

DOI: 10.1002/sml.200800753

Enhanced Environmental Mobility of Carbon Nanotubes in the Presence of Humic Acid and Their Removal from Aqueous Solution**

Peng Wang, Qihui Shi, Hongjun Liang, David W. Steuerman, Galen D. Stucky,* and Arturo A. Keller*

Carbon nanotubes (CNTs) are important structural blocks for the preparation of composites with unique optical, electrical, and mechanical properties, and their production is expected to increase drastically in the years to come.^[1] This may increase the risk of human and environmental exposure to CNTs.^[1d-h] CNTs are extremely hydrophobic and prone to aggregation, as they are subject to higher van der Waals forces along their length axis, and therefore are not readily dispersed in aqueous or non-aqueous solutions; this has been a major obstacle for the application of CNTs in industry.^[2] As a result, significant attention has been directed towards methods of CNT dispersion in aqueous solution. Two methods of exohedral functionalization of CNTs have been developed to disperse them; covalent^[3] and non-covalent methods.^[4] Non-covalent methods are more desirable since they incur little damage to the CNTs' intrinsic structures and properties. Dispersants tested in the laboratory for non-covalent functionalization of CNTs include surfactants, synthetic polymers, and biopolymers.^[4]

Therefore, even though some studies have shown that CNTs are biologically active and cause toxic responses in some cell cultures,^[5] CNTs are not usually considered as potential environmental toxins in the aqueous and soil environment^[6]

because of their strong hydrophobicity and propensity to form insoluble aggregates in aqueous solution. Given the increase in production of CNTs, their potential release to the environment, and possible toxicity, of particular concern are two recent separate studies^[6,7] reporting that natural organic matter (NOM), in particular its major component, humic acid (HA), can disperse CNTs in the aqueous phase. HA constitutes a major fraction of soil organic matter, and of surface water organic matter, and is the most abundant naturally occurring organic macromolecule on Earth.^[8] The ubiquitous presence of HA will facilitate the dispersion of CNTs in the environment. Estimating the risk, both to humans and to the environment, of CNTs requires an understanding of their mobility in the environment, their bioavailability, and their toxicity.^[1d-h] For this reason, an investigation on the transport of solubilized CNTs in the presence of HA within environmental media, such as soils, is necessary and important. In addition, given the possibility that CNTs will be dispersed by HA in ambient waters, a removal strategy for dispersed HA-stabilized CNTs is needed to reduce their potential environmental hazard.

Thus, the objective of this study is to investigate the environmental behavior of CNT released in powder form into aqueous media and to develop a method for removing HA-stabilized CNTs from these waters. Single-walled CNTs (SWNTs) and multi-walled CNTs (MWNTs) were considered. Although CNTs dispersed using synthetic surfactants or polymers can also be released, they are outside the scope of this study.

The SWNTs, with a diameter of 1.4 nm, were synthesized by the high-pressure decomposition of CO (HiPco process purchased from Tubes@Rice) and the MWNTs, with a diameter of 35 nm, were produced by chemical vapor deposition (CVD). Dispersions of either SWNTs or MWNTs were prepared using HA at environmentally relevant concentrations ($\leq 25 \text{ mg L}^{-1}$).^[8] Although higher HA concentrations could be considered to disperse more CNTs, the objective was to study conditions that would lead to environmental mobility. UV/Vis absorption spectroscopy was used to determine the dispersion of CNTs in aqueous solution in the presence of HA.^[6,9] The concentration of HA-coated CNTs was determined by measuring the absorbance of the solution at 600 nm and by using an extinction coefficient of $2.23 \times 10^4 \text{ cm}^2 \text{ g}^{-1}$ for SWNTs and of $2.88 \times 10^4 \text{ cm}^2 \text{ g}^{-1}$ for MWNTs (see Supporting Information).

Aromaticity, and the resulting π - π interactions, has been identified as an important parameter in CNT dispersion by various surfactants and polymers.^[4,6,7] The structure of HA is usually described as assemblies of covalently linked aromatic and aliphatic residues, in which the aromatic fraction ranges from ≈ 10 –40%. Presumably, the aromatic fractions of HA preferentially associate with CNTs via π - π interactions.^[8] HA was found to be very effective in promoting the dispersion of both SWNTs and MWNTs in aqueous solution. The strong interaction between CNTs and HA molecules was demonstrated by Liu et al.^[7] through Raman spectroscopy.

Sonicated a mixture of CNTs in an aqueous HA solution, followed by centrifugation to remove undispersed CNTs, resulted in dark-colored CNT suspensions (Figure S1 in the

[*] Prof. G. D. Stucky, Q. H. Shi, Dr. H. J. Liang
Department of Chemistry and Biochemistry
University of California
Santa Barbara, CA 93106 (USA)
E-mail: stucky@chem.ucsb.edu

Prof. A. A. Keller, Dr. P. Wang
Bren School of Environmental Science and Management
University of California
Santa Barbara, CA 93106 (USA)
E-mail: keller@bren.ucsb.edu

Prof. D. W. Steuerman
Department of Chemistry
The University of Victoria
PO Box 3065
Victoria BC V8W3V6 (Canada)

[**] P. W. and Q. H. S. contributed equally to this work. This work was partially supported by the University of California Lead Campus for Nanotoxicology Training and Research, funded by the University of California Toxic Substances Research & Training Program (UC TSR&TP) and in part by the NASA University Research, Engineering and Technology Institute on Bio Inspired Materials (BIMat) under award no. NCC-1-02037.

Supporting Information is available on the WWW under <http://www.small-journal.com> or from the author.

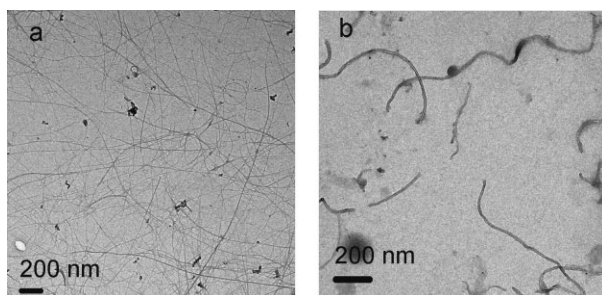


Figure 1. TEM images of HA-coated a) SWNTs and b) MWNTs.

Supporting Information), which were very stable. No significant phase separation or aggregation of CNTs was observed, even after one month. Transmission electron microscopy (TEM) was used to visualize the structure of CNTs dispersed in the HA solution. As seen in Figure 1, SWNTs exfoliated into thin bundles or individual tubes at an HA concentration of 25 mg L^{-1} , while MWNTs were completely isolated in the HA solution. For an initial HA concentration of 25 mg L^{-1} , the concentration of HA-coated SWNTs was 53 mg L^{-1} , and 36 mg L^{-1} for MWNTs. Although the toxicology of CNTs is still under study, these concentrations are high enough to raise some concern, and warrant developing means for removing HA-coated CNTs from solution. As compared to surfactant- or polymer-wrapped CNTs, in which very high surfactant or polymer concentrations are usually involved,^[7,10] HA exhibits an ability to disperse CNTs even at low HA concentrations.

Humic acids are amphiphilic molecules, containing $\approx 3.6 \text{ mol kg}^{-1}$ carboxylic groups, which can almost fully dissociate at the experimental pH value of around 7.^[8] Zeta-potential measurements showed highly negative surface charges of HA-dispersed CNTs (Figure 2a, and Figure S3 in the Supporting Information), which indicates that HA molecules coat CNTs, turning them electrostatically repulsive and therefore stable in aqueous solution. Pristine CNTs have little or no charge at neutral pH values, which explains their inability to form a stable suspension in water.^[11] In light of the negative surface charges of HA-coated CNTs, their transport within natural porous media, such as soils, can be expected because these media are usually negatively charged. The ionic strength of natural systems may vary considerably and will affect particle aggregation and transport. For this reason, potassium chloride (KCl) and calcium chloride (CaCl_2) were used as background electrolytes and their concentrations were adjusted to be environmentally relevant. The zeta potential of HA-coated CNTs became less negative with increasing bulk KCl or CaCl_2 concentration (see Figure 2a, and Figure S3 in the Supporting Information), with a local minimum at a KCl concentration of 0.01 M. This anomalous behavior of the zeta potential has also been observed for other nanoparticles (e.g., latex nanoparticles) in the presence of monovalent cations.^[12a] The HA-coated CNTs had a higher zeta potential with CaCl_2 in the bulk solution than with KCl at the same molarity, which is attributable to the higher charge density of Ca^{2+} , resulting in a significant decrease in the net effective negative charge of the HA molecules.^[13] CNTs are thus dispersible in aqueous HA

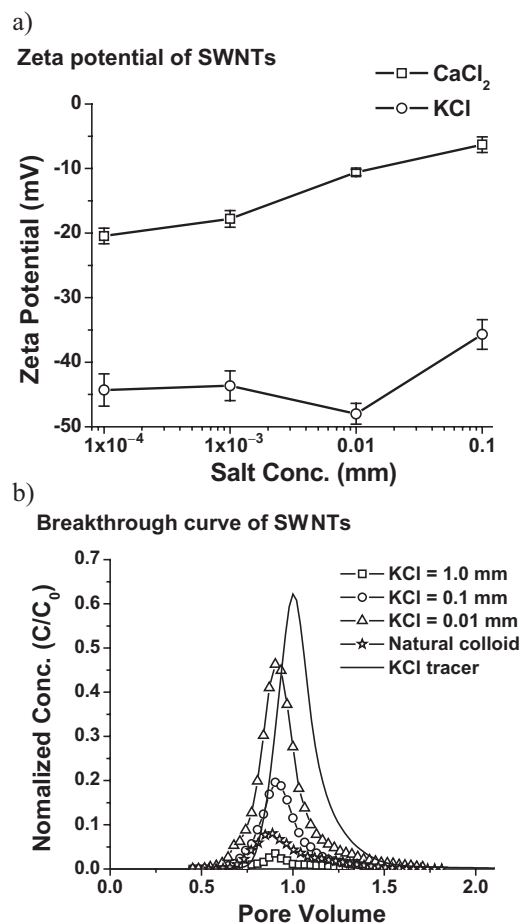


Figure 2. a) Zeta-potential and b) breakthrough curves of HA-coated SWNTs in porous media. The KCl concentration for the natural colloids experiment in Figure 2b is 0.10 mM.

solutions within a wide range of ionic strengths. It is worth mentioning that we used the Smoluchowski model for zeta-potential determination even though it is rigorously valid only for spherical particles (see Supporting Information). O'Brien and Ward have extended the Smoluchowski model to higher-aspect-ratio structures, taking into account the change in the ion densities induced by the applied electric field.^[12b] Depending on the magnitude of the zeta potential, the spherical Smoluchowski approximation may overestimate the actual zeta-potential by up to 20%.

In addition to the stabilization of CNTs in surface waters, it is important to understand their transport in porous media, such as soils or filter media. The transport of small particles has been discussed in detail in the colloid-transport literature.^[14] Recent work has investigated the transport of nanoparticles ranging from one to one hundred nm in size, with an emphasis on the effect of velocity and ionic strength on the transport of various nanoparticles.^[15] The setup of the present column transport experiment is presented in Figure S4, Supporting Information. A constant flow rate (1.0 mL min^{-1} or 7.7 m day^{-1}) was employed. For comparison, the transport of natural soil colloids ($\approx 700 \text{ nm}$) was also investigated. Figure 2b and Figure S5, Supporting Information, present

the breakthrough curves of HA-coated CNTs and natural soil colloids along with a KCl or CaCl₂ tracer. The percent particle recovery is calculated as the ratio between the total mass of the particles recovered at the end of the column and the initial mass of the particles injected into the column, at different bulk KCl or CaCl₂ concentrations (see Table S1 in Supporting Information). At low ionic strength particle recovery was high (e.g., >70% for KCl concentration at 0.01 mM). Given their small size, straining of nanoparticles is insignificant. Straining is defined as particle deposition at grain-grain junctions.^[16] It is more likely that the deposition occurs on soil grain surfaces.^[17]

The deposition rate coefficients (*k*) for HA-coated CNTs and the natural soil colloids were calculated using the following formula^[18] and are presented in Table 1;

$$k = -\frac{1}{t_p} \ln \left[\frac{q}{N_0} \int_0^{t_f} C(t) dt \right] \quad (1)$$

where *t_p* is the average travel time of the HA-coated CNTs through the column, *C(t)* is the concentration of HA-coated CNTs in solution; *q* is the volumetric flow rate; *N₀* is the total amount of HA-wrapped CNTs injected into the column, and *t_f* is the time at which the particle pulse has completely moved through the column. The term in brackets in Equation (1) corresponds to the percent recovery of the particles presented in Table S1. The maximum travel distance, defined by the distance at which 99.9% of the particles have been removed from the solution, can be expressed by:^[18c]

$$L_{\max} = -\frac{v}{k} \ln(C/C_0) \quad (2)$$

where *v* is the water flow rate (m h⁻¹) and *C/C₀* = 0.001. The calculated *L_{max}* is presented in Table 1 along with the calculated *k*.

As can be seen, even with a non-spherical, rod-like shape, the HA-coated CNTs showed considerably higher breakthrough (≈2×) and lower deposition rates than the natural soil colloids (Table 1, and Table S1, Supporting Information), indicating higher mobility within porous media. As a result, the *L_{max}* of the HA-wrapped CNTs were significantly greater than the natural soil colloids. The particle recovery, deposition rate coefficient (*k*), and maximum travel distance (*L_{max}*) of SWNTs and MWNTs did not show significant difference, presumably because of their relatively similar diameters

relative to the large pore sizes of the medium. The breakthrough of the HA-coated CNTs and the natural soil colloids occurred earlier than the solute tracer (e.g., KCl) which can be attributed to charge and size exclusion. Earlier work in our lab demonstrated that particles tend to stay within central flow lines within pore spaces, where the flow rate is high, resulting in fast transport and thus earlier breakthrough.^[19] The recovery of HA-coated CNTs was much lower in the presence of CaCl₂ than KCl because of the higher efficiency of Ca²⁺ in neutralizing the negative surface charges of the HA-coated CNTs. Furthermore, particle recovery, *k* and *L_{max}* are strong functions of bulk ionic strength because the deposition of the colloids onto the soil grains increases with increasing ionic strength, as the electrostatic double-layer is compressed.^[20] Although a constant flow rate was employed in this study, previous colloid studies indicate that a higher flow rate would increase the mobility of the HA-coated CNTs.^[21]

While the HA-coated CNTs were transported through the porous media, unbound HA in aqueous solution was completely adsorbed on the porous medium, indicated by the lack of breakthrough of pure HA solution at the same concentration. The solution with HA-coated CNTs that passed through the column was stable for 4 weeks, even without free HA in the bulk solution, suggesting a strong interaction between HA molecules and CNTs, and that once coated with HA, HA-coated CNTs may remain stable even if there is no HA present along their path in the aqueous phase. This also supports the hypothesis that the adsorption of the HA onto the CNTs is mainly via site-specific π-π interactions and that adsorption via non site-specific interactions, such as entropy driven hydrophobic adsorption, is not significant.

The transport of CNTs in the presence of HA can be summarized as follows. CNTs remain stable in aqueous solutions once coated by HA, and mobile within porous media. Even though the HA-coated CNTs deposited onto the porous medium to a significant extent under high bulk ionic strength, under transient environmental conditions (e.g., precipitation, irrigation) the deposited HA-coated CNTs might detach from the soil surfaces and transport further. Thus, HA-coated CNTs would be expected to transport longer distances, potentially placing drinking-water supplies at risk.

To remove the HA-coated CNTs from aqueous solution, one can reduce the system pH to the point of zero charge (PZC) of the HA-coated CNTs or increase the ionic strength to destabilize the HA-coated CNTs and cause them to

Table 1. Deposition-rate coefficient (*k*) (h⁻¹) and maximum travel distance (*L_{max}*) (m) of HA-wrapped CNTs and natural colloids.

Ionic strength (mM)		0.01		0.10		1.00		10.00	
		KCl	CaCl ₂	KCl	CaCl ₂	KCl	CaCl ₂	KCl	CaCl ₂
SWNT	<i>k</i>	0.6	2.1	2.2	4.7	5.7	9.3	8.5	20.5 ^[a]
	<i>L_{max}</i>	4.0	1.0	1.0	0.5	0.4	0.2	0.3	0.1
MWNT	<i>k</i>	0.8	2.0	2.3	4.8	5.3	10.0	9.3	20.5 ^[a]
	<i>L_{max}</i>	2.8	1.1	1.0	0.5	0.4	0.2	0.2	0.1
Natural colloids	<i>k</i>	2.1	3.4	4.0	6.6	6.9	10.7	20.5 ^[a]	20.5 ^[a]
	<i>L_{max}</i>	1.1	0.7	0.6	0.3	0.3	0.2	0.1	0.1

[a] To avoid undesirably high numbers generated by the Equation 1 at low percent recovery of the particles (<0.1%), the *k* was calculated by setting the particle percent recovery to be 0.1% when it was below 0.1%.

precipitate. However, these measures may have significantly adverse ecological effects and, more importantly, the CNT removal may only be temporary, since, as environmental conditions change, the precipitated CNTs might re-suspend. In addition, the HA-coated CNTs were found to strongly prefer to partition into the aqueous phase rather than into different organic solvents (octanol-water partitioning coefficient, K_{ow} , from $10^{2.33}$ to $10^{5.18}$), indicating a significant increase in the hydrophilicity of the CNT surface when coated with HA (Figure S6, Supporting Information). Filtration through commercial media may also not result in sufficient removal, given the small size of these particles.

As an alternative, affinity-based strategies have been widely used to enrich and separate target molecules with low concentration in bulk solutions because of their high efficiency and specificity, such as in the enrichment of phosphorylated peptides from proteolytic peptide mixtures by immobilized metal-affinity chromatography (IMAC)^[22] or metal-oxide super-paramagnetic nanoparticles,^[23] or in the removal of heavy metals from contaminated water by thiol-functionalized super-paramagnetic nanoparticles.^[24] Since HA has many hydrophilic functional groups, such as carboxylic acid, phenolic hydroxyl, and aliphatic hydroxyl, different transition metal oxides (iron oxide, titania, zirconia, etc.) can be used as adsorbents because of their strong interaction with these hydrophilic functional groups, especially the carboxylic groups. For example, the affinity between carboxylic groups and magnetite nanoparticles has been demonstrated by adsorption of acidic peptides onto magnetite nanoparticles^[23a] and thiol functionalization of magnetite nanoparticles by dimercaptosuccinic acid.^[24,25b] It is either a hydrogen-bonding interaction through the OH group (under acidic conditions) or a direct Fe–carboxylate linkage (at more alkaline pH values in this study).^[26]

To increase the removal of HA-coated CNTs, a new method combining affinity-nanoparticle adsorption with magnetic separation was developed. The uptake process occurs via external surface adsorption, resulting in a very short adsorption time. The separation of the affinity nanoparticles from treated solutions can be achieved via an external magnetic field. In this study, we synthesized ≈ 200 nm magnetite (Fe_3O_4) nanoparticles (Fe-NPs) and ≈ 80 nm $\gamma\text{-Fe}_2\text{O}_3@SiO_2@TiO_2$ core/shell super-paramagnetic nanoparticles (Ti-NPs). The Fe-NPs were synthesized according to Deng et al.,^[25a] and the Ti-NPs were synthesized by a sol-gel-based coating strategy of titania on $\gamma\text{-Fe}_2\text{O}_3@SiO_2$ nanoparticles (see Supporting Information). Figure 3a shows HA-coated MWNTs with adsorbed Fe-NPs that have been separated from solution via an external magnetic field. Scanning electron microscopy (SEM) showed that MWNTs were adsorbed and enriched on the surface of the Fe-NPs (Figure 3b and c). The adsorption kinetics of HA-coated CNTs by Fe-NPs and Ti-NPs are presented in Figure 3d. It can be seen that the rate of CNT uptake was initially quite high, followed by a much slower subsequent removal rate leading gradually to an equilibrium condition. About 88% of the SWNTs and 85% of the MWNTs were removed by Fe-NPs during the first 5 min of the reaction, while only a very small part of the additional removal occurred during the following

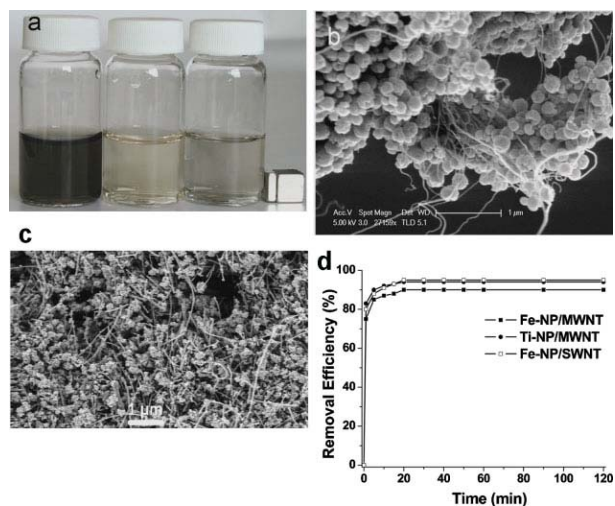


Figure 3. a) Left, HA-coated MWNT suspension (MWNT = 35 mg L^{-1} and initial HA = 25 mg L^{-1}); middle, HA only (25 mg L^{-1}); right, HA-coated MWNT separated from solution by an external magnetic field; b) SEM image of the HA-coated MWNT adsorbed onto Fe-NPs; c) SEM image of the HA-coated MWNT adsorbed onto Ti-NPs; d) kinetics of adsorption of HA-coated CNTs by Fe-NPs and Ti-NPs. The amount of Fe-NPs and Ti-NPs used to adsorb CNTs was 0.1 g and the concentration of HA-coated CNT solutions was 35 mg L^{-1} .

15 min of contact. Rapid adsorption of CNT onto the magnetic nanoparticles is necessary for an efficient removal process. At equilibrium, the removal efficiency for SWNTs and MWNTs was found to be 95% and 90%, respectively. Ti-NPs showed higher removal efficiency than Fe-NP, for which 90% of MWNTs were removed in the first 5 min and the removal efficiency at equilibrium was found to be 94%. The increased removal efficiency can be attributed to a higher surface area resulting from a smaller particle size. Thus, magnetic metal-oxide nanoparticles can be used for the removal of HA-coated CNTs from ambient water and drinking water. The utilization of this technology in real-world applications deserves more research attention to optimize operating conditions.

In summary, HA-coated CNTs were found to be stable in aqueous solution, and readily transport through porous media. Use of magnetic metal-oxide nanoparticles to adsorb the HA-coated CNTs can be a permanent and efficient removal approach.

Experimental Section

Highly purified SWNTs, 1.4 nm in diameter, were synthesized by using the HiPco process. MWNTs were produced by the chemical vapor deposition (CVD) method, and were 35 ± 10 nm in diameter. HA with a purity of $>99\%$ was purchased from MP Biomedicals, Inc. The HA was composed of 49.5 wt% carbon, 43.3 wt% oxygen, and 5.1 wt% hydrogen. The preparation of HA-coated CNT solutions, the column setup and the procedure of the transport experiment, the synthesis of Fe_3O_4 nanoparticles (Fe-NPs) and super-paramagnetic $\gamma\text{-Fe}_2\text{O}_3@SiO_2@TiO_2$ nanoparticles (Ti-NPs), and the procedure for removing HA-coated CNTs using magnetic nanoparticles are described in detail in the Supporting Information.

Keywords:

affinity-based enrichment · carbon nanotubes · environmental effects · humic acid

- [1] a) P. M. Ajayan, *Chem. Rev.* **1999**, *99*, 1787; b) H. Dai, *Acc. Chem. Res.* **2002**, *35*, 1035; c) A. M. Thayer, *Chem. Eng. News* **2007**, *85*, 29; d) B. Nowack, T. D. Bucheli, *Environ. Pollut.* **2007**, *150*, 5; e) C. A. Poland, R. Duffin, I. Kinloch, A. Marynard, W. A. H. Wallace, A. Seaton, V. Stone, S. Brown, W. MacNee, K. Donaldson, *Nat. Nanotech.* **2008**, *3*, 423; f) J. Miyawaki, M. Yudasaka, T. Azami, Y. Kubo, S. Iijima, *ACS Nano* **2008**, *2*, 213. g) J. M. Worle-Knirs, K. Pulskamp, H. F. Krug, *Nano Lett.* **2006**, *6*, 1261. h) S. K. Manna, S. Sarkar, J. Barr, K. Wise, E. V. Barrera, O. Jejelowo, A. C. Rice-Ficht, G. T. Ramesh, *Nano Lett.* **2005**, *5*, 1676.
- [2] L. A. Girifalco, M. Hodak, R. S. Lee, *Phys. Rev. B* **2000**, *62*, 13104.
- [3] a) J. Liu, A. G. Rinzler, H. Dai, J. H. Hafner, R. K. Bradley, P. J. Boul, A. Lu, T. Iverson, K. Shelimov, C. B. Huffman, F. Rodriguez-Macias, Y.-S. Shon, T. R. Lee, D. T. Colbert, R. E. Smalley, *Science* **1998**, *280*, 1253; b) J. Chen, M. A. Hamon, H. Hu, Y. Chen, A. M. Rao, P. C. Eklund, R. C. Haddon, *Science* **1998**, *282*, 95; c) P. J. Boul, J. Liu, E. T. Mickelson, C. B. Huffman, L. M. Ericson, I. W. Chiang, K. A. Smith, D. T. Colbert, R. H. Hauge, J. L. Margrave, R. E. Smalley, *Chem. Phys. Lett.* **1999**, *310*, 367; d) J. E. Riggs, Z. Guo, D. L. Carroll, Y.-P. Sun, *J. Am. Chem. Soc.* **2000**, *122*, 5879; e) C. Dyke, J. M. Tour, *J. Am. Chem. Soc.* **2003**, *125*, 1156; f) R. Blake, Y. K. Gun'ko, J. Coleman, M. Cadek, A. Fonseca, J. B. Nagy, W. J. Blau, *J. Am. Chem. Soc.* **2004**, *126*, 10226.
- [4] a) M. J. O'Connell, S. M. Bachilo, C. B. Huffman, V. C. Moore, M. S. Strano, E. H. Haroz, K. L. Rialou, P. J. Boul, W. H. Noon, C. Kittrell, J. Ma, R. H. Hauge, R. B. Weisman, R. E. Smalley, *Science* **2002**, *297*, 593; b) A. Star, D. W. Steuerman, J. R. Heath, J. F. Stoddart, *Angew. Chem. Int. Ed.* **2002**, *41*, 2508; c) M. Zheng, A. Jagota, E. D. Semke, B. A. Kiner, R. S. McLean, R. E. R. Tassi, *Nat. Mater.* **2003**, *2*, 338; d) H. P. Li, B. Zhou, Y. Lin, L. R. Gu, W. Wang, K. A. S. Fernando, S. Kumar, L. F. Allard, Y. P. Sun, *J. Am. Chem. Soc.* **2004**, *126*, 1014; e) K. S. Chichak, A. Star, M. V. R. Altoe, J. F. Stoddart, *Small* **2005**, *1*, 452; f) Y. Maeda, M. Kanda, M. Hashimoto, T. Hasegawa, S. Kimura, Y. F. Lian, T. Wakahara, T. Akasaka, S. Kazaoui, N. Minami, T. Okazaki, Y. Hayamizu, K. Hata, J. Lu, S. Nagase, *J. Am. Chem. Soc.* **2006**, *128*, 12239; g) A. Ikeda, Y. Tanaka, K. Nobusawa, J. Kikuchi, *Langmuir* **2007**, *23*, 10913; h) M. F. Islam, E. Rojas, D. M. Bergey, A. T. Johnson, A. G. Yodh, *Nano Lett.* **2003**, *3*, 269.
- [5] a) A. A. Shvedova, V. Castranova, E. R. Kisin, D. Schwegler-Berry, A. R. Murray, V. Z. Gandelman, A. Maynard, P. Baron, *J. Toxicol. Environ. Health Part A* **2003**, *66*, 1909; b) S. K. Manna, S. Sarkar, J. Barr, K. Wise, E. V. Barrera, O. Jejelowo, A. C. Rice-Ficht, G. T. Ramesh, *Nano Lett.* **2005**, *5*, 1676; c) D. X. Cui, F. R. Tian, C. S. Ozkan, M. Want, H. J. Gao, *Toxicol. Lett.* **2005**, *155*, 73; d) A. E. Porter, M. Gass, K. Müller, J. N. Skepper, P. A. Midgley, M. Welland, *Nat. Nanotechnol.* **2007**, *2*, 713; e) G. Jia, H. Wang, L. Yan, X. Wang, R. Pei, T. Yan, Y. Zhao, X. Guo, *Environ. Sci. Technol.* **2005**, *39*, 1378; f) S. Pulskamp, S. Diabate, H. Krug, *Toxicol. Lett.* **2007**, *168*, 58.
- [6] H. Hyung, J. D. Fortner, J. B. Hughes, J. H. Kim, *Environ. Sci. Technol.* **2007**, *41*, 179.
- [7] Y. Q. Liu, L. Gao, S. Zheng, Y. Wang, J. Sun, H. Kajiura, Y. M. Li, K. Noda, *Nanotechnology* **2007**, *18*, 365702.
- [8] a) K. H. Tan, *Humic Matter in Soil and the Environment*, Marcel Dekker, New York 2003; b) M. Terashima, S. Nagao, *Chem. Lett.* **2007**, 302; c) M. Schnitzer, S. U. Khan, *Soil Organic Matter*, Elsevier, Amsterdam 1978; d) P. Quagliotto, E. Montoeri, F. Tambone, F. Adani, R. Gobetto, G. Viscardi, *Environ. Sci. Technol.* **2006**, *40*, 1686.
- [9] J. L. Bahr, E. T. Mickelson, M. J. Bronikowski, R. E. Smalley, J. M. Tour, *Chem. Commun.* **2001**, 193.
- [10] R. Shvartzman-Cohen, E. Nativ-Roth, E. Baskaran, Y. Levi-Kalishman, I. Szleifer, R. Yerushalmi-Rozen, *J. Am. Chem. Soc.* **2004**, *126*, 14850.
- [11] a) H. Hu, A. P. Yu, E. Kim, B. Zhao, M. E. Itkis, E. Bekyarova, R. C. Haddon, *J. Phys. Chem. B* **2005**, *109*, 11520; b) B. White, S. Banerjee, S. O'Brien, N. J. Turro, I. P. Herman, *J. Phys. Chem. C* **2007**, *111*, 13684.
- [12] a) M. Elimelech, C. R. O'Melia, *Colloids Surf. A* **1990**, *44*, 165; b) R. R. O'Brien, D. N. Ward, *J. Colloid Interface Sci.* **1988**, *121*, 402.
- [13] A. Amirbahman, T. M. Olson, *Colloids Surf. A* **1995**, *99*, 1.
- [14] a) M. B. McGechan, D. R. Lewis, *Biosystems Eng.* **2002**, *83*, 255; b) T. K. Sen, K. C. Khilar, *Adv. Colloid Interface Sci.* **2006**, *119*, 71; c) S. Sirivithayapakorn, A. A. Keller, *Water Resour. Res.* **2003**, *39*, 1346.
- [15] a) K. A. Dunphy Guzman, D. L. Finnegan, J. F. Banfield, *Environ. Sci. Technol.* **2006**, *40*, 7688; b) H. F. Lecoanet, J. Y. Bottero, M. R. Wiesner, *Environ. Sci. Technol.* **2004**, *38*, 5164; c) H. F. Lecoanet, M. R. Wiesner, *Environ. Sci. Technol.* **2004**, *38*, 4377.
- [16] a) S. A. Bradford, N. Toride, *J. Environ. Qual.* **2007**, *36*, 1346; b) M. Auset, A. A. Keller, *Water Resour. Res.* **2006**, *42*, W12S02, doi:10.1029/2005WR004639.
- [17] S. A. Bradford, S. R. Yates, M. Bettahar, J. Simunek, *Water Resour. Res.* **2002**, *38*, 1327.
- [18] a) R. Kretzschmar, K. Barmettler, D. Grolimund, Y. D. Yan, M. Borkovec, H. Sticher, *Water Resour. Res.* **1997**, *33*, 1129; b) R. Kretzschmar, H. Sticher, *Phys. Chem. Earth* **1997**, *23*, 133; c) R. Kretzschmar, H. Sticher, *Environ. Sci. Technol.* **1997**, *31*, 3497.
- [19] S. Sirivithayapakorn, A. A. Keller, *Water Resour. Res.* **2003**, *39*, 1109.
- [20] D. Grolimund, M. Elimelech, M. Borkovec, K. Barmettler, R. Kretzschmar, H. Sticher, *Environ. Sci. Technol.* **1998**, *32*, 3562.
- [21] M. Elimelech, J. Gregory, X. Jia, R. A. Williams, *Particle Deposition and Aggregation: Measurement, Modeling, and Simulation*, Butterworth-Heinemann, Oxford **1995**.
- [22] a) L. Andersson, J. Porath, *Anal. Biochem.* **1986**, *154*, 250; b) M. C. Posewitz, P. Tempst, *Anal. Chem.* **1999**, *71*, 2883.
- [23] a) C. T. Chen, Y. C. Chen, *Anal. Chem.* **2005**, *77*, 5912; b) C. T. Chen, W. Y. Chen, P. J. Tsai, K. Y. Chien, J. S. Yu, Y. C. Chen, *J. Proteome Res.* **2007**, *6*, 316; c) C. Y. Lo, W. Y. Chen, C. T. Chen, Y. C. Chen, *J. Proteome Res.* **2007**, *6*, 887.
- [24] W. Yantasee, C. L. Warner, T. Sangvanich, R. S. Adleman, T. G. Carter, R. J. Wiacek, G. E. Fryxell, M. G. Warner, *Environ. Sci. Technol.* **2007**, *41*, 5114.
- [25] a) H. Deng, X. L. Li, Q. Peng, X. Wang, J. P. Chen, Y. D. Li, *Angew. Chem. Int. Ed.* **2005**, *44*, 2782; b) S. H. Sun, H. Zeng, *J. Am. Chem. Soc.* **2002**, *124*, 8204; c) M. S. Toprak, B. J. McKenna, M. Mikhaylova, J. H. Waite, G. D. Stucky, *Adv. Mater.* **2007**, *19*, 1362.
- [26] A. Ulman, *An Introduction to Ultrathin Organic Films. From Langmuir-Glodgett to Self-Assembly*, Academic, San Diego, CA **1991**, pp. 239–245.

Received: May 28, 2008

Revised: July 8, 2008