

# “Colloidal Properties of Aqueous Suspensions of Acid-Treated, Multi-Walled Carbon Nanotubes”

*Environmental Science & Technology*

10/13/2008

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Submitted to: Environmental Science and Technology

June, 2008

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## Additional Experimental Details

Electrophoretic mobility measurements (Zetasizer-3000HSa Malvern Instruments) of the O-MWCNTs were measured as a function of NaCl concentration and pH using a capillary cell. In electrophoretic mobility and aggregation studies, salt solutions and Milli-Q water were filtered through a 0.2  $\mu\text{m}$  PES syringe-filter prior to use.

The surface-charge density of O-MWCNTs as a function of pH was determined by isothermally (25°C) titrating a known quantity of O-MWCNTs and solving the charge balance equation:

$$[\text{O-MWNT}]_{\text{charge}} = [\text{Cl}^-] + [\text{OH}^-] - [\text{H}^+] - [\text{Na}^+] \quad (1)$$

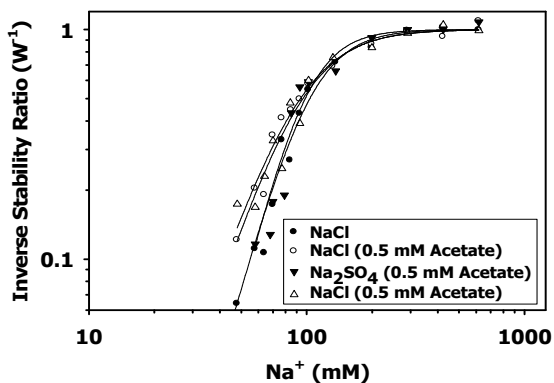
In these experiments, 8.2 mg of O-MWCNT were dispersed by sonication for 10 minutes in a known volume of Milli-Q water (98.1 mL). The suspension was then transferred to a custom titration vessel, with ports for a nitrogen sparge line, titrant delivery, and pH probe. Isothermal conditions were maintained by a temperature-controlled water circulator. Before initiating the titration sequence, the pH was set to ~4 using 0.02 M HCl. During the titration sequence, 20  $\mu\text{L}$  aliquots of 0.02 M NaOH were added. The pH was allowed to equilibrate after each NaOH aliquot. Calculated surface charge measurements were based upon a measured BET surface area of 270  $\text{m}^2/\text{g}$  (ASAP 2000, Micometrics Corp.).(18)

The length distribution and aggregation state of sonicated O-MWCNTs prior to aggregation experiments was evaluated with Atomic Force Microscopy (AFM), Pico SPM LE (Agilent). To preserve the aggregation state upon drying, colloidal suspensions (4.6 mg O-MWCNTs/L) were misted and flash deposited onto a heated, atomically smooth silicon substrate. A sufficient number of 11.4  $\mu\text{m}^2$  AFM images were then acquired to fully resolve and measure

~1,000 O-MWCNTs. Measured values were then classified into bins to display a histogram of length distribution.

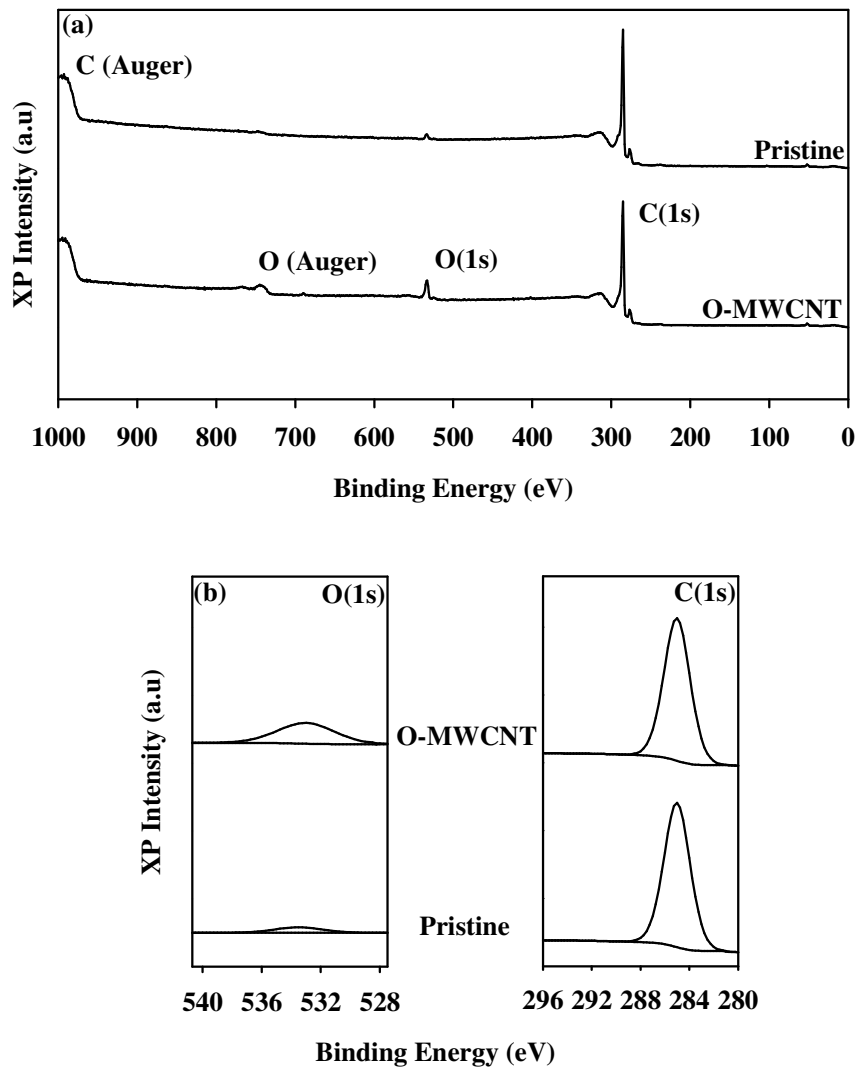
**Figure S1:** Control studies to determine the influence of acetate buffer on the colloidal stability of O-MWCNTs.

To probe the effect of the acetate buffer, separate aggregation experiments were performed in the presence and absence of 0.5 mM acetate at pH 6. Results from these studies (shown in Figure S1) revealed that the colloidal stability of oxidized MWCNTs were, within experimental error, unaffected by the presence of acetate ions in solution.



**Figure S1.** Stability profiles of O-MWCNTs with and without the 0.5 mM acetate buffer. Critical coagulation concentrations calculated for each system with respect to the sodium cation concentration were 103 mM NaCl (No Acetate), 98 mM Na<sub>2</sub>SO<sub>4</sub> (Acetate), 96 mM and 93 mM NaCl (Acetate).

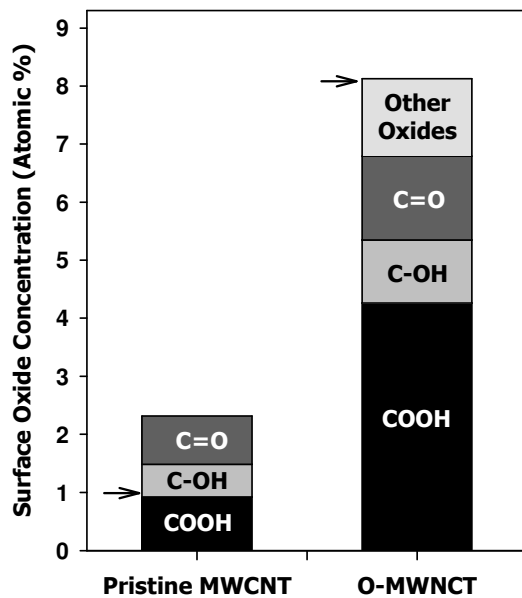
**Figure S2:** High and low resolution XP spectra for pristine and oxidized MWCNTs.



**Figure S2.** (a) Low and (b) high resolution XP scans of both the pristine and O-MWCNTs. High resolution scans of the C(1s) and O(1s) regions were used to quantify the concentration of surface oxides.

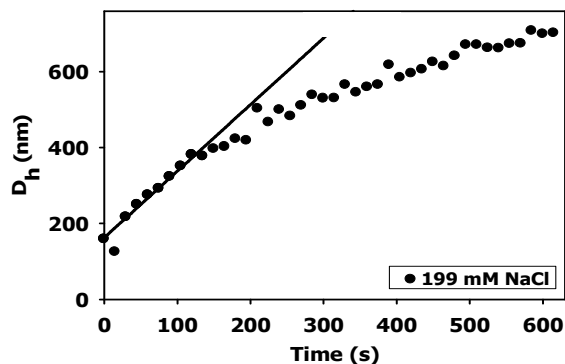
**Figure S3:** Distribution of oxygen functional groups on pristine and acid-treated multi-walled carbon nanotubes determined by chemical derivatization used in conjunction with XPS.

The arrows in Figure S3 indicate the total level of oxidation measured by XPS. For the pristine MWCNTs the slight overestimation of the oxygen concentration obtained by summing the concentration of hydroxyl, carbonyl and carboxyl groups determined by chemical derivatization can be attributed to the presence of a small (< 0.1 %), apparent F(1s) XPS signal on all samples analyzed due to imperfect background subtraction.



**Figure S3.** Total oxygen content (indicated by arrows) and functional group distribution before and after MWCNT oxidation.

**Figure S4:** Example of the initial aggregation kinetics of O-MWCNTs.



**Figure S4.** Initial aggregation profile of O-MWCNTs (0.75 mg/L) in the presence of 199 mM NaCl. Results of linear fit are shown as solid line between  $D_h \sim 150$  to 400 nm.

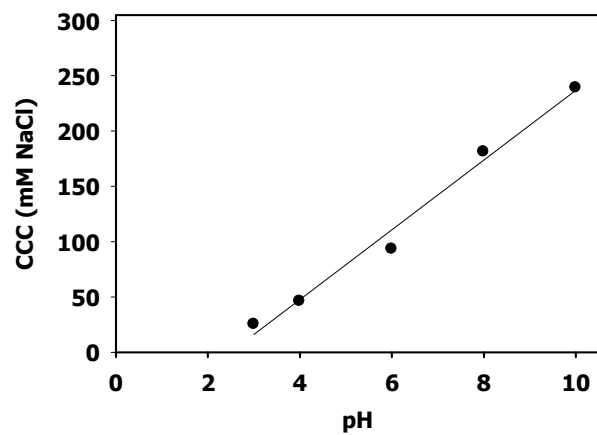
All of the results obtained in our study are consistent with the idea that changes in the intensity weighted hydrodynamic radius caused by the addition of electrolyte are due to the effects of aggregation rather than conformational changes. Our evidence for this includes the following

1. Initial particle attachment efficiencies,  $\alpha / \alpha_{\text{fast}}$  (shown in Figure 4(b)) exhibit a functional dependence on electrolyte concentration which adhere to the commonly used empirical relationship used to determine stability curves for aggregating particles, (3)(27,43)

$$\frac{k_a}{k_{a,\text{fast}}} = \frac{1}{1 + (\text{CCC} / [\text{M}^{n+}])^\beta}$$

2. The critical coagulation concentration (CCC) is proportional to  $Z^{-6}$  (where  $Z$  is the counter ion valence); a relationship which is derived for particle aggregation phenomena.
3. The trends we observe by DLS on the basis of aggregation are supported by pictorial evidence (Figure S5).

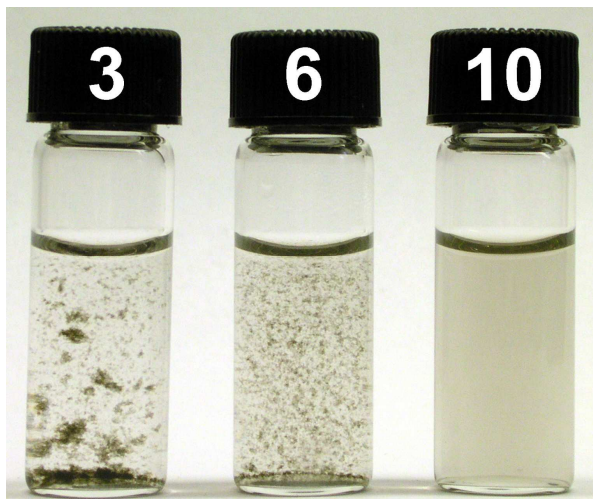
**Figure S5:** Influence of pH on the colloidal stability of O-MWCNTs



**Figure S5.** The relationship between pH and the critical coagulation concentration of O-MWCNTs.

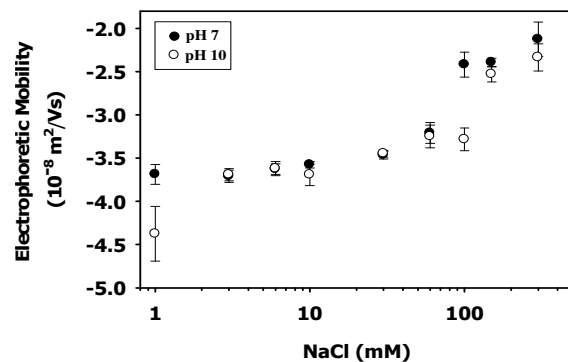


**Figure S6:** Pictorial representation of the influence of pH on the colloidal stability of O-MWCNTs.



**Figure S6.** Photograph illustrating the influence of pH (shown on the cap of each vial) on the perikinetic aggregation behavior of O-MWCNT's (4.2 mg/L). Each aggregation experiment was carried out in the presence 64 mM NaCl.

**Figure S7:** Influence of electrolyte concentration on the electrophoretic mobility of O-MWCNTs, measured at pH 7 and 10.



**Figure S7.** Electrophoretic mobility of O-MWCNTs at pH 7 and 10 measured as a function of NaCl concentration.