# Light-Controlled Single-Walled Carbon Nanotube Dispersions in Aqueous Solution

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We have succeeded in dispersing single-walled carbon nanotubes (SWNTs) into an aqueous solution of poly(ethylene glycol)-terminated malachite green derivative (PEG-MG) through simple sonication. It was found that UV exposure caused reaggregation of these predispersed SWNTs in the same aqueous medium, as adsorbed PEG-MG photochromic chains could be effectively photocleavaged from the nanotube surface. The observed light-controlled dispersion and reaggragation of SWNTs in the aqueous solution should facilitate the development of SWNT dispersions with a controllable dispersity for potential applications.

## 1. Introduction

Since their discovery in 1991,[1] carbon nanotubes (CNTs) have attracted enormous interest for their unique electronic, mechanical, and structural properties.[2–4] Because of these interesting properties, CNTs are promising for applications in nanoscience and nanotechnology. However, their applications have been extremely limited by their low solubility in all conventional solvents. Therefore, the improvement of the solubility of CNTs, especially single-walled carbon nanotubes (SWNTs), has become a hot topic of both fundamental and practical significance.[4,5] For solubilization of SWNTs, a general strategy is to modify SWNTs with soluble moieties via covalent[6] or noncovalent[7] approaches. Among various modification processes, noncovalent methods using polymer surfactants as the dispersion reagent are particularly interesting since well-dispersed SWNTs with unchanged intrinsic

**Scheme 1. Schematic Diagram of the Dispersion of SWNTs by PEG-MG and Their Reaggregation with UV Irradiation**
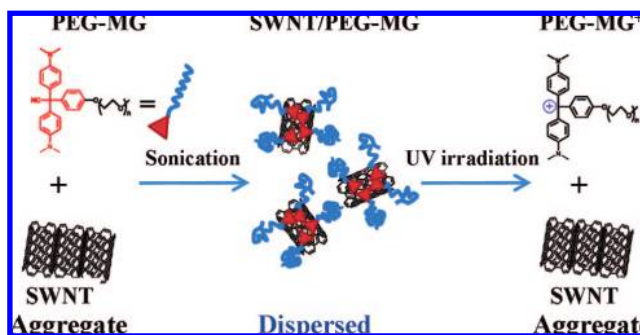


structure and properties can be readily prepared.[8] However, many potential applications, including smart sensors and drug and gene delivery systems, often require stimuli-responsive dispersion/aggregation of SWNTs in certain solvents.[9] Examples include poly(acrylic acid)-,[10] poly-L-lysine-,[11] and lysozyme-dispersed[12] SWNTs with a pH-responsive dispersity, SWNTs dispersed in thermosensitive poly(*N*-isopropylacrylamide) for a temperature-responsive dispersion,[11] and SWNTs dispersed in 2,2′-bipyridine derivative for oxidation–reduction reactions of $Cu^I/Cu^{II}$.[13]

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(1) Iijima, S. *Nature* **1991**, *354*, 56.
(2) Haddon, R. C. *Acc. Chem. Res.* **2002**, *35*, 997.
(3) (a) Liu, J.; Rinzler, A. G.; Dai, H. J.; Hafner, J. H.; Bradley, R. K.; Boul, P. J.; Lu, A.; Iverson, T.; Shelimov, K.; Huffman, C. B.; Rodriguez-Macias, F.; Shon, Y. S.; Lee, T. R.; Colbert, D. T.; Smalley, R. E. *Science* **1998**, *280*, 1253. (b) Chen, J.; Hamon, M. A.; Hu, H.; Chen, Y. S.; Rao, A. M.; Eklund, P. C.; Haddon, R. C. *Science* **1998**, *282*, 95. (c) Baughman, N. R.; Zakhidov, A. A.; de Heer, W. A. *Science* **2002**, *297*, 787. (d) Qu, L.; Dai, L. *J. Am. Chem. Soc.* **2005**, *127*, 10806.
(4) Tasis, D.; Tagmatarchis, N.; Bianco, A.; Prato, M. *Chem. Rev.* **2006**, *106*, 1105.
(5) (a) Hirsch, A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1853. (b) Britz, D. A.; Khlobystov, A. N. *Chem. Soc. Rev.* **2006**, *35*, 637.
(6) (a) Georgakilas, V.; Kordatos, K.; Prato, M.; Guldi, D. M.; Holzinger, M.; Hirsch, A. *J. Am. Chem. Soc.* **2002**, *124*, 760. (b) Hu, H.; Zhao, B.; Hamon, M. A.; Kamaras, K.; Itkis, M. E.; Haddon, R. C. *J. Am. Chem. Soc.* **2003**, *125*, 14893. (c) Baskaran, D.; Mays, J. W.; Zhang, X. P.; Bratcher, M. S. *J. Am. Chem. Soc.* **2005**, *127*, 6916.
(7) (a) Nakashima, N.; Tomonari, Y.; Murakami, H.; Yoshinaga, K. *Chem. Lett.* **2002**, 638. (b) Moore, V. C.; Strano, M. S.; Haroz, E. H.; Hauge, R. H.; Smalley, R. E. *Nano Lett.* **2003**, *3*, 1379. (c) Zorbas, V.; Acevedo, A. O.; Dalton, A. B.; Yoshida, M. M.; Dieckmann, G. R.; Draper, R. K.; Baughman, R. H.; Yacaman, M. J.; Musselman, I. H. *J. Am. Chem. Soc.* **2004**, *126*, 7222. (d) Ogoshi, T.; Takashima, Y.; Yamaguchi, H.; Harada, A. *J. Am. Chem. Soc.* **2007**, *129*, 4878. (e) Ikeda, A.; Tanaka, Y.; Nobusawa, K.; Kikuchi, J. *Langmuir* **2007**, *23*, 10913. (f) Florent, M.; Shvartzman-Cohen, R.; Goldfarb, D.; Yerushalmi-Rozen, R. *Langmuir* **2008**, *24*, 3773.

(8) (a) Wang, D.; Ji, W. X.; Li, Z. C.; Chen, L. W. *J. Am. Chem. Soc.* **2006**, *128*, 6556. (b) Karajanagi, S. S.; Yang, H. C.; Asuri, P.; Sellitto, E.; Dordick, J. S.; Kane, R. S. *Langmuir* **2006**, *22*, 1392. (c) Chatterjee, T.; Yurekli, K.; Hadjiev, V. G.; Krishnamoorti, R. *Adv. Funct. Mater.* **2005**, *15*, 1832. (d) Dieckmann, G. R.; Dalton, A. B.; Johnson, P. A.; Razal, J.; Chen, J.; Giordano, G. M.; Munoz, E.; Musselman, I. H.; Baughman, R. H.; Draper, R. K. *J. Am. Chem. Soc.* **2003**, *125*, 1770. (e) Nakayama-Ratchford, N.; Bangsaruntip, S.; Sun, X.; Welsher, K.; Dai, H. *J. Am. Chem. Soc.* **2007**, *129*, 2448.
(9) Barone, P. W.; Strano, M. S. *Angew. Chem., Int. Ed.* **2006**, *45*, 8138.
(10) Grunlan, J. C.; Liu, L.; Kim, Y. S. *Nano Lett.* **2006**, *6*, 911.
(11) Wang, D.; Chen, L. *Nano Lett.* **2007**, *7*, 1480.
(12) Nepal, D.; Geckeler, K. E. *Small* **2006**, *2*, 406.
(13) Nobusawa, K.; Ikeda, A.; Kikuchi, J.; Kawano, S.; Fujita, N.; Shinkai, S. *Angew. Chem., Int. Ed.* **2008**, *47*, 4577.
(14) (a) Uda, R. M.; Oue, M.; Kimura, K. *Chem. Lett.* **2004**, *33*, 586. (b) Uda, R. M.; Kimura, K. *J. Phys. Org. Chem.* **2007**, *20*, 802.
(15) (a) Willner, I.; Sussan, S.; Rubin, S. *J. Chem. Soc., Chem. Commun.* **1992**, 100. (b) Willner, I.; Rubin, S.; Shatzmiller, R.; Zor, T. *J. Am. Chem. Soc.* **1993**, *115*, 8690.
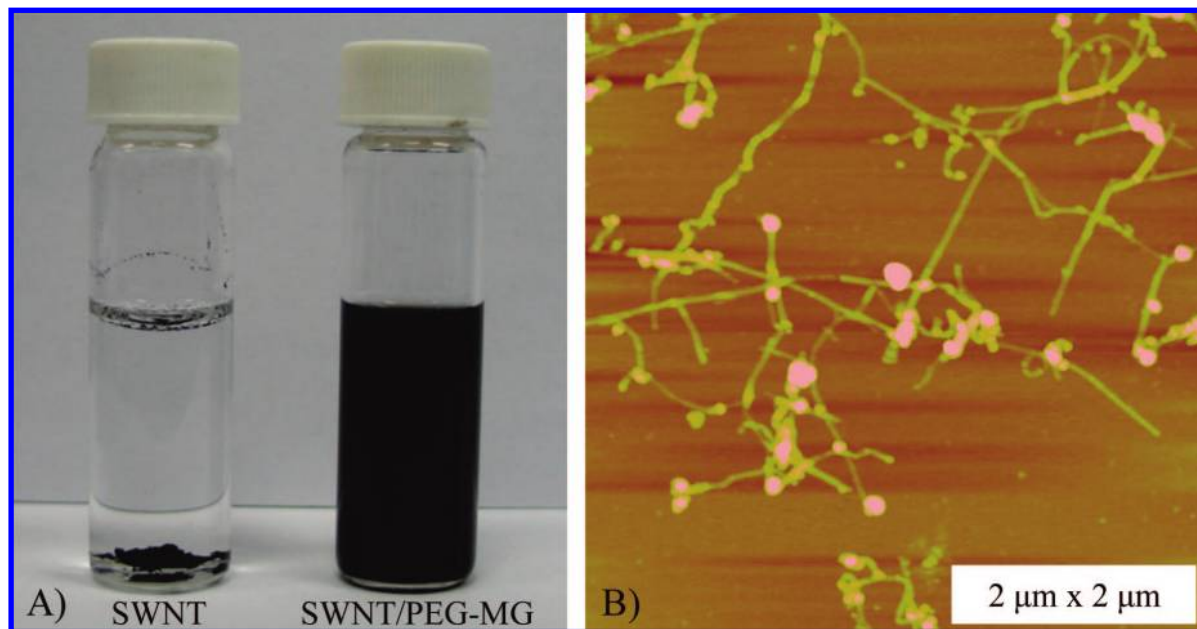
**Figure 1.** (A) Photograph of aqueous solution of SWNTs (left) and SWNT/PEG-MG complex (right). (B) AFM image of SWNT/PEG-MG complex with a scan area of 2 $\mu$m × 2 $\mu$m.

Apart from the pH-/temperature-responsive nanotube dispersion, it is highly desirable to control the nanotube dispersion by photoexposure in a clean environment free of any additional reagent.[14,15] Recently, we have reported that a poly(ethylene glycol)-terminated malachite green derivative (PEG-MG; a triphenylmethane photochromic dye that generates positive charges upon photoirradiation) can reversibly form vesicles and disassemble upon UV exposure.[16] The combination of the $\pi-\pi$ stacking, van der Waals interaction, and hydrophobic interactions could lead to an efficient dispersion of SWNTs in a PEG-MG aqueous solution (Scheme 1). Upon UV irradiation, the malachite green group turned into a cation (MG$^+$), leading to a significantly reduced or even eliminated $\pi-\pi$ stacking interaction between the malachite green group and SWNTs. Consequently, the predispersed SWNTs underwent through a reaggregation process, providing a new way to control the dispersion or aggregation of SWNTs by photoirradiation.

## 2. Experimental Section

**Materials.** SWNTs were kindly provided by Prof. Xuming Xie (Department of Chemical Engineering, Tsinghua University). The UV-responsive PEG-MG ($M_n \approx 2456$ g/mol, $n \approx 47$) was synthesized according to previously published procedures.[16] All other chemicals were analytical-grade reagents and used as received. Deionized water was used for all aqueous solutions.

**Sample Preparation and Characterization.** SWNT/PEG-MG complexes were prepared by sonication of 1.2 mg of SWNTs in 5 mL of 2.30 mg/mL PEG-MG aqueous solution in the dark for 3 h in an ice−water bath. The color of the solution changed from colorless to black during the sonication, indicating that SWNTs were dispersed in the aqueous solution of PEG-MG. The resultant dark suspension was then centrifuged at $1.6 \times 10^4$ rpm for 5 h to remove insoluble SWNTs, if any. The supernatant was subsequently dialyzed (7000 Da MWCO, Solarbio) over 2 weeks to ensure a complete removal of unbound PEG-MG chains.

Atomic force microscopy (AFM) images were taken at room temperature in air tapping mode on a commercial instrument Nanoscope IV (Veeco Company, U.S.A.) using Si cantilevers

(200−300 kHz, Veeco Company, U.S.A.). Silicon wafers were purchased from Wafer Net GmbH, Germany, and treated with piranha (7:3 v:v of sulfuric acid and 30% hydrogen peroxide), and then washed with water and dried with high pure nitrogen flow to get a hydrophilic surface. The freshly prepared hydrophilic silicon wafers were incubated in the aqueous solution of SWNT/PEG-MG for 10 min and dried in air.

UV−visible/near-infrared (UV−vis−NIR) Spectra were obtained by using a Jasco V-570 UV/vis/NIR Spectrophotometer. $^1$H NMR spectra were recorded at 600 MHz on a JEOL JNM-ECA600 to verify the interaction between malachite green and SWNTs. UV−vis spectra were performed on a Hitachi U-3010 spectrophotometer. For UV−vis measurements, a concentration of 0.23 mg/mL for PEG-MG was used to achieve a suitable absorbance, as any higher concentration of PEG-MG would lead to absorbance exceeding the measurement limit. A high-pressure mercury lamp with an optical fiber with output power of 200 W was used as the UV irradiation light source. The emissive wavelength was centered on 360 nm. This UV light source was used directly, without any filters. X-ray photoelectron spectroscopy (XPS) was carried out on a PHI Quantera SXM spectrometer with an Al K$\alpha$ X-ray source. The base pressure in the XPS analysis chamber during spectral acquisition was $6.7 \times 10^{-8}$ Pa, and the substrates were silicon wafers.

## 3. Results and Discussion

We have demonstrated that SWNTs are dispersed very well in an aqueous solution of PEG-MG through simple sonication, centrifugation, and dialyses. As shown in Figure 1a, the gray solution of SWNT/PEG-MG complex is homogeneous and stable, and can stand over 1 month without significant change. As observed by AFM (Figure 1b), SWNTs are well dispersed, and the size of the SWNTs bundles is 1.5−2.3 nm in height, 15−20 nm in width, and several micrometers in length. These results indicate that the PEG-MG has a strong ability not only to keep SWNTs well-dispersed for a long time but also to dissolve such long SWNTs. To further prove the solubility of SWNTs, UV−vis−NIR spectra were employed to investigate the dispersion of SWNTs, as shown in Figure 2. There exist two bands peaked around 740.9 and 837.5 nm, respectively, which are characteristic absorptions of van Hove transitions of SWNTs. These characteristic absorptions are usually not observable

(16) Jiang, Y.; Wang, Y.; Ma, N.; Wang, Z.; Smet, M.; Zhang, X. *Langmuir* **2007**, *23*, 4029.
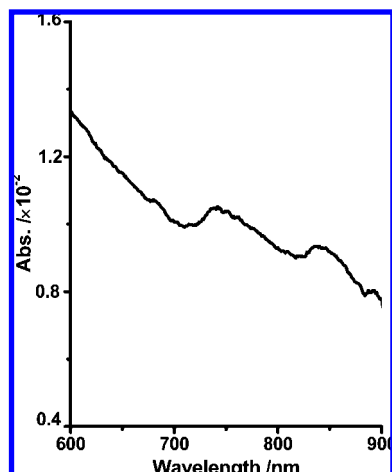
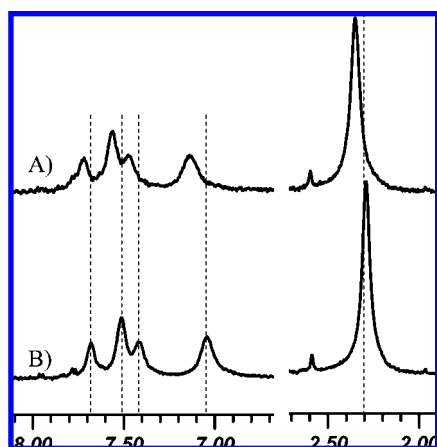**Figure 2.** UV−vis−NIR spectrum of SWNT/PEG-MG complex.



**Figure 3.** ^{1}H NMR of SWNT/PEG-MG (A) and PEG-MG (B) in $D_2O$.



**Figure 4.** XPS survey of SWNT/PEG-MG complex on the substrate of silicon.

**Table 1. XPS Peak Assignments and Atomic Composition of SWNT/PEG-MG Complex on Silicon Substrates[a]**

|        | BE/eV   | atom %  |
|--------|---------|---------|
| C 1s   | 285.46  | 71.37   |
| N 1s   | 399.41  | 1.58    |
| O 1s   | 532.18  | 27.05   |

[a] BE: binding energy.

because of the poor solubility of SWNTs. In the case of addition of PEG-MG, the appearance of characteristic absorptions of SWNTs clearly indicates the homogeneous dispersion of SWNTs in aqueous solution.[7]

As malachite green has a conjugate structure, it should exhibit a strong $\pi-\pi$ stacking interaction with SWNTs. To understand this point, we used ^{1}H NMR spectroscopy in $D_2O$ to investigate the interaction between SWNTs and PEG-MG. As shown in Figure 3, all the ^{1}H NMR signals assigned to the aromatic rings (7.04 ∼ 7.68 ppm) in PEG-MG solution shift to a significantly lower magnetic field upon complexing with SWNTs in the SWNT/PEG-MG solution (7.14 ∼ 7.72 ppm), indicating that malachite green undergoes strong $\pi-\pi$ stacking interactions with SWNTs. Furthermore, it was also noted that the ^{1}H NMR signal of hydrogen atoms in the −N(CH3)2 group at 2.29 ppm shifts to 2.35 ppm upon complexing with PEG-MG, presumably because the distance between −N(CH3)2 and SWNTs became very close as a result of the strong $\pi-\pi$ stacking between PEG-MG and SWNTs. Therefore, the above observed change in chemical shifts provides direct evidence for the strong $\pi-\pi$ stacking between PEG-MG and SWNTs in the solution.

As different lengths of PEG have different solubilities,[17] the PEG chain length has an effect on the dispersion of SWNTs. When decreasing the chain length of PEG, the solubility of PEG-MG decreases too. The low solubility of PEG-MG cannot make
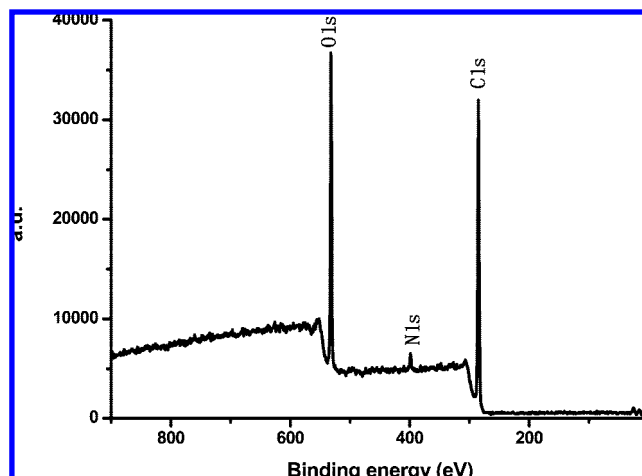
(17) Padmavathi, N. C.; Chatterji, P. R. *Langmuir* **1995**, *11*, 767.

the SWNTs disperse into water. When increasing the chain length of PEG, which also increases the solubility of PEG-MG, it is favorable for dispersing the SWNTs. So an appropriate PEG chain length ($n = 47$) is chosen to disperse the SWNTs.

How many SWNTs can be dispersed into the PEG-MG solution? To answer this question, we have employed XPS to estimate the ratio of SWNTs dispersed into PEG-MG. The XPS peaks of C 1s, N 1s, and O 1s are clearly shown in Figure 4, indicating the existence of the complex of SWNT/PEG-MG. From the integrated peak area of the signals for different elements in the XPS spectrum (Table 1), the atomic composition of the SWNT/PEG-MG on silicon surfaces could be estimated. On the basis of the content of N 1s, it is easy to calculate the content of PEG-MG in the complex of SWNT/PEG-MG. By so doing, it was estimated that about 1.32 g of SWNTs could be dispersed in 1.00 g of PEG-MG. In other words, the weight percentage of SWNTs in the complex of SWNT/PEG-MG is 56.9 wt %.

Having established the dispersion of SWNTs in PEG-MG aqueous solution, we wonder whether the dispersion of SWNTs could be controlled by UV irradiation. As shown in Figure 5, the peak absorbance characteristic of malachite green at 263.7 nm reduced with the UV irradiation time, which was accompanied by the appearance of two continuously enhanced new peaks of its cationic form at 455.4 and 610.4 nm. It should be pointed out that the ionization of PEG-MG can happen within 5 min of UV light irradiation; however, to guarantee the full saturation of reaggregation of the SWNTs, 60 min of UV irradiation is fixed for all the control experiments. After 1 h of UV irradiation, the solution of SWNT/PEG-MG turned from gray to dark green. Subsequent standing in air for several hours led to some observable (even with the naked eye) black precipitate at the bottom of the bottle. These observations indicate that disassembly of PEG-MG chains from the SWNT/PEG-MG complex through the photoreaction characteristic of malachite green is most likely (Scheme 1). This is, at least partially, supported by a control experiment where the interactions between SWNTs and PEG-MG[+] (PEG-MG cation) were investigated by ^{1}H NMR measure-
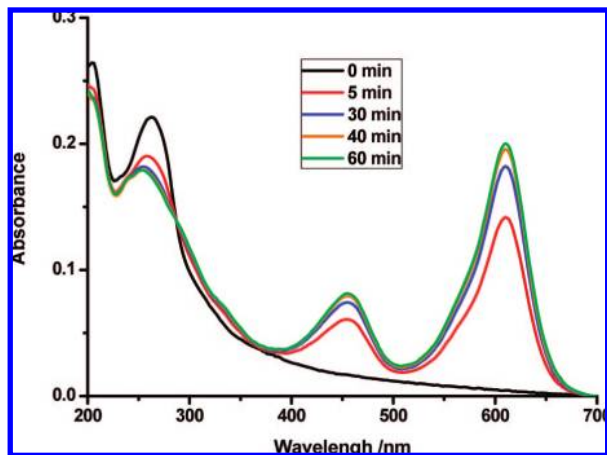
**Figure 5.** UV−vis spectra of SWNT/PEG-MG with different irradiation times.
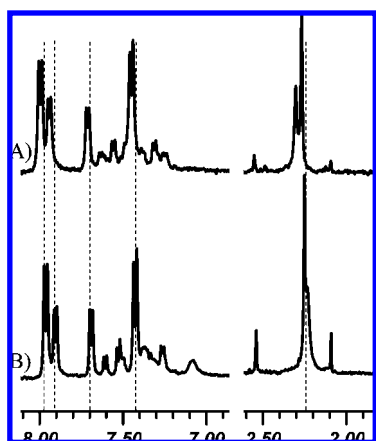


**Figure 6.** $^1$H NMR of PEG-MG$^+$ in D$_2$O with (A) and without (B) SWNTs.

ments. As shown in Figure 6, there is almost no shift for either the aromatic or N(CH$_3$)$_2$ proton peaks in the presence and absence of SWNTs, indicating no $\pi$−$\pi$ stacking interaction between SWNTs and PEG-MG$^+$. This is probably because the photochemically ionized PEG-MG$^+$ exhibits a superstrong hydrophilicity, arising from both the triphenylmethyl cation and long PEG chain,[16] which keeps the PEG-MG$^+$ free chains fully soluble in water in the control experiment and causes the split of PEG-MG$^+$ from the SWNT/PEG-MG complex upon photoirradiation.

To prove that SWNTs cannot be dispersed in a PEG-MG$^+$ aqueous solution, we applied the same sonication procedure described above to a mixture aqueous solution of newly prepared PEG-MG$^+$ and pristine SWNTs. As expected, no nanotube dispersion was observed in the PEG-MG$^+$ aqueous solution. To further confirm the photoinduced reaggregation of SWNTs, we carried out AFM imaging for the SWNTs aggregates formed after UV irradiation. Figure 7 clearly shows the aggregate structure of SWNT bundles (cf. Figure 1B). Therefore, it can be concluded that SWNTs dispersed with PEG-MG could be reaggregated
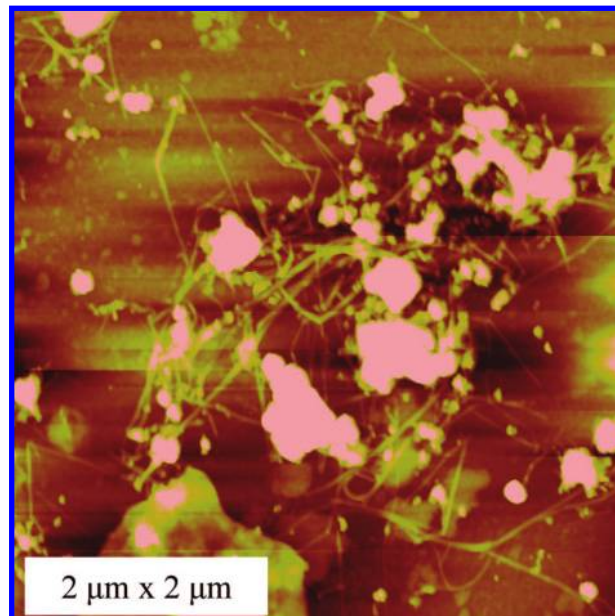


**Figure 7.** AFM image of SWNT/PEG-MG after 1 h of UV irradiation and the scan area is 2 $\mu$m × 2 $\mu$m.

simply by photoirradiation of the nanotube solution to convert the preadsorbed PEG-MG into PEG-MG$^+$.

We are wondering whether the recombination of the anion with the triphenyl methyl cation should control the aggregation of the CNTs. To answer this question, we have done the control experiments to find out the relationship between the recovery speed of PEG-MG and the concentration of the anion OH$^-$. It is found that the concentration of OH$^-$ has little effect on the recovery speed of PEG-MG. However, the recovery extent of PEG-MG increases with increasing the concentration of OH$^-$. When the molar ratio of PEG-MG and OH$^-$ is 1:1, the recovery extent of PEG-MG can be 2 times more than that in the absence of OH$^-$. However, it should be pointed out that the reversibility of the dispersion−aggregation was not that good indeed, and it can only stand one recycle probably because of the fatigue of the photo reaction.

## 4. Conclusion

We have demonstrated that SWNTs can be dispersed well in an aqueous solution of PEG-MG, and that subsequent UV irradiation can cause reaggregation of the predispersed SWNTs. The photoirradiation is know to convert PEG-MG into cationic PEG-MG$^+$, and the superhydrophilic nature of PEG-MG$^+$ is believed to be responsible for the observed reaggregation. This light-responsive SWNT/PEG-MG complex could have potential applications in many fields, including nanoelectronics, sensors, and drug and gene delivery systems.