Pd-induced ordering of 2D Pt Nanoarrays on phosphonated calix[4]arene stabilised graphene

Jianli Zou, Adam D. Martin, Bogdan Zdyrko, Igor Luzinov, Colin L. Raston and K. Swaminathan Iyer*

Supporting information

Experimental procedure:

p-Phosphonic acid calix[4]arene was synthesised according to literature using a five step procedure.[1] Briefly, the parent calix[4]arene was brominated at the upper rim, followed by protection of the lower rim with an acetyl group. A nickel-catalysed Arbuzov reaction was then employed to attach a phosphoryl group to the upper rim, and this was followed by subsequent deacetylation and deesterification to give the desired product.

Graphene was synthesized according to the recently reported procedure. [2-4] Graphite was first oxidised by H_2SO_4 and $KMnO_4$. And the resulting graphite oxide underwent exfoliation to afford graphene oxide. A mixture of hydrazine and ammonia were subsequently used to reduce graphene oxide to graphene.

The synthesis palladium nanoparticles coated graphene sheet involved in incubating 1 mg/mL *p*-phosphonic acid calix[4]arene solution with graphene solution overnight. Calix[4]arene stabilised graphene (CSG) was vacuum-filtrated using a membrane (pore size 0.2 μm, Sigma) and then washed several times using MilliQ water. CSG was re-dispersed in MilliQ water, and incubated with H_2PdCl_4 overnight. The resulting mixture was filtrated through a filter membrane and redispersed in MilliQ water to remove excess Pd precursors. The solution was purged with hydrogen gas 2-3 min under magnetic stirring. Following this the solution was centrifuged for 30 min at 4000 rpm, and re-dispersed in MilliQ water.

For a typical platinum nanoparticles growth we used a modified experimental protocol previously described by Xia *et al.*[5-7] Briefly, CSG-Pd(0) solution 100 μL was

heated in air to remove water and then dissolved with 4 mL EG (ethylene glycol). 22.5 mg PVP (MW 55,000) was dissolved in 1 mL EG and 0.2 mL of 0.1 $molL^{-1}$ H_2PtCl_6 was dissolve in 1 mL EG (heated to remove water before use). PVP and H_2PtCl_6 solution were added simultaneously to the CSG-Pd(0) mixture dropwise at 110 °C and the reaction was allowed to continue for 2 h before adding different amount of $FeCl_3$ solution (0, 10, 20 and 200μL of 12 mM $FeCl_3$). At 110 °C some of the EG decomposed to aldehyde which in turn reduces the H_2PtCl_6 to Pt^{II} intermediate. The Pt^{II} undergoes replacement reaction with Pd to form Pt nanoparticles.

TEM images:

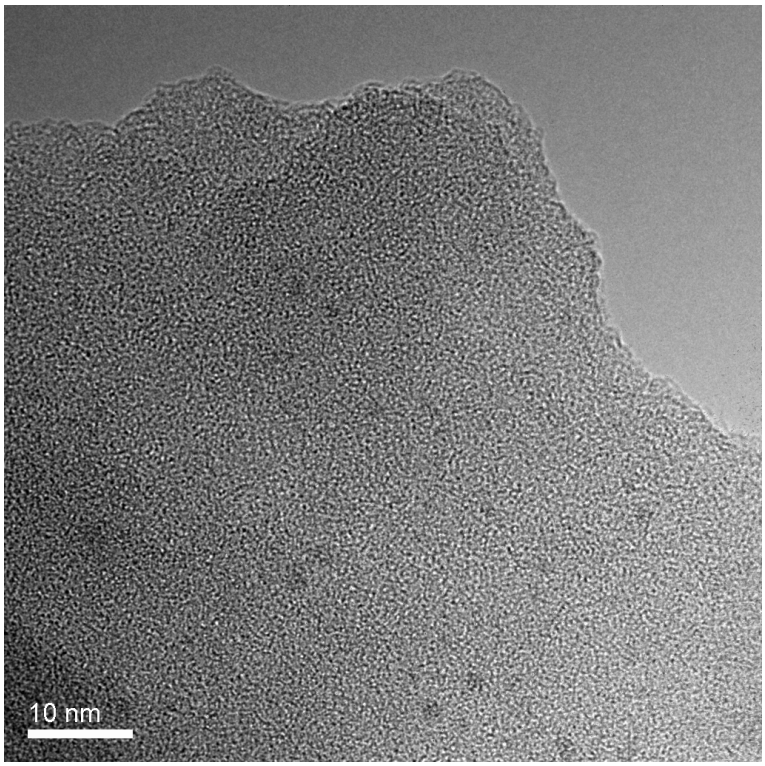

Figure S1 TEM image of graphene-Pd without phosphonated calix[4]arene.

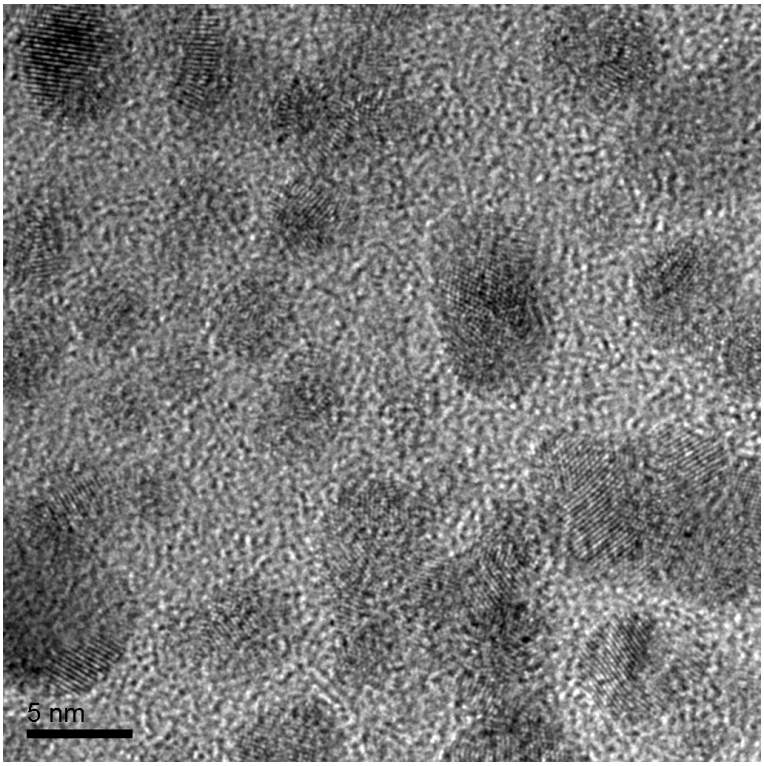

Figure S2. High resolution TEM image of CSG-Pd.

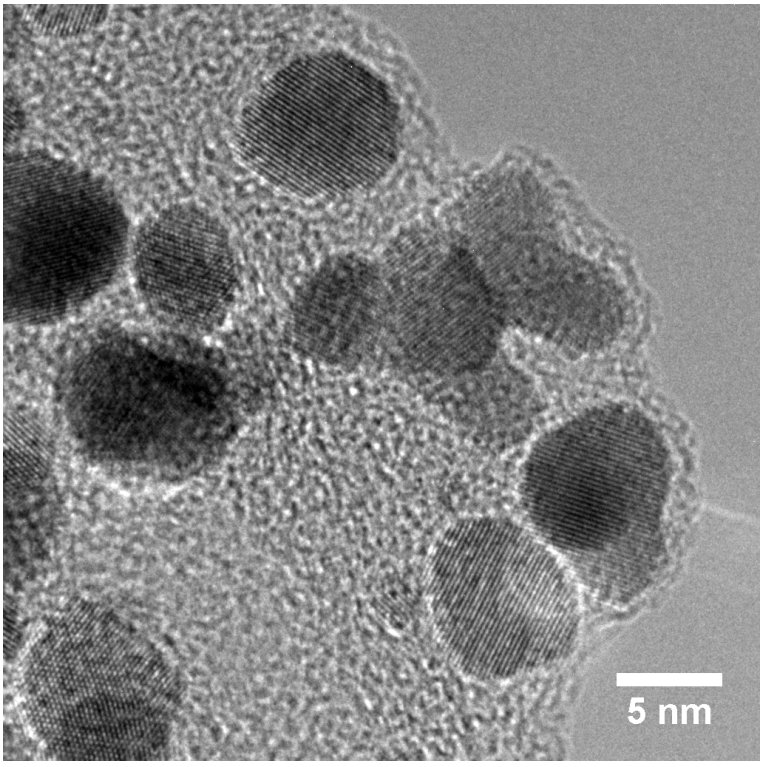

Figure S3. High resolution TEM image of Pt nanoparticles on the CSG.

1. T. E. Clark, M. Makha, A. N. Sobolev, D. Su, H. Rohrs, M. L. Gross, J. L. Atwood and C. L. Raston, *New J. Chem.*, 2008, **32**, 1478.
2. W. S. Hummers and R. E. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339.
3. N. I. Kovtyukhova, P. J. Ollivier, B. R. Martin, T. E. Mallouk, S. A. Chizhik, E. V. Buzaneva and A. D. Gorchinskiy, *Chem. Mater.*, 1999, **11**, 771.
4. D. Li, M. B. Muller, S. Gilje, R. B. Kaner and G. G. Wallace, *Nat. Nanotechnol.*, 2008, **3**, 101.
5. J. Chen, T. Herricks, M. Geissler and Y. Xia, *J. Am. Chem. Soc.*, 2004, **126**, 10854.
6. J. Chen, T. Herricks and Y. Xia, *Angew. Chem. Int. Ed.*, 2005, **44**, 2589.
7. E. P. Lee, J. Y. Chen, Y. D. Yin, C. T. Campbell and Y. N. Xia, *Adv. Mater.*, 2006, **18**, 3271.