Electronic Supplementary Material (ESI) for Environmental Science: Nano.

Supporting Information for

Graphene Oxides in Water: Assessing Stability as a Function of Material and Natural Organic Matter Properties

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1. Extended Experimental Methods

***Synthesis of Graphene Oxide*.** The graphene oxide nanosheets were prepared by using the modified Hummers method.[1] Graphite powders (45 μm, Sigma-Aldrich) were used as the raw materials. In this method, 50 ml of concentrated sulfuric acid (H_2SO_4) was added into a beaker containing 2 g of graphite at room temperature. The beaker was cooled to 0°C by using an ice bath. 6 g potassium permanganate ($KMnO_4$) was then slowly added to the above mixture while it was allowed to warm to room temperature. The suspension was stirred for 2 h at 35°C. After the suspension was cooled in an ice bath, it was diluted by 350 ml of deionized (DI) water. Then, hydroperoxide aqueous solution (H_2O_2, 30%) was added drop wise until the gas evolution ceased in order to reduce residual permanganate. The suspension was then filtered, thoroughly washed by DI water, and dried at room temperature for 24 h to obtain brownish graphite oxide powder. The dry graphene oxide powder was redispersed in DI water and sonicated for 2 h to get exfoliated single nanosheets. The suspension was then centrifuged at 10,000 rpm for 30 min and the supernatant was used as the precursor for crumpled graphene oxide preparation.

Characterization of GO/CGOs. The morphology and size of the GO/CGO samples were examined by transmission electron microscopy (TEM, TecnaiTM Spirit, FEI Co.) and atomic force microscopy (AFM, Veeco Nanoman). For AFM imaging, diluted samples were drop casted onto a silicon wafer substrate. Surface chemistry information regarding molecular bond and functionality were obtained with fourier transform infrared spectrometer (FTIR, Nicolette Nexus 470) and X-ray photoelectron spectroscopy (XPS, PHI 5000 VersaProbe II equipped with monochromatic Al Kα (1486.6 eV) X-ray source). The XPS peaks were fitted to a mixed function having 80% Gaussian and 20% Lorentzian characters using the software PHI Multipak, after performing a Shirley background subtraction. In the fitting procedure, the FWHM values were fixed at 1.2 ± 0.2 eV for all peaks, and the peak positions were constrained within 0.2 eV deviated from the assigned position. Calibration was carried out by alignment of the spectra with reference to the C 1s line at 284.8 eV associated with graphitic carbon. At least three measurements were performed at different samples (or locations). ζ-potential and hydrodynamic diameter (D_h) (in 40 mg/L aqueous solution) were measured with a ZetaSizer Nano ZS (Malvern Instruments, Worcestershire).

2. Relationship between surface potential and CCC.

When considering only electrostatic repulsion and vdW attraction, the relationship between CCC (n as the cation number concentration) and surface potential of particles can be approximated by the following equation:[2]

$$n = \frac{\lambda tanh^4(\frac{a\psi_0}{4})(4\pi\varepsilon_0\,\varepsilon_r)^3(k_BT)^5 48^2}{a^5(a+b)k_3^6\ e^6 A_{GWG}{}^2\pi exp(2)},$$

$$\lambda = \left[1 - \frac{1}{2k_3X_0}(1 - \exp(-2k_3X_0))\right]^2$$

Thus CCC is proportional to ζ-potential (when assume the A_{GWG} values are the same for CGOs) by:

$$n/\lambda \propto tanh^4(\frac{a\psi_0}{4})$$

Where ψ_0 is dimensionless surface potential $\psi_0 = \frac{e\Phi_0}{k_BT}$; X_0 is the dimensionless radius of the particle, $X_0 = \kappa r_0$ (r_0 is the particle radius); L is the surface-to-surface distance between two particles. The reciprocal Debye length κ is calculated by $\kappa^2 = \frac{a(a+b)ne^2}{\varepsilon_0\,\varepsilon_r\,k_BT}$, where a and b are the valences of the cation and anion of the electrolyte, ε_0 and ε_r are the permeability of a vacuum and the relative permeability of the liquid phase (water) respectively, T is the absolute temperature (298 K), e is the elementary charge (1.6×10^{-19} C), k_B is the Boltzmann constant (1.38×10^{-23} $m^2\cdot Kg\cdot s^{-2}\cdot K^{-1}$), n is the number concentration of cations in bulk phase. A_{GWG} is the Hamaker constant of the GO-water system (i.e., GO separated by water). k_3 is a parameter related to a and b, for NaCl, $k_3=1$; for $CaCl_2$ and $MgCl_2$, $k_3 \approx 1.078$.

For the above hyperbolic function $y = tanh^4(\frac{e\Phi_0}{4k_BT})$, the plot will appear as follows (Figure S1). As the shows, when the surface potential decreases from -29 to -45 mV, the function y increases from 0.006 to 0.029 (about 5 times).

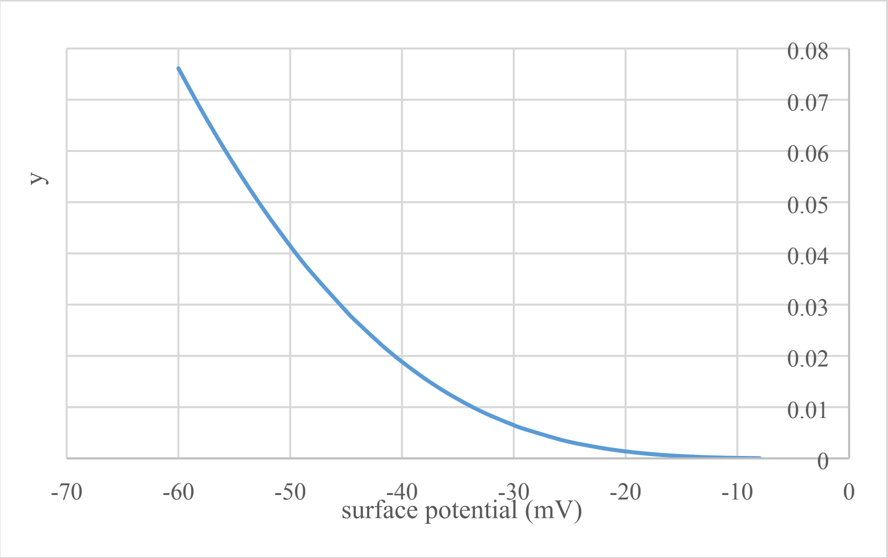

Figure S1. y as a function of surface potential Φ_0, $y = tanh^4(\frac{e\Phi_0}{4k_BT})$

References

1. Hummers, W. S.; Offeman, R. E., Preparation of Graphitic Oxide. *J Am Chem Soc* **1958,** *80*, (6), 1339.
2. Jiang, Y.; Raliya, R.; Fortner, J. D.; Biswas, P., Graphene Oxides in Water: Correlating Morphology and Surface Chemistry with Aggregation Behavior. *Environ. Sci. Technol.* **2016,** *50*, (13), 6964–6973.