

# Supporting Information

## Interaction of Fullerene (C<sub>60</sub>) Nanoparticles with Silica Surfaces Coated with Humic Acid and Alginate: Measurements, Mechanisms, and Environmental Implications

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Additional Details on Materials and Methods

FIGURE S1. Electrophoretic mobilities (EPM) of fullerene nanoparticles in the presence of 1 mM KCl as a function of pH.

FIGURE S2. Representative frequency shift  $\Delta f_{(3)}$  when silica surface is pre-coated with humic acid.

FIGURE S3. Representative aggregation and deposition profiles of fullerene nanoparticles obtained through DLS and QCM, respectively, at 10 and 60 mM NaCl presented simultaneously on the same axis.

FIGURE S4. Representative aggregation profiles of fullerene nanoparticles in the presence of humic acid and alginate (both at 1 mg/L TOC) obtained through DLS.

## **Additional Details on Materials and Methods**

**Fullerene Nanoparticle Synthesis.** First, 120 mg of 99.9% pure C<sub>60</sub> powder (MER Corporation, Tucson, AZ) were dissolved in 90 mL of HPLC-grade toluene (Sigma-Aldrich, St. Louis, MO) by stirring for a few hours. A volume of 5 mL of this mixture was introduced into a solution made up of 50 mL of deionized water (Millipore) and 1.5 mL of HPLC-grade ethanol (Sigma-Aldrich, St. Louis, MO). The entire mixture was sonicated with a sonicating probe (450 Sonifier, Branson Ultrasonics Corporation, Danbury, CT) to allow for the evaporation of toluene and ethanol. Throughout this sonication process, the mixture was topped off with deionized water every 20 min to compensate for water loss by evaporation. The final solution was filtered first through a 0.45 µm cellulose-based membrane filter followed by a 0.2 µm membrane (Fisher Scientific) under vacuum. The resulting clear yellow filtrate containing the fullerene nanoparticles was collected and stored in the dark at 4 °C. Twelve such batches were synthesized and combined to form about 600 mL of fullerene nanoparticle stock suspension.

**Preparation of the Humic Acid and Alginate Stock Solutions.** The humic acid stock solution was prepared by introducing 28.3 mg of the dry Suwannee River humic acid powder (Standard II, International Humic Substances Society) into 52 mL of deionized water and stirring the solution for 2 hours. The sodium alginate stock solution was prepared by introducing 1.55 g of dry sodium alginate powder (A2158, Sigma-Aldrich, St. Louis, MO) into 480 mL of deionized water and stirring for 2 days. The solutions were then filtered through 0.22 µm cellulose acetate membranes (Corning Incorporated, Corning, NY) under vacuum. The pH of both solutions was raised to 5.5 by adding NaOH, and the solutions were subsequently stored in the dark at 4 °C. Through high-temperature oxidation, the total organic carbon (TOC) contents of the humic acid and sodium alginate stock solutions were found to be 192.7 and 885.9 mg/L, respectively.

**Modification of Silica Surface with Poly-L-lysine (PLL) Polyelectrolyte.** The PLL (93.8 kDa) was prepared in a solution made up of 10 mM N-(2-Hydroxyethyl) piperazine-N'-(2-ethanesulfonic acid) (HEPES, H4034-100G, Sigma-Aldrich, St. Louis, MO) and 100 mM NaCl filtered through a 0.22 µm cellulose acetate filter. The concentration of the PLL in the solution was 0.1 g/L. The crystal was first equilibrated by flowing 2 mL of the PLL-free solution (10 mM HEPES and 100 mM NaCl) at 0.1 mL/min across the substrate surface, which resulted in the normalized third overtone frequency attaining a constant value. Next, 2 mL of the PLL solution

was flowed across the silica surface. PLL quickly adsorbed onto the silica surface, leading to a sudden frequency shift  $\Delta f_{(3)}$  of about 7 Hz. The baseline stabilized after a few minutes, indicating the end of adsorption after the complete coverage of the silica surface with PLL. Following that, 2 mL of the HEPES solution was flowed through the module to rinse the PLL layer. Finally, the PLL layer was rinsed with the electrolyte of interest.

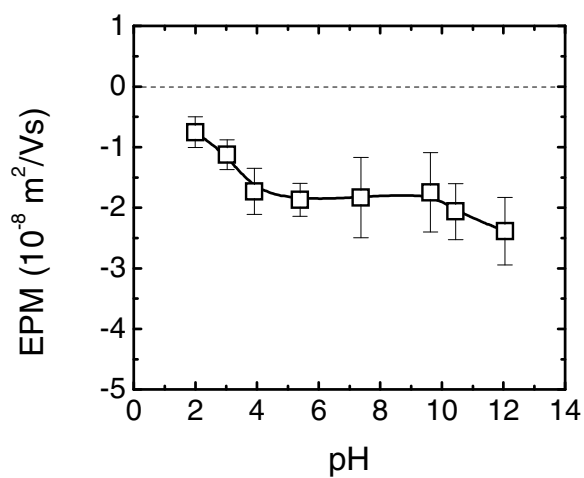


FIGURE S1. Electrophoretic mobilities (EPM) of fullerene nanoparticles in the presence of 1 mM KCl as a function of pH. Each data point represents the mean of a minimum total of 30 measurements of at least three different samples at each pH condition, and the error bars represent standard deviations. The line is meant to guide the eye. Measurements were conducted at 25 °C.

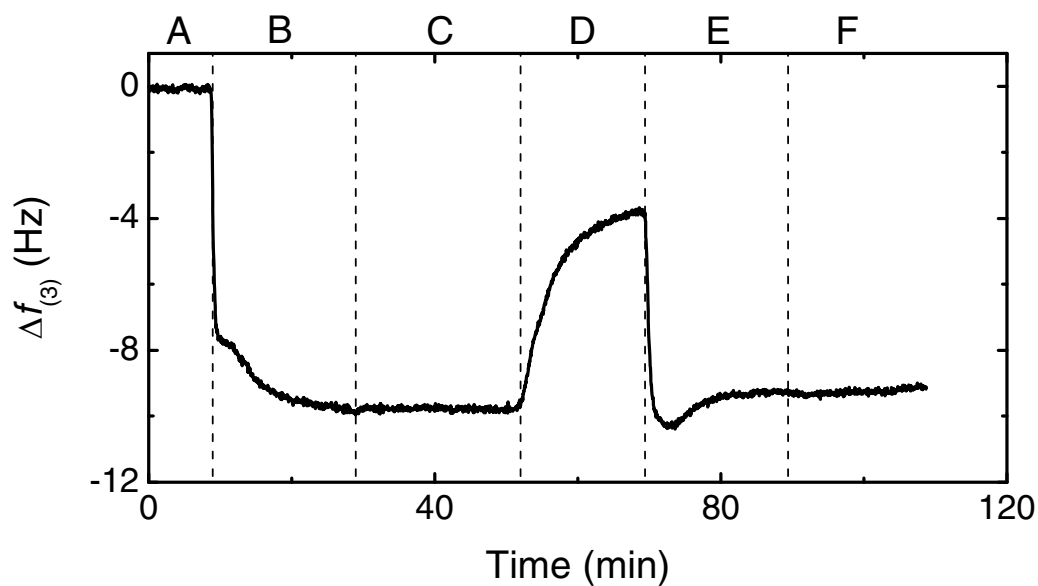


FIGURE S2. Representative frequency shift  $\Delta f_{(3)}$  when silica surface is pre-coated with humic acid. Baseline is first collected in HEPES (A), before PLL is adsorbed on the silica surface (B). The PLL layer is rinsed with HEPES (C) followed by 1 mM NaCl solution (D). Humic acid is adsorbed on the PLL layer (E), resulting in a frequency shift of about 5 Hz. The humic acid layer is then rinsed with 1 mM NaCl solution (F).

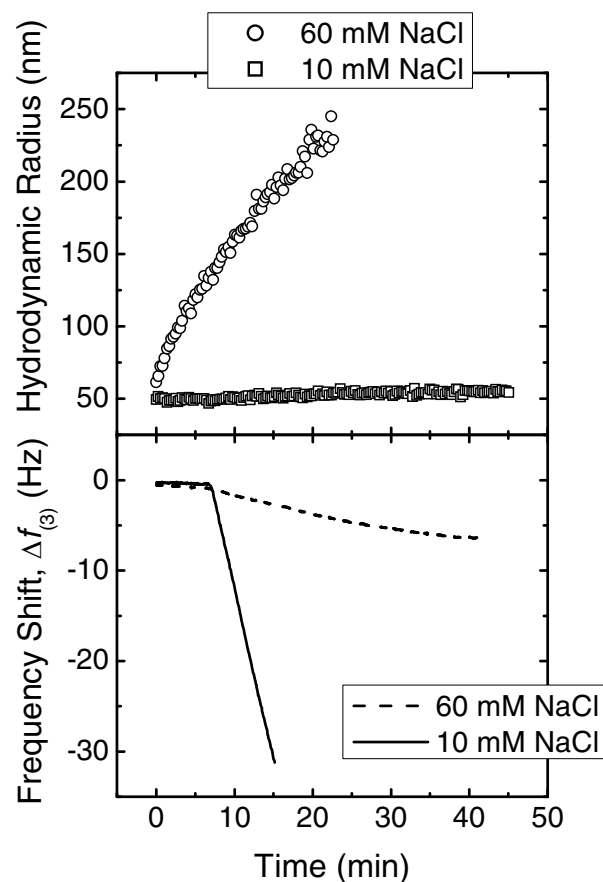


FIGURE S3. Representative aggregation and deposition profiles of fullerene nanoparticles obtained through DLS and QCM, respectively, at 10 and 60 mM NaCl presented simultaneously on the same axis. The aggregation experiments were conducted at the same fullerene nanoparticle concentrations used for the deposition experiments of 5.81 mg/L total carbon content. Deposition was conducted under favorable conditions (onto PLL-coated silica surfaces). After the introduction of electrolyte into the stable fullerene nanoparticle suspension, it took about 7 min for the suspension to reach the silica crystal when deposition occurred.

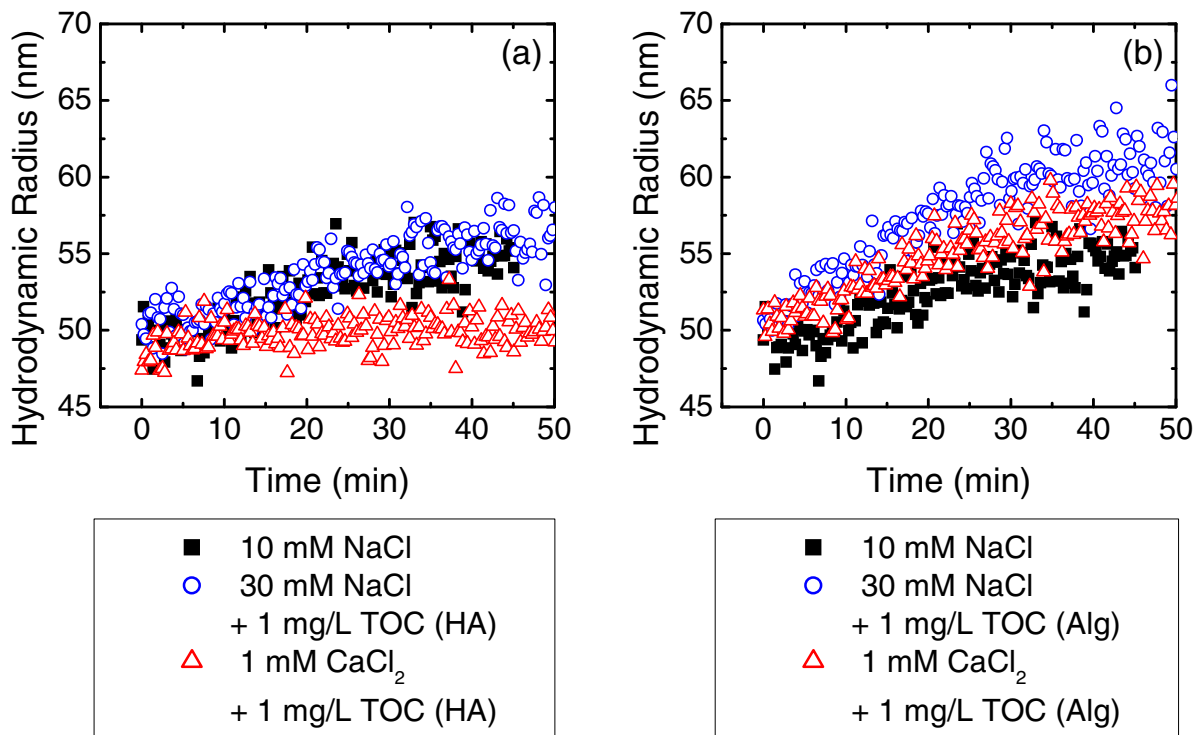


FIGURE S4. Representative aggregation profiles of fullerene nanoparticles in the presence of humic acid and alginate (both at 1 mg/L TOC) obtained through DLS. The aggregation experiments were conducted at the same fullerene nanoparticle concentrations of 5.81 mg/L total carbon content. The results show that insignificant aggregation occurs in the presence of background (a) humic acid and (b) alginate at 30 mM NaCl and 1 mM  $\text{CaCl}_2$  (compared to the case of 60 mM NaCl as presented in Figure S3). The aggregation profile obtained in the absence of macromolecules at 10 mM NaCl was included for comparison purposes. Thus, deposition attachment efficiencies under such conditions can be calculated by using the favorable deposition rate obtained at 1 mM NaCl (which is similar to the one at 10 mM NaCl, as shown in Figure 2).