This work is on a Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International (CC BY-NC-ND 4.0) license, <u>https://creativecommons.org/licenses/by-nc-nd/4.0/</u>. Access to this work was provided by the University of Maryland, Baltimore County (UMBC) ScholarWorks@UMBC digital repository on the Maryland Shared Open Access (MD-SOAR) platform.

Please provide feedback

Please support the ScholarWorks@UMBC repository by emailing <u>scholarworks-group@umbc.edu</u> and telling us what having access to this work means to you and why it's important to you. Thank you. Supporting Information for: Synthesis and bacterial toxicity of nitrogen and phosphorus codoped amorphous polymeric carbon dots

Bo Zhi^a, Miranda J. Gallagher^b, Benjamin P. Frank^b, Taeyjuana Y. Lyons^c, Tian A. Qiu^a, Joseph Da^b, Arielle C. Mensch^d, Robert J. Hamers^d, Zeev Rosenzweig^c, D. Howard Fairbrother^b, Christy L. Haynes^{a*}

a. Department of Chemistry, University of Minnesota, Minneapolis, MN 55455,

b. Department of Chemistry, The Johns Hopkins University, Baltimore, MD 21218,

c. Department of Chemistry and Biochemistry, University of Maryland, Baltimore County, MD 21250,

d. Department of Chemistry, University of Wisconsin, Madison, WI, 53706, United States.

Experimental Section

Determination of Photon Flux

The photon flux in terms of quanta/s was determined through an actinometry measurement. Potassium ferrioxalate was decomposed by the UV-B light from the photoreactors into Fe^{2+} ions. Longer exposure of the ferrioxalate to UV-B light results in a linear increase in Fe^{2+} ions. Adding o-phenanthroline buffered with sodium acetate to these solutions causes the Fe^{2+} ions to form a red colored complex with an absorption maximum at 510 nm. The presence of more Fe^{+2} corresponds to a solution with higher absorbance. In this way, measuring the absorbance allows for determination of Fe^{2+} present in the solution. Because each photon yields a single Fe^{2+} ion, the number of photons absorbed by the sample can be calculated through this technique. By plotting the absorbance of the solution at 510 nm as a function of UV-B exposure, a slope can be obtained to calculate quantum flux of the UV reaction chamber. For more details, see the supporting information of Bitter et al.[1]



Fig. S1. Photographs of solid (a) CACDs and (b) MACDs.



Fig. S2. X-ray diffraction patterns for (a) CACDs and (b) MACDs.



Fig. S3. AFM images of (a) CACDs and (b) MACDS, particle height distribution of (c) CACDs and (d) MACDs.



Fig. S4. Excitation emission matrices (EEM) of (a) CACDs, (b) MACDs, (c) CA-P-CDs-4 and (d) MA-P-CDs-4.



Fig. S5. FTIR spectra of (a) CACDs and (b) MACDs as well as spectral band assignments (oop means out of plane bending).^[2]



Fig. S6. ¹³C NMR spectra of (a) CA-CDs (b) CA-P-CDs-4, (c) MA-CDs and (d) MA-P-CDs-4.

XPS Surface Area Report	%С	%O	%N	%P
CACDs (N=4)	62 ± 3	24.3 ± 1.6	13.6 ± 1.6	0.02 ± 0.03
CA-P-CDs-1	64.8	18.5	16.7	0.0
CA-P-CDs-2	62.7	22.0	14.2	1.1
CA-P-CDs-3	63.1	22.2	13.8	0.9
CA-P-CDs-4	61.7	24.1	11.4	2.9
MACDs (N=4)	62.6 ± 1.8	22 ± 3	15 ± 2	0.0 ± 0.0
MA-P-CDs-1	60.5	22.0	16.4	1.1
MA-P-CDs-2	58.0	23.2	17.0	1.8
MA-P-CDs-3	58.0	23.3	15.9	2.8
MA-P-CDs-4	61.2	21.5	14.9	2.4

 Table S1. XPS element analysis results of all of samples.

TEM Size Analysis Method:

The particle counting was performed in ImageJ software. Specifically, oval tools were used to measure the Feret diameter of carbon dots, as the Feret diameter measures the size of an object along a specific direction. In addition, to minimize human error and improve reproducibility, the measurement was repeated three times on different days, and more than 500 particles were included each time. Counting results were imported into OriginPro 9.0 for further statistical analysis, such as frequency counts and peak analysis. Since the values for particle size are positive, a lognormal function was applied to fit the size distribution. Thus, the data shown report the mean size and peak width (FWHM).



Fig. S7. TEM images and corresponding size distribution of (a) & (b) CA-P-CDs-1, (c) & (d) CA-P-CDs-2, (e) & (f) CA-P-CDs-3, and (g) & (h) CA-P-CDs-4 (scale bar inside: 20 nm).



Fig. S8. TEM images and corresponding size distribution of (a) & (b) MA-P-CDs-1, (c) & (d) MA-P-CDs-2, (e) & (f) MA-P-CDs-3, and (g) & (h) MA-P-CDs-4 (scale bar inside: 20 nm).

Sample Name	τ _{avg} (ns)	QY (%)	Sample Name	τ _{avg} (ns)	QY (%)
CACDs	11.17 ± 0.65	48.34	MACDs	4.77 ± 0.34	12.07
CA-P-CDs-1	9.11 ± 0.37	40.98	MA-P-CDs-1	5.43 ± 0.39	15.56
CA-P-CDs-2	9.12 ± 0.07	39.29	MA-P-CDs-2	4.45 ± 0.15	11.58
CA-P-CDs-3	8.88 ± 0.09	35.56	MA-P-CDs-3	5.63 ± 0.30	10.19
CA-P-CDs-4	9.72 ± 0.80	44.23	MA-P-CDs-4	4.32 ± 0.06	11.99

Table S2. Lifetime and quantum yield (QY) data of citric acid CDs series (left) and malic acid

 CDs series (right).



Fig. S9. Comparison of fluorescent lifetimes (τ) among (a) citric acid carbon dots, and (b) malic acid carbon dots using one-way ANOVA.



Fig. S10. Photograph showing the layout of drop plate colony counting with S. oneidensis MR-1.



Fig. S11. (a) 15-min and (b) 1-hour exposure results of MA-P-CDs-4 (5 mg/mL) in dark condition and under lab light condition.



Fig. S12. Cubic baseline and Gaussian distribution fit to obtain peak absorbance for a degraded citric acid carbon dot.

Reference

[1] J.L. Bitter, J. Yang, S.B. Milani, C.T. Jafvert, D.H. Fairbrother, Transformations of oxidized multiwalled carbon nanotubes exposed to UVC (254 nm) irradiation, Environmental Science-Nano 1(4) (2014) 324-337, 10.1039/c4en00073k.

[2] D. Pavia, G. Lampman, G. Kriz, J. Vyvyan, Introduction to spectroscopy, Cengage Learning2008.