

Nanoscale

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

COMMUNICATION

Self-assembled calixarene aligned patterning of noble metal nanoparticles on graphene

Cite this: DOI: 10.1039/x0xx00000x

Xianjue Chen,^a Kasturi Vimalanathan,^a Wenzhe Zang,^b Ashley D. Slattery,^a Ramiz A. Boulos,^a Christopher T. Gibson^a and Colin L. Raston^{a,*}

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Patterns of noble metal nanoparticles (NMNPs) of ruthenium and platinum are formed on *p*-phosphonic acid calix[8]arene stabilised graphene in water. This involves hydrogen gas induced reduction of metal ions absorbed on the stabilised graphene, with TEM revealing the patterns being comprised of domains of parallel arrays of NMNPs ~7 nm apart. The domains are orientated in three directions on each graphene sheet at an angle of ~60° or ~120° with respect to each other. AFM of self-assembled *p*-phosphonic acid calix[8]arene on the surface of a highly ordered pyrolytic graphite (HOPG) revealed a similar pattern, implying that the orientation of the assembly of *p*-phosphonic acid calix[8]arene is governed by the hexagonal motif of graphite/graphene.

Manipulation of nanoparticles for assembly into specific arrangements at the nanoscale shows great promise for the fabrication of novel functional materials with unique electronic, optical, and magnetic properties.¹⁻⁴ A variety of routes to achieve the directed self-assembly of nanoparticles have been explored, including the use of polymer scaffolds,^{2,5} programmable DNA linkers,⁶ crystal step edges,⁷ and lithography for assisting the assemblies on predefined surfaces.^{8,9} However, to facilitate and precisely control the spatial organization of nanoparticles down to a few nanometre, especially with the ability to directly obtain scalable functional nano-composites, is a challenge.

Herein we report a simple method of patterning of noble metal nanoparticles (NMNPs) on *p*-phosphonic acid calix[8]arene stabilised graphene sheets in water. This involves initially the self-assembly of calixarene molecules onto the graphene at the time of exfoliation from graphite, followed by reduction using hydrogen of noble metal complex precursors bound to the calixarene functional groups through primary or secondary coordination interactions.

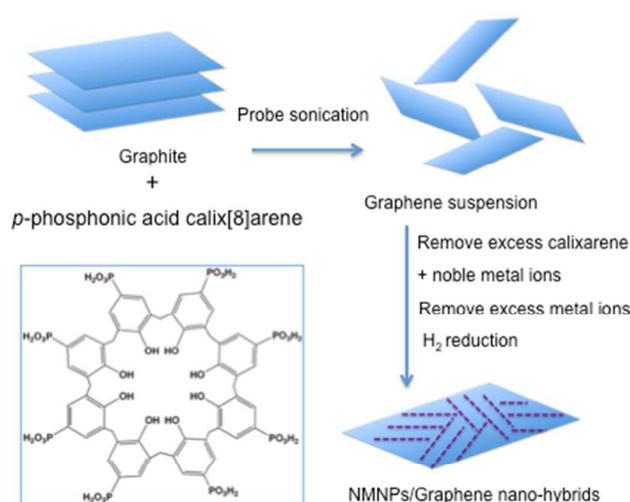


Figure 1. Exfoliation of graphite in water involving probe sonication in the presence of *p*-phosphonic acid calix[8]arene, followed by NMNP pattern formation using hydrogen gas.

NMNPs in general are a family of nanoparticles which have received intense interest.^{10,11} In most colloidal routes to NMNPs, stabilisers are introduced in order to produce mono-dispersed nanoparticles with unique properties.¹²⁻¹⁴ In recent years, there has been a trend in dispersing the NMNPs directly on supporting materials, to avoid underplaying the catalytic performance caused by the capping of the NMNP surface in the presence of stabilisers.¹⁵⁻¹⁸ Graphene has great potential as such a supporting material, given its large specific surface area, extraordinary physical properties,¹⁹ and strong interactions towards noble metals.²⁰⁻²²

Covalently or non-covalently modified graphene is stabilised with surfactants under acidic conditions prior to the addition and binding of precursors metal complexes.²³⁻²⁴ The use of surfactants is also a

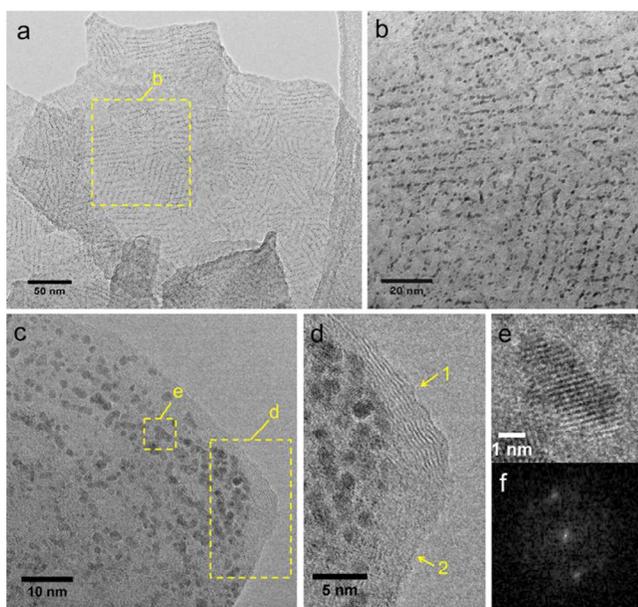


Figure 2. TEM of (a) graphene sheets decorated with Ru nanoparticles, (b) zoomed-in area as indicated in (a) showing the nanoparticles arrays, and (c) a closer view of the Ru/graphene nano-hybrids, with HRTEM in (d) showing the edge of the graphene sheet, and (e), showing an individual Ru nanoparticle with lattice fringe. (f) Corresponding FFT pattern of the Ru nanoparticle in (e).

prerequisite for generating well-dispersed nanoparticles decorated on graphene. That said, there are limited studies on the interactions between metal complexes, surfactants and graphene, prior to reduction to the formed metal nanoparticles, despite the importance of these interactions in understanding the formation of NMNPs and further controlling their arrangements on graphene.²⁵

p-Phosphonic acid calix[8]arene has versatile properties, effectively facilitating the exfoliation of graphene and other laminar inorganic materials, and stabilising the resulting two-dimensional sheets in water, which relates to its amphiphilic nature, bearing ‘upper rim’ phosphonate groups and ‘lower rim’ hydroxyl groups.²⁶ The extended family of *p*-phosphonic acid calix[*n*]arene, *n*=4, 5, 6, and 8, are effective in solubilizing and separating different diameter single-walled carbon nanotubes, encapsulating anti-cancer drugs, templating the growth of metal nanoparticles, and stabilising graphene oxide, with the latter material effective in removing nitrate from aquatic effluents.^{27–33} *p*-Phosphonic acid calix[*n*]arenes are highly soluble in basic aqueous solutions through ionization of the phosphonate groups, but they have limited solubility in acidic solutions. Electrostatic potential analysis suggests that the largest macrocycle in the series, namely *p*-phosphonic acid calix[8]arene has the highest solubility in both acidic and basic conditions.³⁴

Decoration of NMNPs on *p*-phosphonic acid calix[8]arene functionalized two-dimensional materials is possible without the need for adjusting the pH.³⁵ This involved probe sonicating pristine graphite in water in the presence of the macrocycle, in affording stable graphene suspensions. Low-speed centrifugal washing (~1800×*g*, 30 min) was used to remove non-exfoliated graphite flakes, with high-speed centrifugation (~16900×*g*, 30 min) used to remove excess calixarene. Any excess calixarene provides additional nucleation sites, resulting in the formation of unwanted calixarene capped NMNPs devoid of the graphene. Noble metal precursors of

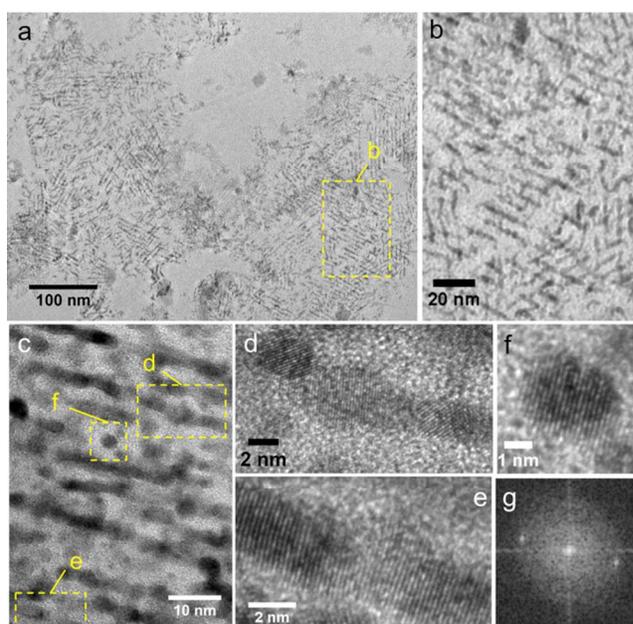


Figure 3. TEM of (a) Pt/graphene nano-hybrids, with (b) a zoomed-in area of the pattern indicated in (a). (c) Closer view of the pattern, with indicated areas for HRTEM in (d, e, and f), showing the lattice fringes of Pt nanoparticles. (g) Corresponding FFT pattern of the Pt nanoparticles in (f).

hydrated ruthenium(III) chloride (RuCl_3) and chloroplatinic acid (H_2PtCl_6) were directly added to the aforementioned washed graphene suspensions. The resulting mixtures were left for 12 hours before high-speed centrifugal washing to remove any freestanding noble metal species. This is necessary because high concentrations of metal species result in strong kinetically driven diffusion, which could lead to aggregation and branching of the NMNPs, and also because metal ions can be reduced using hydrogen in forming freestanding metal particles. After washing and re-dispersing in Milli-Q water, hydrogen gas was bubbled through the solutions for 20 minutes with two subsequent centrifugal washing steps resulted in NMNPs/graphene nano-hybrid material. A schematic of the overall process is shown in Figure 1, with full experimental details given in ESI.

Distinct patterns of NMNPs patterns were present on the graphene sheets for both Ru/graphene and Pt/graphene nano-hybrid materials, as established using transmission electron microscopy (TEM). Figure 2a shows patterns of decorated nanoparticles on as synthesized Ru/graphene nano-hybrids material. A zoomed-in image of the indicated area is given in Figure 2b, establishes an average NMNP particle size of ~2–3 nm, and that they are aligned in parallel domains ~7 nm apart. In Figure 2d, the edge of the graphene sheet can be seen, and interestingly, a few lines are visible at the upper boundary, indicated by Arrow 1, whereas only one layer can be observed at the lower boundary, indicated by Arrow 2. A plausible explanation is that it is a monolayer graphene sheet, and the lines at the upper region were caused from slight scrolling of the graphene edge, where two-dimensional structures are energetically more unstable.³⁶ HRTEM image of a Ru nanoparticle (Figure 2e) reveals the lattice fringe of the crystalline nanoparticle. Fast Fourier transform (FFT) diffraction pattern of the nanocrystal is given in Figure 2f, affording a lattice spacing ~0.21 nm, which corresponding to the Ru(101) plane.

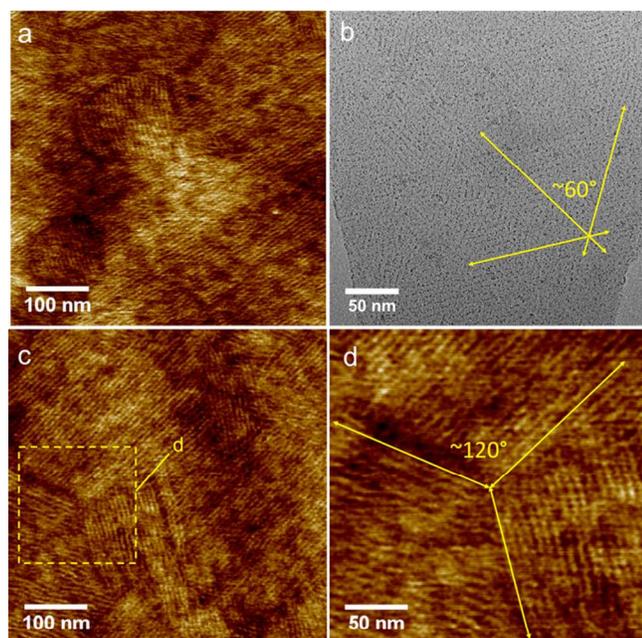


Figure 4. AFM (a, c, and d) of self-assembled *p*-phosphonic acid calix[8]arene patterns on HOPG surface. (b) TEM image of a graphene sheet decorated with patterns of Ru nanoparticles.

TEM was also carried out on the Pt/graphene nano-hybrids. Figure 3a and 3b reveal aligned patterns of nanoparticles on graphene with a similar spacing distance to that of the analogous Ru/graphene hybrid material. HRTEM (Figure 3d-3f) was carried out on Pt nanoparticles in different areas indicated in Figure 3c. The HRTEM images can provide insight into the mechanism of growth of the metal nanoparticles. Prior to reduction, it is expected that the noble metal complexes were attached to the phosphonate groups of the calix[8]arene on the graphene. At the beginning of the reduction, ultra small NMNPs will be generated from closely associated metal complexes and these particles will tend to be spherical in shape by undergoing coalescence relaxation in order to maintain lower boundary energy. Subsequently, these nanoparticles will interact with each other. However, different from the freestanding nucleation and growth, the nanoparticles attached to the graphene sheet would be relatively difficult to migrate and rotate to form the same crystallographic orientation for oriented attachment.³⁸ As a result, the nanoparticles maintain their own orientation to form nanopolycrystalline structures, as shown in Figure 3d. In the meantime, some crystal nanochains with similar crystalline orientation can be observed (Figure 3e), which is probably attributed to the post-attachment recrystallization that eliminated any inter-nanoparticle boundary.³⁹ Figure 3f shows the lattice fringe of a Pt nanoparticle, with its corresponding FFT diffraction pattern (Figure 3g), indicating a spacing of ~ 0.23 nm for the Pt(111) plane.

The consistency of the nanoparticle arrangements in both graphene nano-hybrids highlights a critical role of *p*-phosphonic acid calix[8]arene in forming the NMNP patterns. We note that calix[8]arene derivatives in general can self-organize into a monolayer tubular fashion on highly oriented pyrolytic graphite (HOPG) at low concentrations via intermolecular interactions.³⁹ *p*-Phosphonic acid calix[8]arene binds to a freshly cleaved HOPG surface, forming a similar self-assembled structures as that for the above hybrid material, as established using atomic force microscopy (AFM), Figure 4a. Here the calixarene was dissolved in chloroform

($\sim 2 \times 10^{-5}$ mg mL⁻¹), which was then probe sonicated for 10 minutes prior to drop-casting on HOPG. Higher concentration ($\sim 2 \times 10^{-3}$ mg mL⁻¹) led to the formation of disoriented nanofibers, which were microns in length (Figure S1). Water is also used as the solvent for dispersing calixarene, even though its poor wettability on HOPG was an issue for AFM analysis.

A comparison between the AFM images of self-assembled calixarene on HOPG and a TEM image of Ru/graphene (Figure 4b) shows similar patterns of domains of parallel arrays, ~ 7 nm apart. This matches the spacing of metal nanoparticle arrays from TEM. This similarity is consistent with the self-assembled calixarenes controlling the formation of the NMNP patterns. The orientation of the calixarene and NMNP (Figure 4b and 4d), revealed that all the parallel arrays are roughly in three directions at an angle of 60° or 120° with respect to each other, implying that the assembly of calixarene is governed by the hexagonal structure of the graphene/graphite substrate, i.e. the orientation of the calixarene on the surface is predetermined by the orientation of the hexagonal motif of graphene itself.

We have established a simple solution based process for patterning NMNPs on graphene in the presence of *p*-phosphonic acid calix[8]arene. The ability to form patterns of metal nanoparticles in this way, relates to the self-assembly of the calixarene with specific orientation relative to the six membered motif of the graphene. These results provide further understanding of the controlled organization of noble metal nanoparticles decorated on supporting materials, directed by surface bound molecules. This method shows promise for generating novel graphene-based nano-hybrids by selecting different molecules/surfactants or varying the nature of the substrate. More importantly, it offers an effective way to organize particles at the nanometre scale on large area substrates, for example, in selectively generating patterns of metal nanoparticles on large-sized graphene/graphite for electronic/optical applications.

We gratefully acknowledge the Australian Research Council, The Perth Mint, and the Government of South Australia for support of this work. TEM and AFM characterizations were carried out in the Centre for Microscopy, Characterisation and Analysis at the University of Western Australia and the SPM Laboratory in the Centre for Nanoscale Science and Technology at Flinders University, respectively, which are both supported by the Australian Microscopy & Microanalysis Research Facility. This work was performed in part at the Flinders University Node of the Australian National Fabrication Facility. W. Zang sincerely appreciates the Ministry of Education of China for financial support (National Science Fund for Talent Training in Basic Science, Grant No. J1103310).

Notes and references

^a Centre for Nanoscale Science and Technology, School of Chemical and Physical Sciences, Flinders University, Bedford Park SA 5042, Australia.

^b School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, 210093, China

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/c000000x/

- 1 C. T. Black, C. B. Murray, R. L. Sandstrom and S. Sun, *Science*, 2000, **290**, 1131-1134.
- 2 W. A. Lopes and H. M. Jaeger, *Nature*, 2001, **414**, 725-738.

- 3 W. U. Huynh, J. J. Dittmer and A. P. Alivisatos, *Science*, 2002, **295**, 2425-2427.
- 4 S. Glotzer and M. Solomon, *Nat. Mater.*, 2007, **6**, 557-562.
- 5 B. H. Sohn, J. M. Choi, S. I. Yoo, S. H. Yun, W. C. Zin, J. C. Jung, M. Kanehara, T. Hirata and T. Teranishi, *J. Am. Chem. Soc.*, 2003, **125**, 6368-6369.
- 6 F. A. Aldaye, A. L. Palmer and H. F. Sleiman, *Science*, 2008, **321**, 1795-1799.
- 7 F. Favier, E. C. Walter, M. P. Zach, T. Benter and R. M. Penner, *Science*, 2001, **293**, 2227-2231.
- 8 S. A. Maier, P. G. Kik, H. A. Atwater, S. Meltzer, E. Harel, B. E. Koel and A. A. G. Requicha, *Nat. Mater.*, 2003, **2**, 229-232.
- 9 L. M. Demers, D. S. Ginger, S. J. Park, Z. Li, S. W. Chung and C. A. Mirkin, *Science*, 2002, **296**, 1836-1838.
- 10 B. Lim, M. Jiang, P. F. C. Camargo, E. C. Cho, J. Tao, X. Lu, Y. Zhu and Y. Xia, *Science*, 2009, **324**, 1302-1305.
- 11 M. Grzelczak, J. Pérez-Juste, P. Mulvaney and L. M. Liz-Marzán, *Chem. Soc. Rev.*, 2008, **37**, 1783-1791.
- 12 M. P. Pileni, *Nat. Mater.*, 2003, **2**, 145-150.
- 13 O. M. Wilson, R. W. J. Scott, J. C. Garcia-Martinez and R. M. Crooks, *J. Am. Chem. Soc.*, 2005, **127**, 1015-1024.
- 14 S. U. Son, Y. Jang, K. Y. Yoon, E. Kang and T. Hyeon, *Nano Lett.*, 2004, **4**, 1147-1151.
- 15 X. Chen, G. Wu, J. Chen, X. Chen, Z. Xie and X. Wang, *J. Am. Chem. Soc.*, 2011, **133**, 3693-3695.
- 16 Y. Lee, M. A. Garcia, N. A. Frey Huls and S. H. Sun, *Angew. Chem. Int. Ed.*, 2010, **49**, 1271-1274.
- 17 Y. A. Li, N. H. Tai, S. K. Chen and T. Y. Tsai, *ACS Nano*, 2011, **5**, 6500-6506.
- 18 S. Guo, S. Dong and E. Wang, *ACS Nano*, 2010, **4**, 547-555.
- 19 N. Savage, *Nature*, 2012, **483**, S30-S31.
- 20 P. A. Khomyakov, G. Giovannetti, P. C. Rusu, G. Brocks, J. Van den Brink and P. J. Kelly, *Phys. Rev. B*, 2009, **79**, 195425.
- 21 Q. J. Wang and J. G. Che, *Phys. Rev. Lett.*, 2009, **103**, 066802.
- 22 I. Cabria, M. J. López and J. A. Alonso, *Phys. Rev. B*, 2010, **81**, 035403.
- 23 J. D. Qiu, G. C. Wang, R. P. Liang, X. H. Xia and H. W. Yu, *J. Phys. Chem. C*, 2011, **115**, 15639-15645.
- 24 X. Chen, F. Md Yasin, P. K. Eggers, R. A. Boulos, X. Duan, R. N. Lamb, K. S. Iyer and C. L. Raston, *RSC Adv.*, 2013, **3**, 3213-3217.
- 25 J. Granatier, P. Lazar, R. Prucek, K. Šafářová, R. Zbořil, M. Otyepka and P. Hobza, *J. Phys. Chem. C*, 2012, **116**, 14151-14162.
- 26 X. Chen, R. A. Boulos, P. K. Eggers and C. L. Raston, *Chem. Commun.*, 2012, **48**, 11407-11409.
- 27 T. E. Clark, M. Makha, A. N. Sobolev, H. Rohrs, J. L. Atwood and C. L. Raston, *Chem. Eur. J.*, 2008, **14**, 3931-3938.
- 28 L. J. Hubble, T. E. Clark, M. Makha and C. L. Raston, *J. Mater. Chem.*, 2008, **18**, 5961-5967.
- 29 A. D. Martin, R. A. Boulos, L. J. Hubble, K. J. Hartlieb and C. L. Raston, *Chem. Commun.*, 2011, **47**, 7353-7355.
- 30 K. J. Hartlieb, M. Saunders and C. L. Raston, *Chem. Commun.*, 2009, 3074-3076.
- 31 K. J. Hartlieb, A. D. Martin, M. Saunders and C. L. Raston, *New J. Chem.*, 2010, **34**, 1834-1837.
- 32 J. Zou, A. D. Martin, B. Zdyrko, I. A. Luginov, C. L. Raston and K. S. Iyer, *Chem. Commun.*, 2011, **47**, 5193-5195.
- 33 E. Eroglu, W. Zang, P. K. Eggers, X. Chen, R. A. Boulos, M. H. Wahid, S. M. Smith and C. L. Raston, *Chem. Commun.*, 2013, **49**, 8172-8174.
- 34 A. D. Martin and C. L. Raston, *Chem. Commun.*, 2011, **47**, 9764-9772.
- 35 X. Chen, W. Zang, K. Vimalanathan, K. S. Iyer and C. L. Raston, *Chem. Commun.*, 2013, **49**, 1160-1162.
- 36 X. Chen, R. A. Boulos, J. F. Dobson and C. L. Raston, *Nanoscale*, 2013, **5**, 498-502.
- 37 H. B. Dai, X. D. Kang and P. Wang, *Int. J. Hydrogen Energy*, 2010, **35**, 10317-10323.
- 38 D. Li, M. H. Nielsen, J. R. I. Lee, C. Frandsen, J. F. Banfield and J. J. De Yoreo, *Science*, 2012, **336**, 1014-1018.
- 39 J. Zhang, G. Podoprygorina, V. Brusko, V. Böhmer and A. Janshoff, *Chem. Mater.*, 2005, **17**, 2290-2297.