**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 H₂SO₄ and KMnO₄. 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 H₂PdCl₄ overnight. The resulting mixture was filtrated through a filter membrane and re-dispersed 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$_2$PtCl$_6$ was dissolve in 1 mL EG (heated to remove water before use). PVP and H$_2$PtCl$_6$ 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$_2$PtCl$_6$ 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.](image-url)
Figure S2. High resolution TEM image of CSG-Pd.

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


