

Supplementary Information

Nitrate uptake by *p*-phosphonic acid calix[8]arene stabilized graphene

Ela Eroglu^{a,b}, Wenzhe Zang^c, Paul K. Eggers^a, Xianjue Chen^a, Ramiz A. Boulos^d, M. Haniff Wahid^a, Steven M. Smith^b, and Colin L. Raston^{d*}

^a Centre for Strategic Nano-Fabrication, School of Chemistry and Biochemistry, The University of Western Australia, Crawley, WA 6009, Australia.

^b ARC Centre of Excellence in Plant Energy Biology, The University of Western Australia, 35 Stirling Highway, Crawley, WA 6009, Australia.

^c State Key Laboratory of Coordination Chemistry, Coordination Chemistry Institute, Nanjing National Laboratory of Microstructures, Nanjing University, Nanjing, P. R. China

^d Centre for NanoScale Science and Technology, School of Chemical and Physical Sciences, Flinders University, Bedford Park, SA 5042, Australia.
E-mail: colin.raston@flinders.edu.au

1. Methods summary:

Graphite flakes were obtained from Alfa Aesar (043480, 7-10 μm , 99%). *p*-Phosphonic acid calix[8]arene was synthesized by following the previously reported method.¹ The graphite was suspended in distilled water (10 mL) at a 2 $\text{mg}\cdot\text{mL}^{-1}$ concentration. Colloidal suspensions of graphene and *p*-phosphonic acid calix[8]arene mixtures were prepared following the protocol previously developed.² Milli-Q water was used for the preparation of the following solutions. Graphene sheets were produced from aqueous dispersion of graphite (2 $\text{mg}\cdot\text{mL}^{-1}$) via probe sonication (150W at 70% amplitude, Sonifier cell disruptor, Model SLPt, Branson Ultrasonics Corporation) at ambient temperature for 2 hours in the presence of various *p*-H₂O₃P-calix[8]arene (1 $\text{mg}\cdot\text{mL}^{-1}$, 2 $\text{mg}\cdot\text{mL}^{-1}$, 4 $\text{mg}\cdot\text{mL}^{-1}$, 8 $\text{mg}\cdot\text{mL}^{-1}$). The final mixtures were centrifuged at 1500 $\times g$ for 30 min in order to remove any remaining flakes of the graphite (precipitate) from the exfoliated graphene (supernatant). The excess *p*-H₂O₃P-calix[8]arene was separated by consecutive washing and centrifuging at 18400 $\times g$ for 30 min for 4 times. Final

precipitate (0.25 mL) was mixed with 1.25 mL nitrate containing aquatic media.³ The final mixture was mildly sonicated at room temperature for 20 seconds inside an ultrasonic bath (Unisonics Australia) to ensure the homogenous dispersion of the graphene sheets within the solution. The mixtures were let stand on the bench at certain time intervals for sufficient absorption of nitrate ions on the surface of graphene sheets. Before the final nitrate measurements, the mixture was centrifuged at $18400 \times g$ for 30 minutes, and the supernatant was collected for analyzing its final nitrate content. The “cadmium reduction method” was used for the nitrate analysis, using chemical-kits in the form of powder pillows (HACH[®], NitraVer Nitrate Reagent) and a colorimeter (HACH[®] DR/870).⁴ TEM and EFTEM images were performed using JEOL 2100 operating at 120 keV. TEM instrument has a Gatan Orius charged-coupled device camera and a Tridiem energy filter. Resulting TEM data was processed using Image J software. The TEM samples were prepared by placing the graphene dispersions, before and after mixing with nitrate containing solution, onto the 200 mesh holey carbon copper grids and letting them to dry. Zetasizer Nano S (ZEN1600, Malvern Instruments) was used for the Zeta potential measurements.

2. Zeta Potential Measurements

Table S1. Zeta potential analysis of *p*-phosphonic acid calix[8]arene stabilized graphene for different concentrations of calixarene at different time intervals.

Time, h	Zeta potential, mV			
	1 mg/mL	2 mg/mL	4 mg/mL	8 mg/mL
0	-16.2 ± 0.7	-17.3 ± 0.9	-23.1 ± 0.9	-28.6 ± 0.4
6	-17.6 ± 0.9	-16.9 ± 0.4	-24.0 ± 0.4	-27.2 ± 0.3
12	-17.0 ± 0.3	-17.7 ± 0.6	-27.2 ± 0.4	-28.2 ± 0.3
24	-17.2 ± 0.7	-18.0 ± 0.8	-27.1 ± 0.2	-26.1 ± 0.5

3. Removal of nitrate ions from the liquid media using *p*-phosphonic acid calix[8]arene stabilized graphene at various concentrations.

Table S2. Nitrate-nitrogen (NO_3^- -N) concentration of the liquid media at various time intervals after exposure to graphene sheets which were exfoliated from graphite in the presence of various *p*- $\text{H}_2\text{O}_3\text{P}$ -calix[8]arene concentrations.

Time, h	$[\text{NO}_3^-\text{-N}], \text{mg.L}^{-1}$			
	1 mg/mL	2 mg/mL	4 mg/mL	8 mg/mL
0	22.0 ± 0.1	22.0 ± 0.1	22.0 ± 0.1	22.0 ± 0.2
3	18.0 ± 0.4	19.5 ± 0.3	19.5 ± 0.4	18.5 ± 0.7
6	15.0 ± 0.4	16.5 ± 0.4	16.5 ± 0.6	15.5 ± 0.6
12	14.0 ± 0.4	14.5 ± 0.5	13.0 ± 0.5	12.0 ± 0.5
18	13.8 ± 0.5	13.3 ± 0.5	11.8 ± 0.6	10.5 ± 0.5
24	13.5 ± 0.4	12.3 ± 0.5	11.3 ± 0.4	9.75 ± 0.5

4. Release of adsorbed nitrate ions into the liquid media under mild sonication

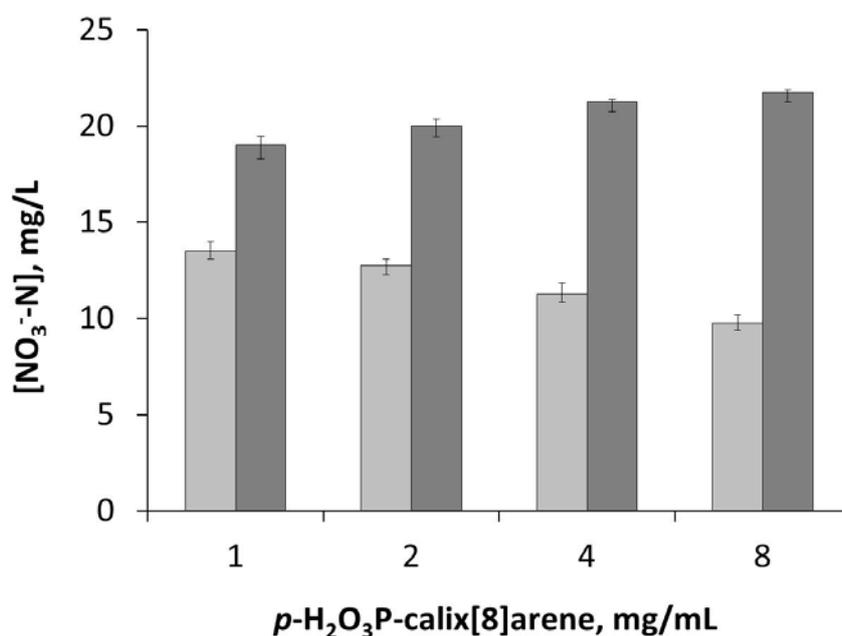


Figure S1. Amount of NO_3^- -N (mg.L^{-1}) for various calixarene/graphene mixtures (i) at 24th hour (light-grey columns), and (ii) after mild-sonication for 2.5 minutes (dark-grey columns).

5. Chemical Modelling

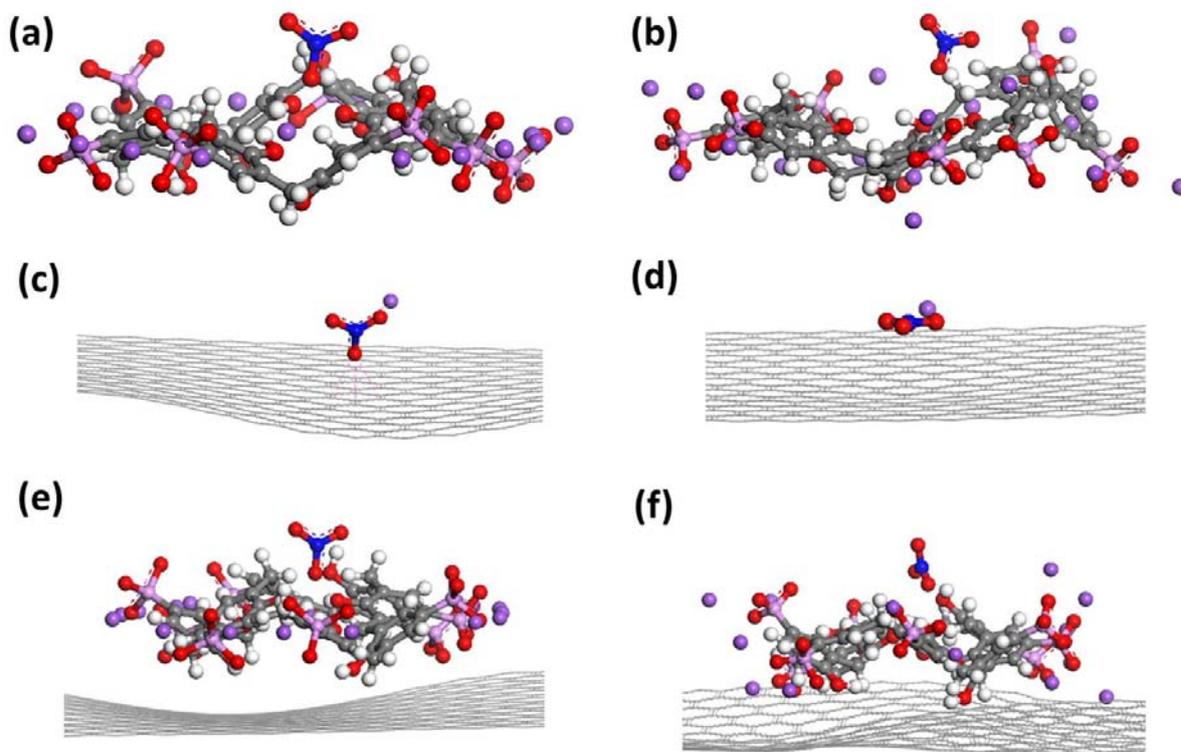


Figure S2. Initial and final configurations of graphene, *p*-H₂O₃P-calix[8]arene and nitrate system studies: (a-b) *p*-H₂O₃P-calix[8]arene & NaNO₃, (c-d) graphene & NaNO₃, (e-f) graphene & *p*-H₂O₃P-calix[8]arene and NaNO₃.

References

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