

Assembly of Fullerene-Carbon Nanotubes: Temperature Indicator for Photothermal Conversion

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Experimental Section

Preparation of alkylated-C₆₀/SWCNT assemblies

Fullerene-C₆₀ derivatives **1**, **2** and **3** were prepared by refluxing the corresponding benzaldehyde with *N*-methylglycine and C₆₀ in dry monochlorobenzene, according to our previous reports.¹⁻³ The alkylated-C₆₀/SWCNT assemblies (**1**-SWCNT, **2**-SWCNT and **3**-SWCNT) were prepared by heating and sonicating 1.0 mM of **1**, **2** or **3** at 70 °C of with 0.1 mg SWNT in 1.0 mL 1,4-dioxane for 30 min, and then cooling to room temperature. The flake-shaped microparticles or microdisks were obtained as precipitates in 1,4-dioxane solutions, and spread onto water from the 1,4-dioxane dispersions to form a very diluted film. Then the diluted film of microparticles or microdisks were transferred onto a glass for the near-infrared (NIR) laser irradiation.

Optical setup

The optical setup is similar with that in our previous report.⁴ Briefly, a continuous wave laser diode at 830 nm with optical power up to 90 mW was used in the experiments. The collimated laser beam in micrometer size was focused onto the sample through a microscope objective, ×100 magnification N.A. = 1.25 (Edmund Scientific, Commercial Grade). The sample was positioned in the field of view by a micrometer resolution XYZ stage. Illumination was made

in transmission mode within seconds, and the images were recorded by a charge coupled device (CCD) camera connected to a computer.

Instruments

Scanning electron microscopy (SEM) images were recorded by means of a Philips XL30 electron microscope at an accelerating voltage of 3 kV. Transmission electron microscopy (TEM) images were obtained with a JEOL model JEM-2200FS microscope. High resolution cryogenic TEM (HR-cryo-TEM) images were obtained with a JEOL model JEM-4000SFX microscope. FT-IR spectra were recorded on Bruker EQUINOX 55/S spectrophotometer. Differential scanning calorimetry (DSC) measurements were carried out using a DSC 204 (Netzsch, Germany) under nitrogen. The scanning speed is a 10 °C/min. Powder X-ray diffraction (XRD) analysis was carried out with a Rigaku Rint-2200 X-ray diffractometer with monochromated CuK α radiation and temperature-controlled heating stage.

Supporting Reference:

1. Nakanishi, T.; Michinobu, T.; Yoshida, K.; Shirahata, N.; Ariga, K.; Möhwald, H.; Kurth, D. G. *Adv. Mater.* **2008**, *20*, 443.
2. Nakanishi, T.; Ariga, K.; Michinobu, T.; Yoshida, K.; Takahashi, H.; Teranishi, T.; Möhwald, H.; Kurth, D. G. *Small* **2007**, *3*, 2019
3. Nakanishi, T.; Shen, Y.; Wang, J.; Li, H.; Fernandes, P.; Yoshida, K.; Yagai, S.; Takeuchi, M.; Ariga, K.; Kurth, D. G.; Möhwald, H. *J. Mater. Chem.* **2010**, *20*, 1253.
4. Skirtach, A. G.; Antipov, A. A.; Shchukin, D. G.; Sukhorukov, G. B. *Langmuir* **2004**, *20*, 6988.

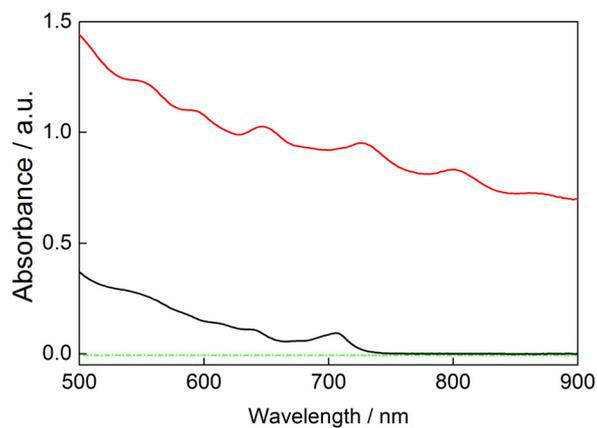


Figure S1 Absorption spectra of **1** (black) and **1**-SWCNT (red) in THF where the concentrations of **1** are the same (0.25 mM).

The black line in the spectra shows that **1** has no absorption at 830 nm, which proves our control experiment indicating that microparticles consisting of **1** itself do not transform the flaked surface morphology upon NIR laser irradiation.

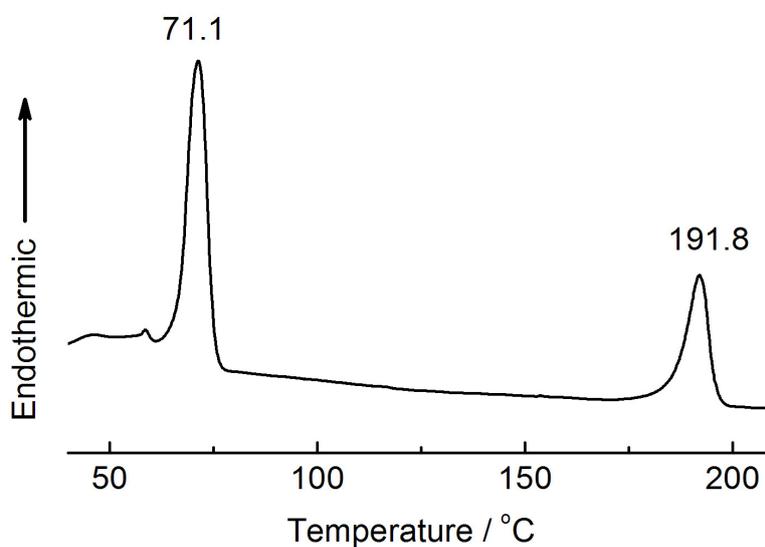


Figure S2 The first heating trace of the DSC thermogram for **1**-SWCNT with the whole temperature range applied.

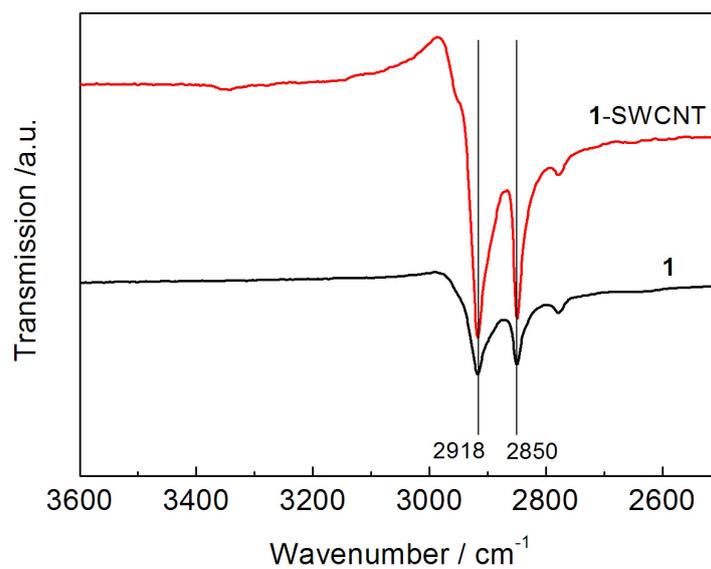


Figure S3 FT-IR spectra of flake-shaped microparticles of **1** (black) and **1-SWCNT** (red) at room temperature.



Figure S4 Photo of SWCNT in THF with the addition of alkylated-C₆₀ derivative **3**.

Here as an example, we show SWCNT dispersed by **3** in THF solution. Our results show that SWCNT can be dispersed by all the alkylated-C₆₀ derivatives **1-3** as seen in this photo.

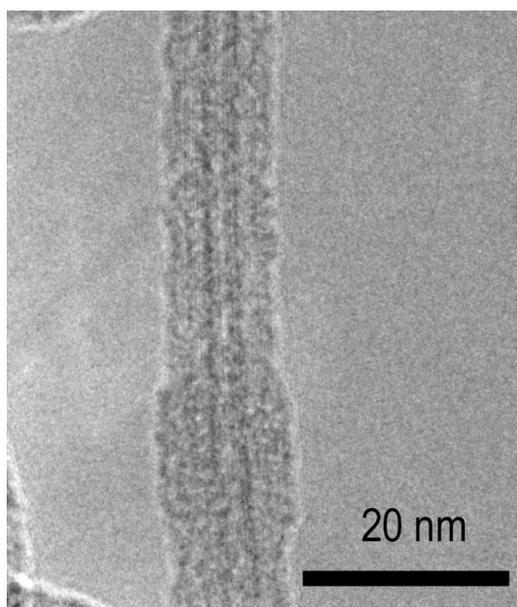


Figure S5 High-resolution TEM of SWCNT debundled by the addition of **1** from THF solution, showing that **1** can adsorb on the SWCNT surface.

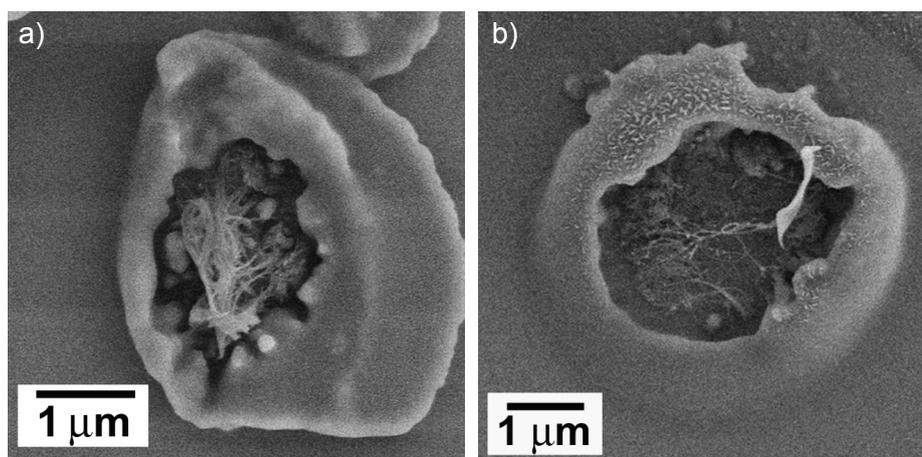


Figure S6 Enlarged SEM images from Fig. 3c and Fig. 3f in the main text: SEM images of a disk assembly of **2**-SWCNT (a) and a flake-shaped microparticle assembly of **3**-SWCNT (b) after NIR laser irradiation (90 mW). In both cases, a “hole” is formed in the middle exposing SWCNT, demonstrating that the morphology of fullerene assemblies changes but that of the SWCNT does not.

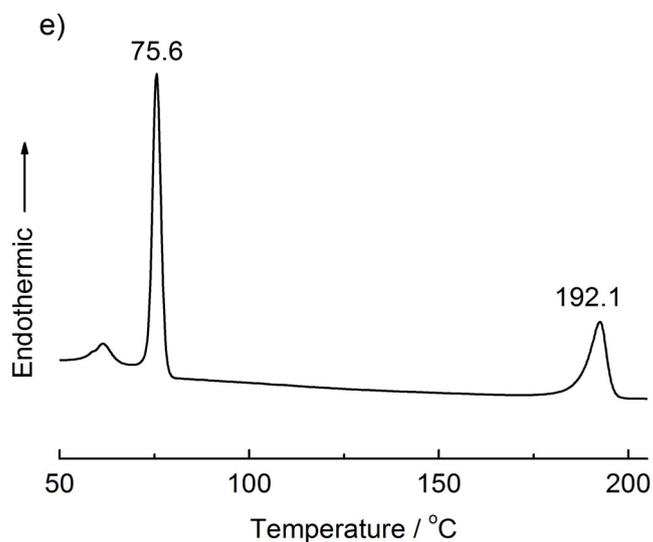
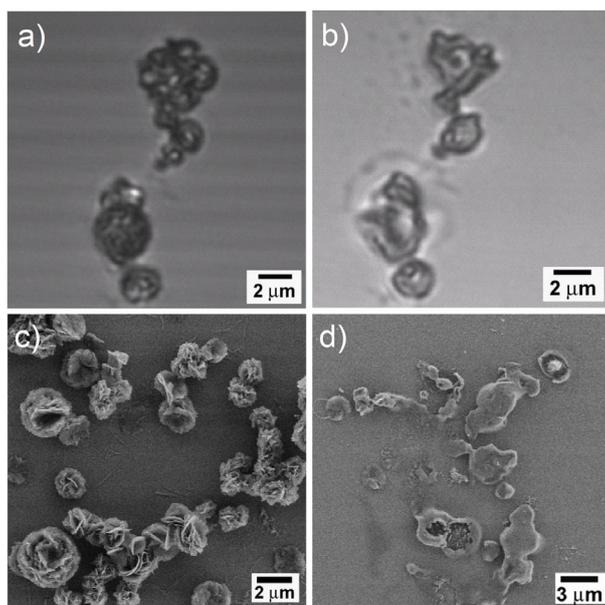


Figure S7 Optical microscopy images of **1-MWCNT** microparticles before (a) and after (b) NIR laser irradiation (90 mW) captured from the same position, and SEM images of **1-MWCNT** microparticles before (c) and after (d) NIR laser irradiation (90 mW) captured from different positions. (e) The first heating trace of the DSC thermogram of **1-MWCNT** microparticles demonstrates the melting point of **1-MWCNT** is about 192 °C. The deformation of **1-MWCNT** microparticles indicates that upon NIR light irradiation the temperature rise of MWCNT in air can be up to 192 °C.

Complete ref 9c:

Nasibulin, A. G.; Pikhitsa, P. V.; Jiang, H.; Brown, D. P.; Krasheninnikov, A. V.; Anisimov, A. S.; Queipo, P.; Moisala, A.; Gonzalez, D.; Lientschnig, G.; Hassanien, A.; Shandakov, S. D.; Lolli, G.; Resasco, D. E.; Choi, M.; Tomanek, D.; Kauppinen, E. I. *Nat. Nanotechnol.* **2007**, 2, 156.