V F-MWCNTs/hexadecane composites after one month of standing. d) Mid-IR spectrum of the F-MWCNTs.

with F-MWCNTs composites, TC of the liquid O-MWCNTs/hexadecane composites enhances slower with the increase of the CNTs volume fraction. In the solid state, TC increases from to 0.2% to 0.4% CNTs volume fraction. From then on, TC starts to decrease with the CNTs loading, which is contrary to F-MWCNTs composites (Supporting Information, Figure S3d). The largest TC contrast ratio is 2.46 times at the volume fraction of 0.4% (Figure 3f), corresponding TC changes from 0.154 W $m^{-1}K^{-1}$(liquid) to 0.379 W $m^{-1}K^{-1}$(solid). The mechanism for the degeneration of the TC in solid composites is still under investigation, but we conjecture that the agglomeration at higher O-MWCNTs loading leads to less conducting path and higher thermal resistance. The pure hexadecane shows EC insulated characteristic in both liquid and solid state, but it also shows TC switching property during the phase transition because of the intrinsic difference of TC in liquid and solid state. The TC variation of pure hexadecane around 18 °C is about 2 times, the corresponding TC changes from 0.141 W $m^{-1}K^{-1}$ (liquid) to 0.285 W $m^{-1}K^{-1}$ (solid) (Figure 3c, d).

The EC cycling behavior of the 1.2% (V/V) F-MWCNTs/hexadecane composites is shown in **Figure 4**a. In the first three cycles, the EC increases from 1.83 × 10^{-7} S m^{-1} to 2.03 × 10^{-7} S m^{-1} in the liquid state, and varies from 1.16 × 10^{-2} S m^{-1} to 3.34 × 10^{-2} S m^{-1} in the solid state. The corresponding EC contrast ratio increases from 61749 to 164532 times. After three times recycle, the ratio of the EC becomes stable and approaches a constant with a contrast by 5 orders of magnitude, the corresponding EC changes from 2.03 × 10^{-7} S m^{-1}(liquid) to 3.34 × 10^{-2} S m^{-1}(solid). Figure 4b shows the EC cycling of the O-MWCNTs/hexadecane composites at the CNTs volume fraction of 0.4%. Different from F-MWCNTs composites, the EC changes little in the solid state. In the liquid state, EC increases in the first six cycles from 4.40 × 10^{-5} S m^{-1} to 1.98 × 10^{-4} S m^{-1}. After first six cycles, the EC does not change anymore, and the contrast ratio stabilizes at 2 orders, the corresponding EC changes from 1.98 × 10^{-4} S m^{-1}(liquid) to 2.73 × 10^{-2} S m^{-1}(solid).

The repeatability test of the TC in 0.4% (V/V) F-MWCNTs/hexadecane composites is shown in Figure 4c. In first three cycles, TC increases from 0.166 W $m^{-1}K^{-1}$ to 0.172 W $m^{-1}K^{-1}$ in the liquid state, but decreases from 0.531 W $m^{-1}K^{-1}$ to 0.518 W $m^{-1}K^{-1}$ in the solid state, the corresponding TC contrast ratio decreases from 3.2 to 3 times. After the first three cycles, the TC turns to stable in both the liquid and the solid state, and the TC contrast ratio stabilizes at about 3 times. Figure 4d shows the repeatability test of the TC in O-MWCNTs/hexadecane composites at the volume fraction of 0.4%. During the first six cycles, TC changes a little in the liquid state, but continually decreases from 0.439 W $m^{-1}K^{-1}$ to 0.379 W $m^{-1}K^{-1}$ in the

could be squeezed and form a percolation networks, which cause the EC of the F-MWCNTs composites increased significantly around phase change point of the hexadecane (18 °C). Though the EC of solid F-MWCNTs composite is not as high as that of solid O-MWCNTs composite, the EC contrast ratio of F-MWCNT composite increases evidently.

Figure 3c shows the TC of the F-MWCNTs/hexadecane composites as a function of temperature. TC of the liquid composite has the similar trend as EC, it changes little with temperature. In the course of freezing, the TC rises sharply. After the composite is completely frozen, the TC stabilizes too. TC contrast is much smaller than the EC since heat also conducts in hexadecane, while electrons can only conduct along the CNTs. The TC contrast ratio peaks 3 times at 0.4% CNTs volume fraction (Figure 3e). The corresponding TC changes from 0.172 W $m^{-1}K^{-1}$ (liquid) to 0.518 W $m^{-1}K^{-1}$ (solid). The TC enhancement is due to phonon heat conduction along the CNTs network in the composite.[24] From 0.2% to 0.4%CNTs volume fraction, the TC of the solid composites enhances a lot, we anticipate that the big enhancement is due to the growth of CNTs networks. As we further increase the CNTs volume fraction, the TC turns to saturate (Supporting Information, Figure S3c).

TC of the O-MWCNTs/hexadecane composites as a function of temperature is shown in Figure 3d. Compare

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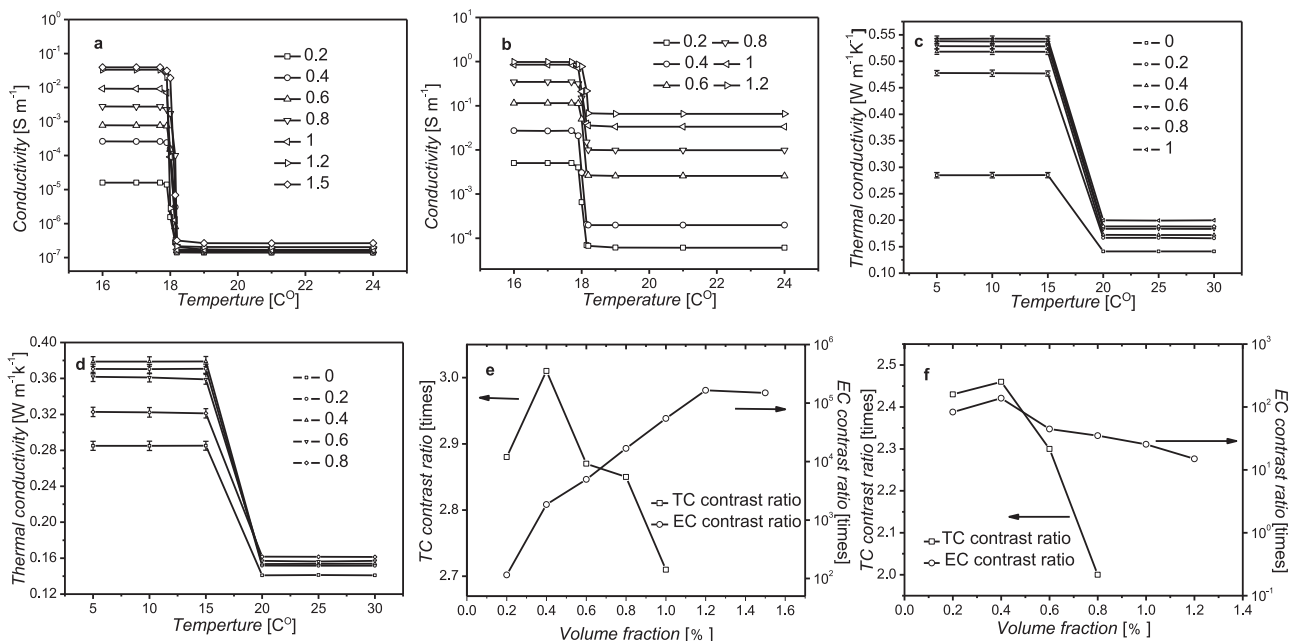ADVANCED
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Figure 3. Variation of EC and TC around the phase transition point. a,b) EC of F-MWCNTs and O-MWCNTs hexadecane composites with different CNTs volume fractions as a function of temperature, respectively. c,d) TC of F-MWCNTs and O-MWCNTs hexadecane composites with different CNTs volume fractions as a function of temperature, respectively. e) EC and TC contrast ratio of F-MWCNTs/hexadecane composites as a function of volume fraction, the EC and TC contrast ratio peak at the volume fraction of 1.2% and 0.4%, respectively. f) EC and TC contrast ratio of O-MWCNTs/hexade-cane composites as a function of volume fraction, both the EC and TC contrast ratio peak at the volume fraction of 0.4%. All dates in the EC and TC switching property tests of the composites (Figure a-d) are taken after 15 times cycles when the materials stabilize.
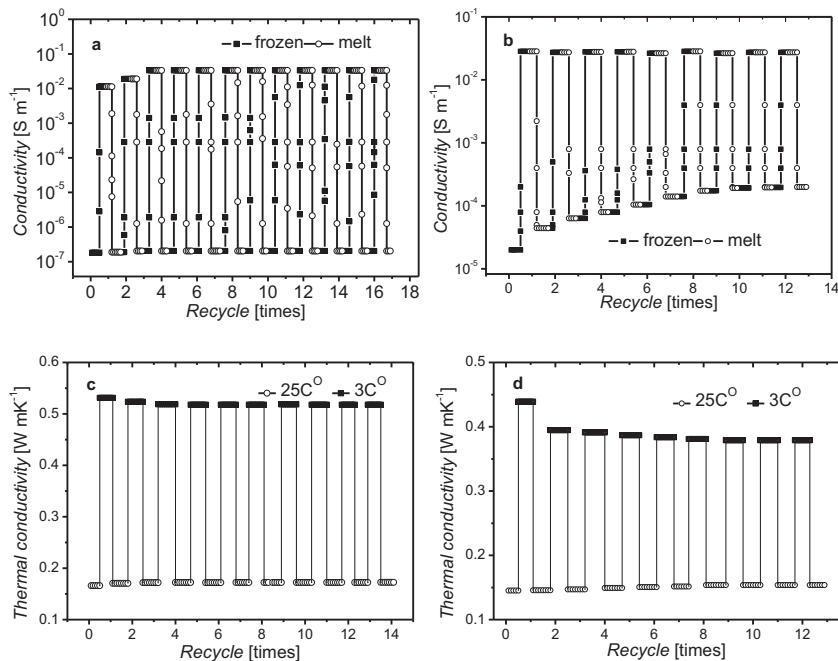

Figure 4. Cyclic freezing-melting tests of the composites. a,b) EC results of a 1.2% F-MWCNTs/hexadecane composite and a 0.4% O-MWCNTs/hexadecane composite, squares and circles indicate the conductivity variance through the processes of freezing and melting, respectively. c,d) TC contrast of 0.4% F-MWCNTs/hexadecane composites and 0.4% O-MWCNTs/hexade-cane composites after different cycles, squares and circles indicate the TC measured at 3 °C and 25 °C during different thermal cycles, respectively.

solid state. After the first six cycles, the TC contrast ratio stabilizes at 2.46 times, the corresponding TC changes from 0.154 W m^{-1}K^{-1} to 0.379 W m^{-1}K^{-1}(See EC and TC measurement method in Supporting Information).

In order to illustrate the variation of EC and TC contrast ratio during the freezing/remelting cycles, the microstructures of the dilute O-MWCNTs and F-MWCNTs hexadecane composites(0.05% volume fraction) during the repeated phase transition are observed by an optical microscope (**Figure 5**). Due to van der Waals interaction, the O-MWCNTs tend to agglomerate and form tens of micrometers size clusters in the original liquid state (Figure 5a). After three cycles, the O-MWCNTs clusters become bigger and bigger because of the repeated squeezing by the hexadecane crystals, the size of most clusters turns to hundred micrometers (Figure 5b). After fifteen cycles, the O-MWCNTs clusters continue to agglomerate with each other and tend to form continuous networks (Figure 5c). The growth of the O-MWCNTs clusters should be responsible for the enhancement of the EC in the liquid state during the first six cycles because of its higher efficiency electron transport,[25] but it
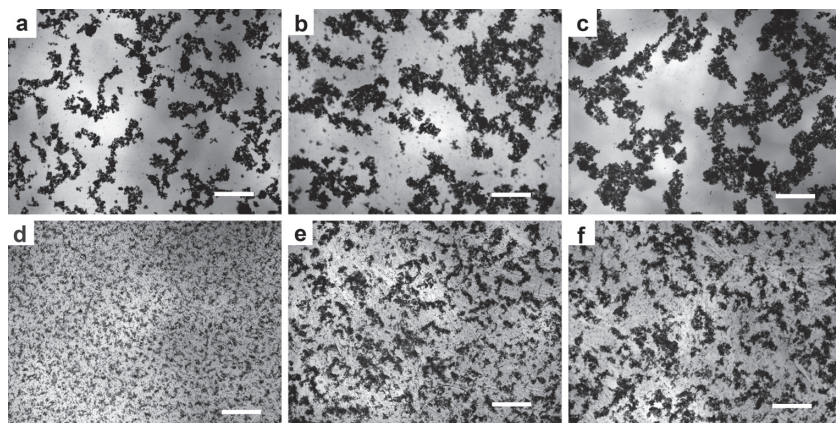
Figure 5. Evolution of MWCNTs microstructures in hexadecane during the remelting process. a-c) Optical microscope images of 0.05%(V/V) O-MWCNTs/hexadecane composites in original state, after three times re-melting, after fifteen times re-melting, respectively. d-f) Optical microscope images of 0.05%(V/V) F-MWCNTs/hexadecane composites in original state, after three times re-melting, after fifteen times re-melting, respectively. Scale bars in a-f are all corresponding to 200 μm.

shows negative effects for TC in the solid state because of the worse dispersion, as other researchers already observed.[26,27] In comparison, the F-MWCNTs show uniform distribution with a few micrometers size clusters in the original liquid phase (Figure 5d), and after three cycles, the size of the clusters of the F-MWCNTs grows to about tens of micrometers, but they are still well separated (Figure 5e). After further twelve cycles, some of the F-MWCNTs clusters grow to around one hundred micrometers, but majority of the clusters are still quite small, which shows a better re-dispersion property compare to O-MWCNTs (Figure 5f). Different from the O-MWCNTs composites, the growth of the F-MWCNTs clusters causes small EC enhancement in the liquid state, but obvious enhancement of EC in solid state during the first three cycles. The functionalization of CNTs should be responsible for this difference. The weak contact among F-MWCNTs could be improved gradually by the repeated squeezing of hexadecane crystals, which should be responsible for the enhancement of the EC in the solid state during the first three cycles. After the first three cycles, when the F-MWCNTs cluster structures stabilize, both the EC and the TC contrasts become a constant too.

Due to the similar structures of the function groups and hexadecane,[18,19] the compatibility between F-MWCNTs and the host is improved and the surface tension of the CNTs is reduced. F-MWCNTs show better dispersion than the O-MWCNTs in hexadecane (Figure 5). The re-dispersion of the F-MWCNTs is caused by the liquid convection, Brownian motion and steric effect. When the host starts to melt, the long-chain amine group will push CNTs away from each other, and enhance the driven force for re-dispersion, which cause F-MWCNTs/hexadecane composites having better repeatability than O-MWCNTs composites. Surface functionalization is beneficial for the durability of composites, which is very important for application of these materials.

In conclusion, based on the first-order phase transition, we have developed a simple and cheap method to prepare room temperature switching CNTs/hexadecane composites with

more than 5 orders in the EC and 3 times of TC variations around 18 °C. The experimental results indicate that surface modification of CNTs will not only enhance the EC contrast, but also improve the stability of composites. The novel smart composite materials show good practicality and durability, which have potential applications in sensors, smart control, thermal storage and other related area.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

[1] B.-J. Kim, Y. W. Lee, B.-G. Chae, S. J. Yun, S.-Y. Oh, H.-T. Kim, Y.-S. Lim, *Appl. Phys. Lett.* **2007**, *90*, 023515.

[2] A. M. Khudhair, M. M. Farid, *Energy Conversion and Management* **2004**, *45*, 263.

[3] A. F. Regin, S. C. Solanki, J. S. Saini, *Renewable Sust. Energy Rev.* **2008**, *12*, 2438.

[4] Q. Lai, Z. Zhu, Y. Chen, S. Patil, F. Wudl, *Appl. Phys. Lett.* **2006**, *88*, 133515.

[5] J. C. Scott, L. D. Bozano, *Adv. Mater.* **2007**, *19*, 1452.

[6] R. Waser, M. Aono, *Nat. Mater.* **2007**, *6*, 833.

[7] D. B. Strukov, G. S. Snider, D. R. Stewart, R. S. Williams, *Nature* **2008**, *453*, 80.

[8] T. W. Hickmott, *J. Appl. Phys.* **1962**, *33*, 2669.

[9] S. E. Ahn, M. J. Lee, Y. Park, B. S. Kang, C. B. Lee, K. H. Kim, S. Seo, D. S. Suh, D. C. Kim, J. Hur, W. Xianyu, G. Stefanovich, H. Yin, I. K. Yoo, J. H. Lee, J. B. Park, I. G. Baek, B. H. Park, *Adv. Mater.* **2008**, *20*, 924.

[10] C. Wu, H. Wei, B. Ning, Y. Xie, *Adv. Mater.* **2010**, *22*, 1972.

[11] R. Oligschlaeger, R. Waser, R. Meyer, S. Karthäuser, R. Dittmann, *Appl. Phys. Lett.* **2006**, *88*, 042901.

[12] K. Szot, W. Speier, G. Bihlmayer, R. Waser, *Nat Mater* **2006**, *5*, 312.

[13] K. H. Kim, M. Uehara, C. Hess, P. A. Sharma, S. W. Cheong, *Phys. Rev. Lett.* **2000**, *84*, 2961.

[14] R. Zheng, J. Gao, J. Wang, G. Chen, *Nat. Commun.* **2011**, *2*, 289.

[15] S. Deville, E. Saiz, R. K. Nalla, A. P. Tomsia, *Science* **2006**, *311*, 515.

[16] K. M. Golden, S. F. Ackley, V. I. Lytle, *Science* **1998**, *282*, 2238.

[17] J. M. Schnorr, T. M. Swager, *Chem. Mater.* **2010**, *23*, 646.

[18] K. Hayashida, H. Tanaka, *Adv. Funct. Mater.* **2012**, *22*, 2338.

[19] J. Liu, *Science* **1998**, *280*, 1253.

[20] J. Chen, *Science* **1998**, *282*, 95.

[21] M. A. Hamon, J. Chen, H. Hu, Y. Chen, M. E. Itkis, A. M. Rao, P. C. Eklund, R. C. Haddon, *Adv. Mater.* **1999**, *11*, 834.

[22] E. Fuente, J. A. Menéndez, M. A. Díez, D. Suárez, M. A. Montes-Morán, *J. Phys. Chem. B* **2003**, *107*, 6350.

[23] Y. Agari, A. Ueda, S. Nagai, *J. Appl. Polym. Sci.* **1991**, *42*, 1665.

[24] R. Zheng, J. Gao, J. Wang, S.-P. Feng, H. Ohtani, J. Wang, G. Chen, *Nano Lett.* **2011**, *12*, 188.

[25] J. Li, P. C. Ma, W. S. Chow, C. K. To, B. Z. Tang, J. K. Kim, *Adv. Funct. Mater.* **2007**, *17*, 3207.

[26] S. H. Song, K. H. Park, B. H. Kim, Y. W. Choi, G. H. Jun, D. J. Lee, B.-S. Kong, K.-W. Paik, S. Jeon, *Adv. Mater.* **2013**, *25*, 732.

[27] J. E. Peters, D. V. Papavassiliou, B. P. Grady, *Macromolecules* **2008**, *41*, 7274.

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