Plasmonic Enhancement of Nitric Oxide Generation

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Electronic Supplementary Information

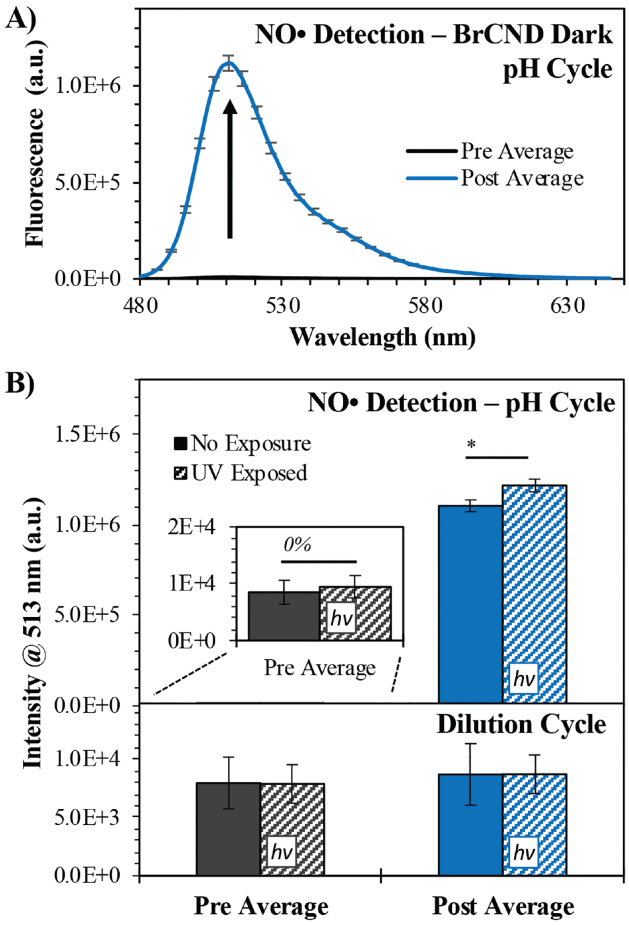

Fig. S1. Nitric oxide (NO•) detection from brominated carbon nanodots (BrCND) under pH cycled conditions. Detection was completed using diaminofluorescein-FM (DAF-FM) probe both "pre" and "post" acid cycling conditions, either under dark or UV-exposed (λ_{ex} = 365 nm, 0.56 ± 0.04 mW) conditions. *A)* Fluorescence spectra of NO• detection under dark conditions. *B)* Average intensities from n = 3 trials, with error from standard deviation (*p < 0.05). Reproduced from Ref. [S1] with permission from The Royal Society of Chemistry.

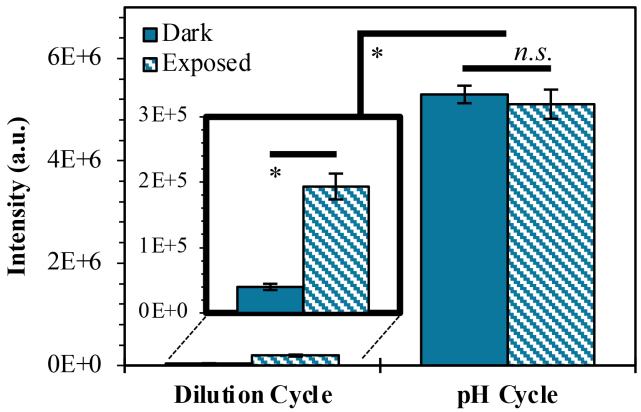

Fig. S2. Photodynamic release of nitric oxide (NO•) from brominated carbon nanodots (BrCND) as detected by *fluorescence-on* probe DAF-FM. Release was detected after 4 minutes of either dark or UV exposure ("Exposed," λ_{ex} = 365 nm, 580 ± $20_{(SD)}$ μW) in blank 96-well plates, both under dilution (pH ~ 12-12.5) and pH cycled (pH < 3) conditions. $N = 5$, $*P << 0.001$, error from standard deviation.

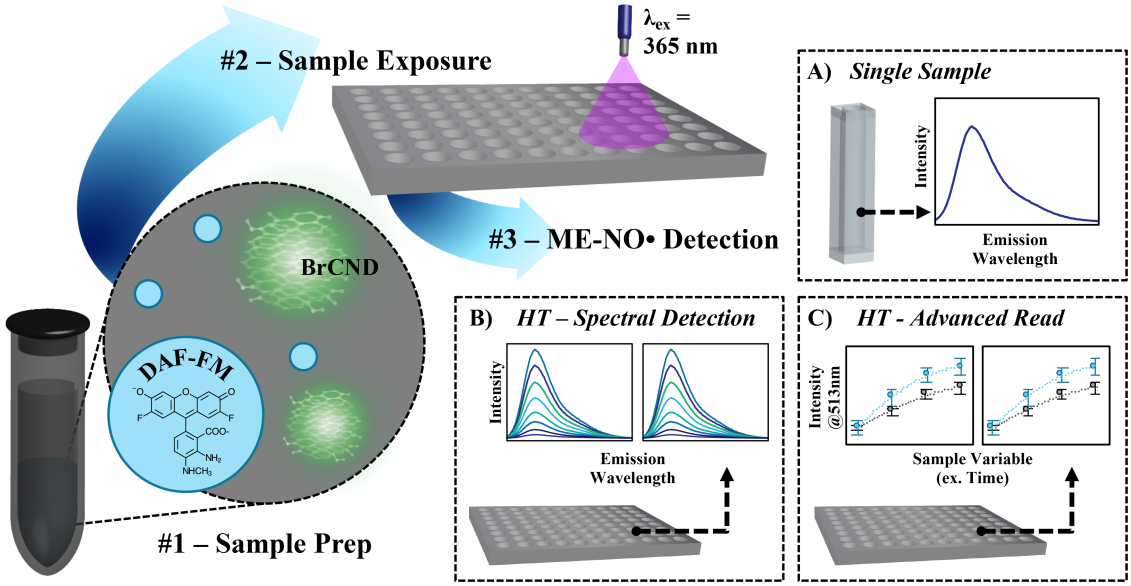

Fig. S3. Schematic of the different detection methods of metal-enhanced nitric oxide (ME-NO•) photodynamic release from brominated carbon nanodots (BrCND), using the *fluorescence-on* probe DAF-FM. Methods include *(A)* single sample, *(B)* high-throughput (HT) spectral detection, and *(C)* HT advanced read, with detection occurring at 513 nm (error from standard deviation of $N = 5$ sample scans).

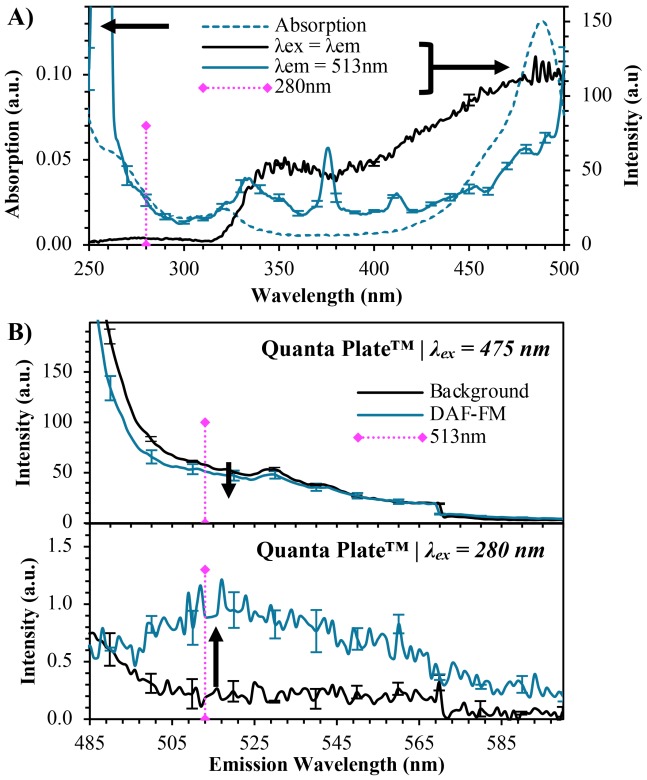

Fig. S4. Selection of excitation parameters for metal-enhanced detection of nitric oxide (NO•) release. *(A)* Spectral overlay of DAF-FM absorption (detected in blank plate, dashed blue line), excitation (detected in Quanta Plate™, λ_{em} = 513 nm, solid blue line) profiles versus Quanta Plate™ well synchronous scattering profile ($\lambda_{ex} = \lambda_{em}$). *(B)* Background excitation scattering versus DAF-FM (10 μM) emission in Quanta Plate™ wells at λ_{ex} = *top* – 475 and *bottom* – 280 nm. Arrows indicate signal change relative to background excitation scattering. All error from standard deviation from $N = 3$ measurements.

Table S1. Metal-Enhanced Generation or Release of Reactive Species.

Species Detected	Plasmonic Substrate	Reactive Species Donor	Enhancement Factor	[Ref.]
Singlet Oxygen ($^1O_2$)	Silver Island Films (SiFs)	Acridine Rose Bengal Chloroquine Indomethacin Riboflavin Naproxen Chlorpromazine Quinidine	~2 ~3 ~6 ~2 ~4 ~17 ~21 ~26	[S2]
$^1O_2$	SiFs	C_{60}	~ 5 - 35	[S3]
$^1O_2$	SiFs	Rose Bengal	~ 2 - 10	[S4]
$^1O_2$	Quanta Plates™	Brominated Carbon Nanodots	~ 2	[S5]
Superoxide anion radical ($O_2^{\bullet-}$)	SiFs	Acridine	~ 4 - 6	[S4]

Table S2. Parameters and Analysis from Varied Energy Density Experiments (Fig. 3).

Fig.	[DAF-FM] (μM)	Time (*t*, sec)	Power (*P*, μW)	Surface Area (*SA*, mm²)	Linear Fit, Slope ($J^{-1}•m^2$)
3*A*	7 μM	0-240 sec int. = 80 sec	$540 \pm 20_{(SD)}$	100% (40 mm²)	$-0.0001 \pm 0.0001_{(SE)}$
3*B*	7 μM	80 sec	$580 \pm 30_{(SD)}$ $950 \pm 140_{(SD)}$ $1590 \pm 60_{(SD)}$	100% (40 mm²)	$3•10^{-6} \pm 30•10^{-6}_{(SE)}$
3*C*	7 μM	80 sec	$570 \pm 20_{(SD)}$	35% (14 mm²) 55% (21 mm²) 100% (40 mm²)	$27•10^{-5} \pm 2•10^{-5}_{(SE)}$
3*E*	1-100 μM	80 sec	$560 \pm 20_{(SD)}$	100% (40 mm²)	N/A

The reader is referred to Fig. 3*A-C,E* of the main text.
"int." = interval

Table S3. Timescales for Detection of Metal-Enhanced Nitric Oxide Release.

Method	Preparation / Exposure	Analysis (Single Trial, *N*)	Analysis (All Samples, *N*)	Total Time
Single sample	~ 15 min	~ 3 min, $N = 1$	~ 1.6 hr, $N = 32$	~ 2 hr
HT, spectral	~ 15 min	12 ± 1 [a] min, $N = 16$	25 ± 2 [b] min, $N = 32$	~ 40 min
HT, adv read	~ 15 min	6.3 ± 0.4 [c] min, $N = 16$	12.6 ± 0.8 [d] min, $N = 32$	~ 30 min

[a] $N = 4$ timed trials, error from standard deviation
[b] Error propagated from (*a*)
[c] $N = 4$ timed trials, error from standard deviation
[d] Error propagated from (*c*)

HT – High throughput, $N = 5$ averaged scan per spectrum
Adv read – advanced read, $N = 5$ averaged scans at 513nm

ESI References

1. R. Knoblauch, A. Harvey, C.D. Geddes, Antimicrobial carbon nanodots: photodynamic inactivation and dark antimicrobial effects on bacteria by brominated carbon nanodots. *Nanoscale* 13, 85-99 (2021). doi:10.1039/D0NR06842J
2. Y. Zhang, K. Aslan, M.J.R. Previte, C.D. Geddes, Plasmonic engineering of singlet oxygen generation. *Proc. Natl. Acad. Sci. U.S.A.* 105, 1798-1802 (2008).
3. X. Ragàs, A. Gallardo, Y. Zhang, W. Massad, C.D. Geddes, S. Nonell, Singlet oxygen production enhancement by silver island films. *J. Phys. Chem. C.* 115, 16275-16281 (2011).
4. J. Karolin, C.D. Geddes, Metal-enhanced fluorescence based excitation volumetric effect of plasmon-enhanced singlet oxygen and superoxide generation. *Phys. Chem. Chem. Phys.* 15, 15740-15745 (2013).
5. R. Knoblauch, A. Harvey, C.D. Geddes, Metal-enhanced photosensitization of singlet oxygen (ME^1O_2) from brominated carbon nanodots on silver nanoparticle substrates. *Nanoscale* in submission (2021).