Electronic Supplementary Material (ESI) for Analytical Methods.

Supporting Information for:

Direct Measurement of the pH of Aerosol Particles using Carbon Quantum Dots

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Summary: A description of the composition of the complex organic mixture as well as further images and notes on the characterization of the carbon quantum dot fluorescence probe including a quantum yield measurement and a stability assay.

Carbon Quantum Dot Fluorescence Replication

Peak maxima for the two major fluorescence peaks (λ_{ex} 350 nm and λ_{ex} 410 nm) produced by the carbon quantum dots synthesized for this study are summarized in Table S1. Carbon dots were shown to give very reproducible fluorescence across many replicate trials (a). Additionally, no significant shift was caused by the addition of inorganic or organic components (b).

Table S1. Peak Maxima for Carbon Quantum Dot Fluorescence Replicate Trials and with Organic and Inorganic Components

	Sample	λ_{max} (λ_{ex} 350 nm)	λ_{max} (λ_{ex} 410 nm)	
a	CQD replicate synthesis 1	461.94 nm	518.05 nm	
	CQD replicate synthesis 2	462.98 nm	517.01 nm	
	CQD replicate synthesis 3	461.94 nm	518.05 nm	
	CQD replicate synthesis 4	464.02 nm	520.00 nm	
	CQD replicate synthesis 5	465.97 nm	518.95 nm	
	CQD replicate synthesis 6	464.02 nm	522.98 nm	
		463.48 nm ± 1.53 nm	519.17 nm ± 2.12 nm	Avg
b	CQD + HCl (pH 3)	465.07 nm	524.02 nm	
	CQD + H_2SO_4 (pH 1)	460.00 nm	520.00 nm	
	CQD + phosphate buffer (pH 3, 0.1M)	465.07 nm	*	
	CQD + phosphate buffer (pH 3, 0.01M)	464.02 nm	*	
	CQD + sucrose	461.94 nm	525.07 nm	
	CQD + phosphate buffer + sucrose	465.97 nm	521.94 nm	
	CQD + phosphate buffer (pH 6)	461.94 nm	522.98 nm	
	CQD + COM	462.98 nm	522.98 nm	

*fluorescence measurement not taken

Composition of the Complex Organic Mixture (COM)

The contents of the COM was adapted from Song et al. (COM-3) with modifications to component identities and quantities based on availability.[1] All reagents were of analytical grade with the highest purity available (>97%).

Table S2. Composition of complex organic mixture (COM)

Component	Relative % (by molarity)
2-methylglutaric acid	12.5
3,5-dihydroxybenzoic acid	12.5
3-hydroxybenzoic acid	6.25
3-methyladipic acid	25
levoglucosan	12.5
malic acid	12.5
malonic acid	12.5
pinolic acid	3.125
pinonic acid	3.125

Characterization of Carbon Quantum Dots

The chemical and physical characteristics of the quantum dots synthesized for this work were investigated and the findings are displayed below. Succinctly, a fluorescent nanoparticle product was confirmed to have formed via imaging and was shown to be chemically distinct from its precursors.

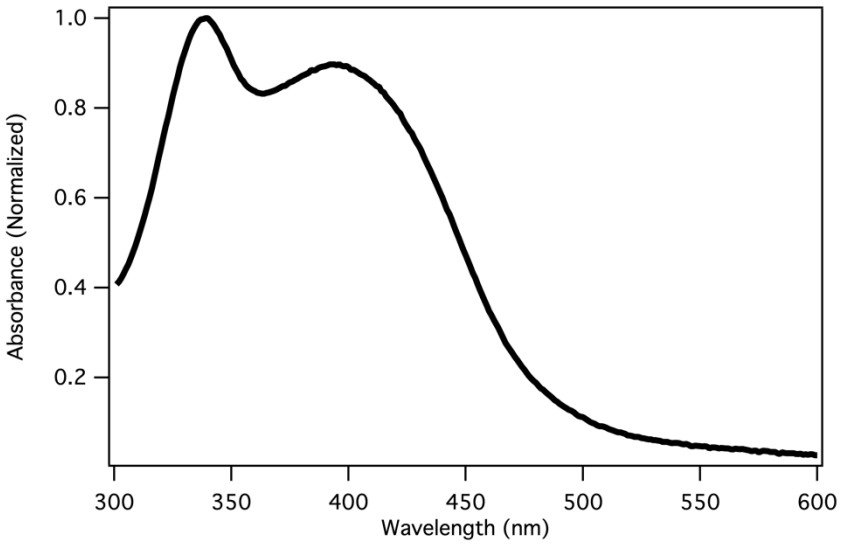

Figure S1: Absorption spectrum for the carbon quantum dot product

A representative TEM image of the synthesized carbon quantum dots on a carbon/copper support is shown in Figure S2. Carbon dots are monodisperse and have a mean diameter of 7.6nm ± 1.8nm. Inset: frequency of particle size plotted against particle diameter shows a monomodal distribution. Scale bar - 50nm.

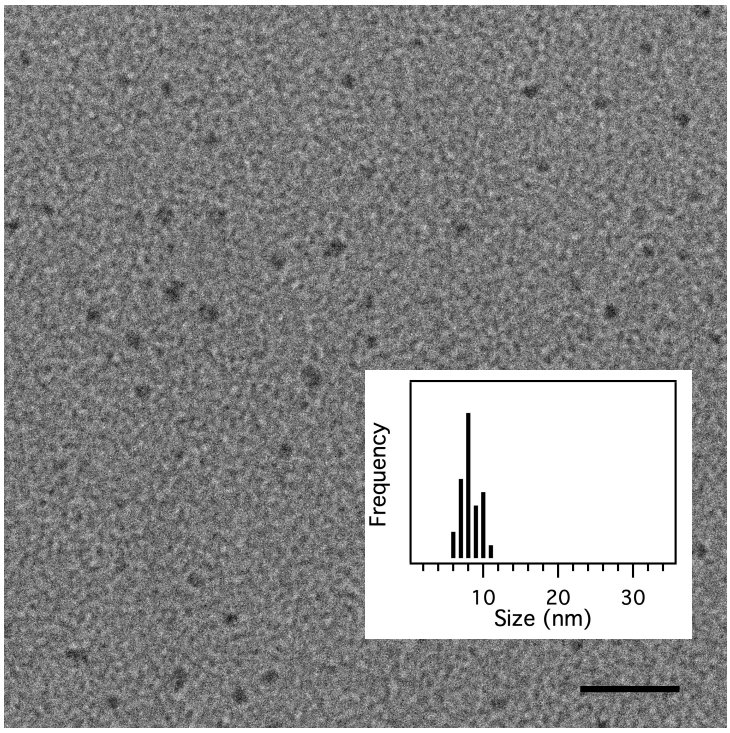

Figure S2: Representative transmission electron microscope image for carbon quantum dots

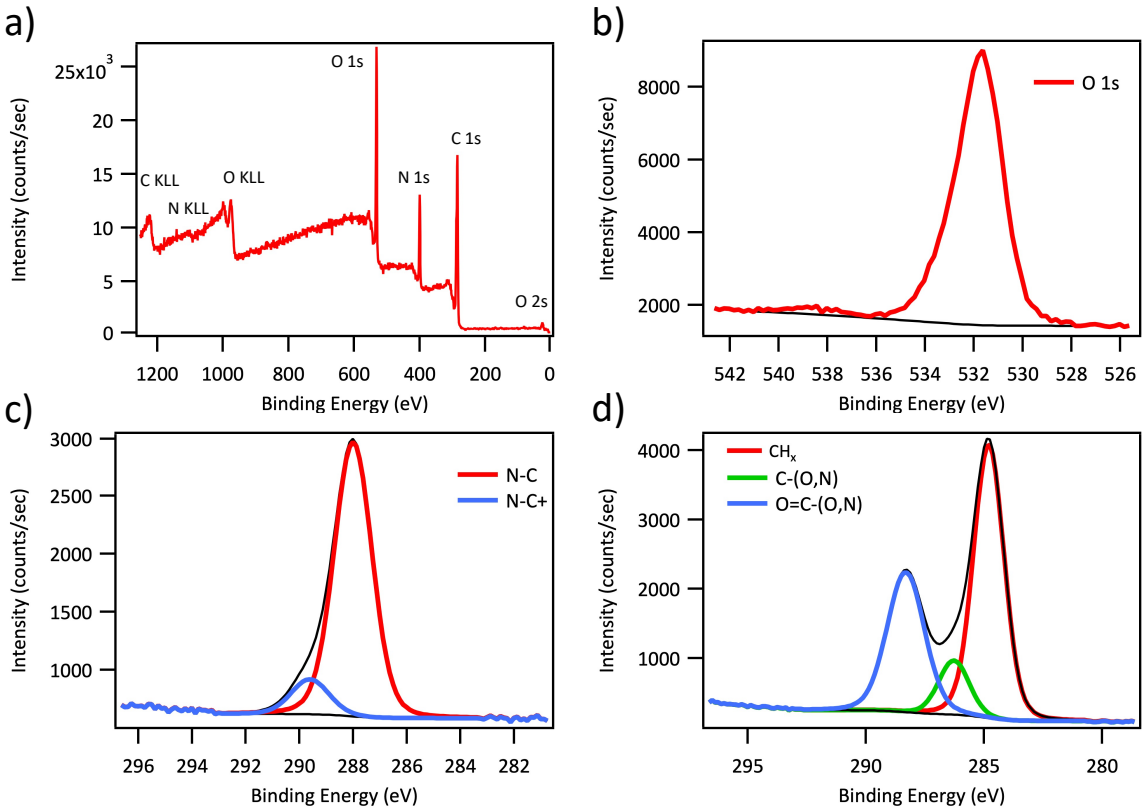

Figure S3: X-ray photoelectron spectra for carbon quantum dots

The FT-IR spectra for the carbon quantum dots (a) differs from those of the synthesis precursors (b, c).

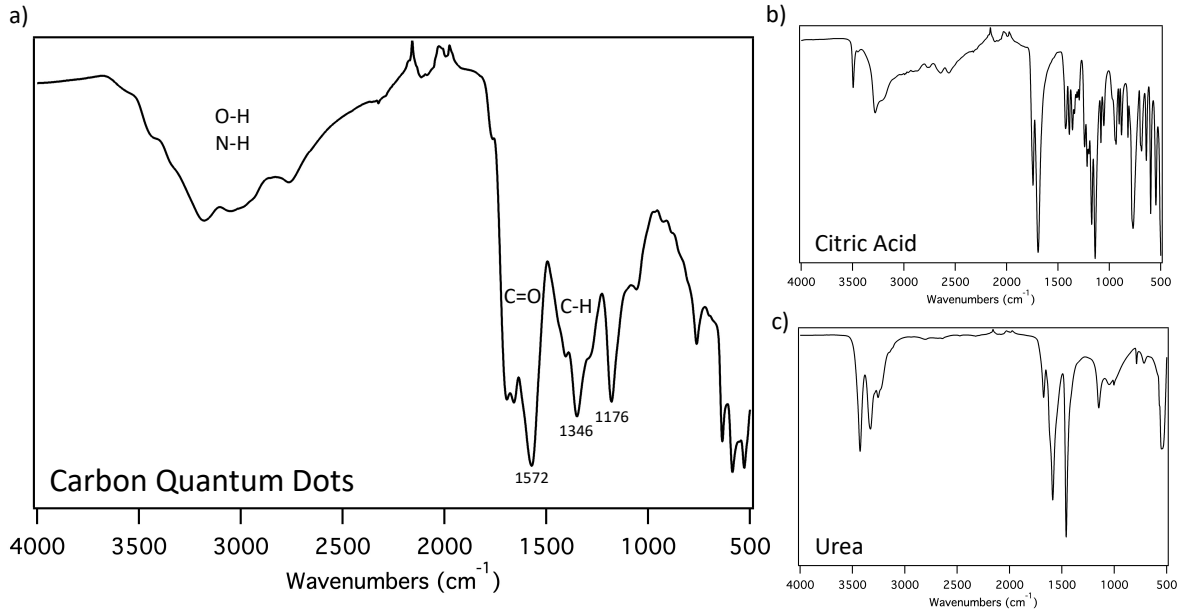

Figure S4: Fourier transform infrared spectrum for carbon quantum dots

Quantum Yield

The integrated fluorescence intensity of the emission peak at λ_{ex} 350nm vs. absorbance at 350 nm for both quinine sulfate in 0.1M H_2SO_4 and carbon quantum dots was plotted at various dilutions. The gradients for each curve were used in Equation S1 where ϕ is the quantum yield for fluorescence, *Grad* is the gradient of the plot of integrated fluorescence vs. absorbance, and η is the refractive index for each solvent. The subscript X refers to the sample of interest (carbon dots) and the subscript S refers to the standard (quinine sulfate).

(ES1) $$\phi_X = \phi_S \left(\frac{Grad_X}{Grad_S}\right)\left(\frac{\eta_X}{\eta_{ST}}\right)^2$$

The literature value for the quantum yield of quinine sulfate in 0.1M H_2SO_4 is 0.54 and the solvent for both the standard and carbon dots was water (refractive index, n=1.333).[2,3]

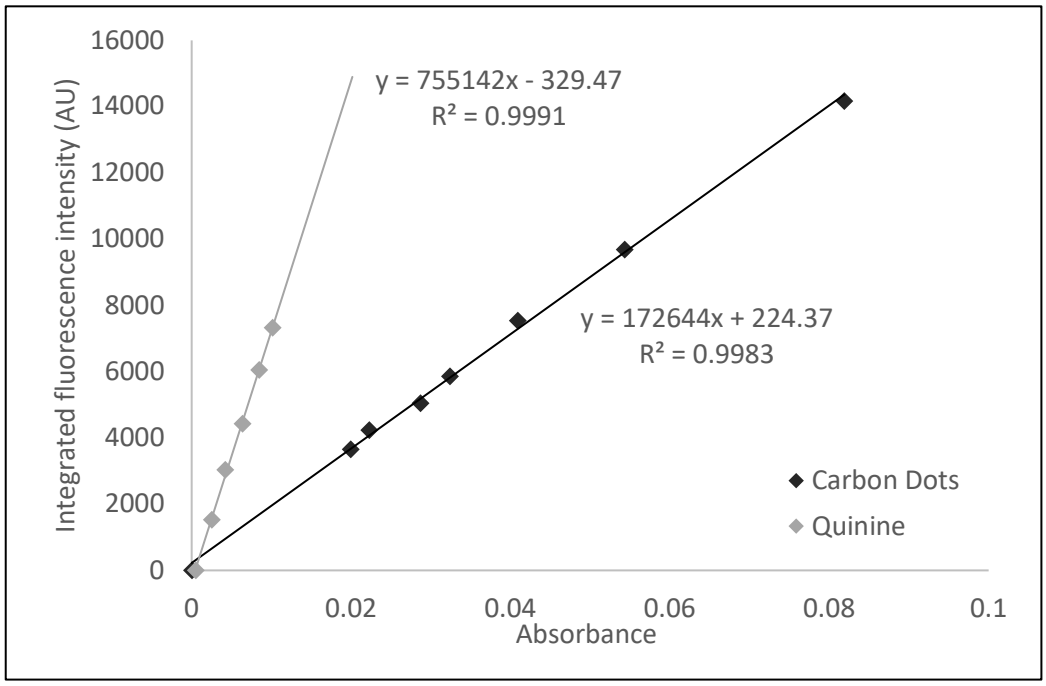

Figure S5: Integrated fluorescence intensity vs. absorbance for carbon quantum dots and quinine sulfate standard

Carbon Quantum Dot Stability

Carbon dots were stable on the time scale of months when stored in concentrate, but were found to degrade slightly during this same time period when stored under acidic conditions. Carbon quantum dot fluorescence spectra (λ_{ex} 350nm) was assessed once per week for 7 weeks at neutral pH and fluorescence intensity was found to remained constant (a). Peak height for these spectra (λ_{ex} 350nm) plotted against weeks after synthesis at neutral pH illustrates the good shelf stability for this product (b). The same plot of the peak height (λ_{ex} 350nm) vs. weeks after synthesis for samples stored under acidic conditions (pH 3) shows degradation under acidic conditions by about 15% of the original intensity (c). Carbon quantum dots stored in acidic conditions experiencing degradation of their surface or internal structure may lose surface functional sites or structural integrity leading to a decrease in fluorescence intensity.

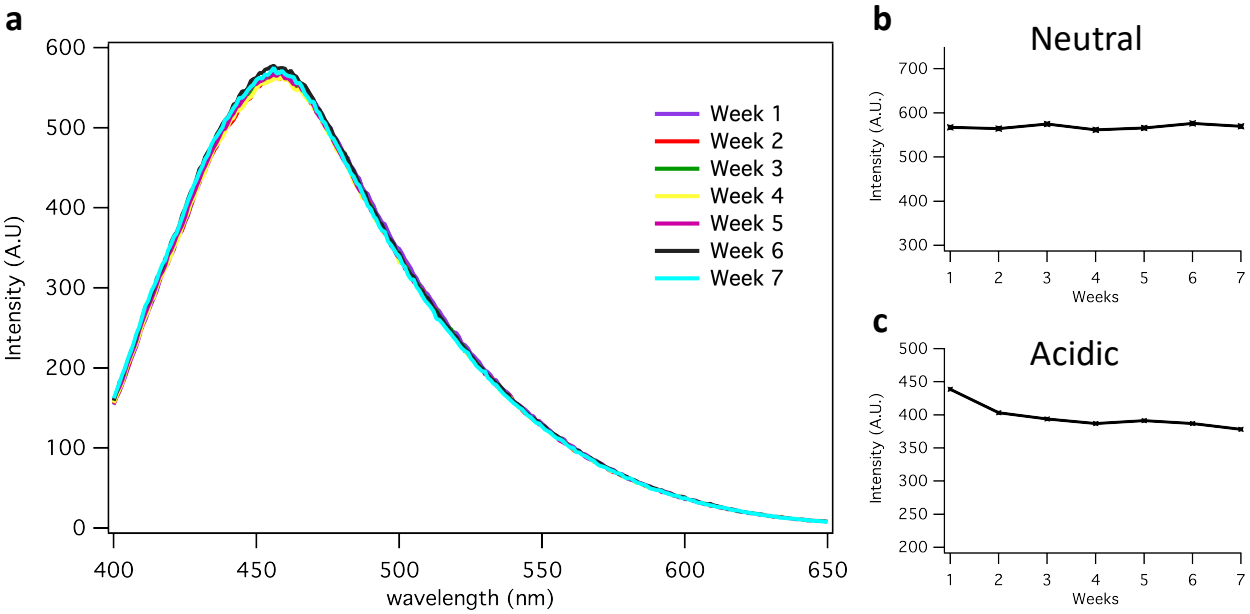

Figure S6: Carbon Dot Stability under Neutral and Acidic Conditions

References:

(1) Song, M.; Marcolli, C.; Krieger, U. K.; Zuend, A.; Peter, T. *Geophys. Res. Lett.* **2012**, *39*, 19.

(2) Stefanakis, D.; Philippidis, A.; Sygellou, L.; George, F.; Ghanotakis, D.; Anglos, D. *J. Nanoparticle Res.* **2014**, *16*.

(3) Menhuish, W. *J. Phys. Chem.* **1961**, *65*, 229–235.