Supporting Information

Non-covalently modified graphene supported ultrafine nanoparticles of palladium for hydrogen gas sensing

Xianjue Chen, Faizah Md Yasin, Paul K. Eggers, Ramiz A. Boulos, Xiaofei Duan, Robert N. Lamb, K. Swaminathan Iyer and Colin L. Raston*

S1 Methods summary

***Materials*:**

Pristine graphite flakes (7-10 μm, 99%) from Alfa Aesar were used as received. *p*-Phosphonic acid calix[8]arene was synthesized following the literature method.[1] Milli-Q water was used for all the aqueous solution preparations. Colloidal suspensions of graphene were prepared using our recently established protocol.[2] A 10 mL aqueous suspensions of graphite (2 mg mL^{-1}) was prepared with the addition of solid *p*-phosphonic acid calix[8]arene in targeting a 1 mg mL^{-1} concentration. The suspensions were probe sonicated continuously for 2 hours at ambient conditions (150W at 70% amplitude, Sonifier cell disruptor, Model SLPt, Branson Ultrasonics Corporation). After 5 minutes for the solution to cool to room temperature, the suspensions were transferred into 15 mL centrifuge vials and centrifugated for 30 min at ~1800 × *g* (Centrifuge 5810, Eppendorf). Thereafter, the supernatant was decanted and kept in a glass vial as a dispersion of graphene.

The as-synthesized graphene dispersions were cleaned twice using high-speed centrifugation (Centrifuge 5418, Eppendorf). For each centrifugation, 1 mL was transferred into a 1.5 mL vial and centrifuged for 30 min at ~16800 × *g*. The supernatants of the resulting products were removed and then Milli-Q water was added. Gentle sonication (Ultrasonic cleaner, Unisonics) for 1 minute was applied to re-disperse the slurry into the water, followed by another round of high speed centrifugation. An aqueous solution of H_2PdCl_4 (0.2 mM) was used directly. The mixture was centrifugated at high-speed (30 min, ~16800 × *g*) to remove freestanding palladium(II) species in solution via a washing process. The slurry was re-dispersed in 1 mL of water for hydrogen gas reduction in a vortex fluidic device (see below for details). After 5 minutes processing, the solution was collected and the product was washed twice with water involving centrifugation (30 min, ~16800 × *g*). The final product was used directly for the subsequent characterizations.

***Characterizations*:**

The as-treated sample was dropped onto 200 mesh holey carbon copper grids for TEM characterizations. A JEOL 2100 LaB_6 TEM equipped with a Gatan Orius charged-coupled device camera operating at 120 kV was used for TEM and HRTEM data acquisition. Image J software was used for processing all the TEM images. For SEM studies, samples were dropped onto 12 mm carbon tabs covered aluminum specimen mounts (SPI supplies), and then coated with 5 nm Pt films after drying in air. A Zeiss 1555 VP-FESEM with a 3 kV accelerating voltage was used for characterization. A NanoMan AFM system (Veeco Instruments Inc.) was used for AFM characterization. The system is a combination of several components which includes the Dimension 3000 Scanning Probe Microscope (SPM) in providing basic imaging platform, with the Dimension Closed Loop XY Scanning Head for precise lateral positioning, and the NanoMan User interface available within a NanoScope controller. Tapping mode AFM was used for size and height profile measurements of the graphene sheets. Samples were prepared by drop casting dispersions in water onto freshly cleaved mica with the water evaporated under a gentle flow of nitrogen gas. The raw data was processed using the Gwyddion software. XPS data was acquired using a VG ESCALAB220i-XL X-ray Photoelectron Spectrometer equipped with a hemispherical analyser. The incident radiation was monochromatic Al Kα X-rays (1486.6 eV) at 220 W (22 mA and 10kV). Survey (wide) and high resolution (narrow) scans were taken at analyser pass energies of 100 eV and 20 eV, respectively. Survey scans were carried out over 1200-0 eV binding energy range with 1.0 eV step size and 100 ms dwell time. Narrow high resolution scans were run over 20 eV binding energy range with 0.05 ev step size and 250 ms dwell time. Base pressure in the analysis chamber was 7.0×10^{-9} mbar. The flood gun was not used considering that the samples were conductive due to graphene. This resulted in the $Pd3d_{5/2}$ peak in sample 2 detected at a higher binding energy (338.4 eV) than that in sample 3 (337.4 eV) due to a less conductive nature of Pd(II) species. XPS data were processed using the CasaXPS software. All high resolution spectra were calibrated to C *1s* (C-C) at 285.0 eV.

***Electrocatalytic testing*:**

Glassy carbon electrode (GCE), 5 mm in diameter (electrode area 0.2 cm^2), polished with alumina to a mirror-finish before electrocatalytic testing, was used as the substrate for supporting the nano-composites. The centrifugation-washed nano-composites in water was drop cast onto the top surface of the GCE and dried in atmosphere. The electrochemical measurements were carried out with a Reference 600 computer-controlled potentiostat/galcanostat/ZRA from Gamry Instruments. The testing was used with a Pt wire as the counter electrode and a saturated Ag/AgCl electrode as reference electrode. All the experiments were carried out at ambient conditions.

***Hydrogen sensing testing*:**

The hydrogen gas sensing testing set-up basically consists of a carrier gas (ultra high purity nitrogen), two gas mass flow controllers, a glass cyclonic mixer, a sensor test chamber, and a potentiostat and an electronic recorder, as described elsewhere.[18] The mass flow controller allows different flow rates of gas passing through (1-1000 mL min^{-1}). The Pd-NPs/graphene nano-composites solution was drop cast onto the interdigitated electrode (IDE) using aliquots of 0.02 μL from a 0.5 μL glass syringe and dried in air. The gas mass flow controllers and measurement instrumentation were all linked and controlled through PC-compatible software, which allows an automatic control of the experiments.

S2 Control of Pd-NPs decoration

A large number of branched palladium structures appeared in the sample when the as-synthesized graphene dispersion in the presence of excess calixarene and palladium(II) was reduced directly, as shown in Figure S2a and S2b. The freestanding solvated calixarene may be responsible for providing extra sites for Pd nucleation. Also, some graphene sheets were not decorated with Pd nanoparticles (indicated by dotted circles in Figure S2b). The result in Figure S2c and S2d shows an extremely improved Pd decoration with small particle size and uniform distribution.

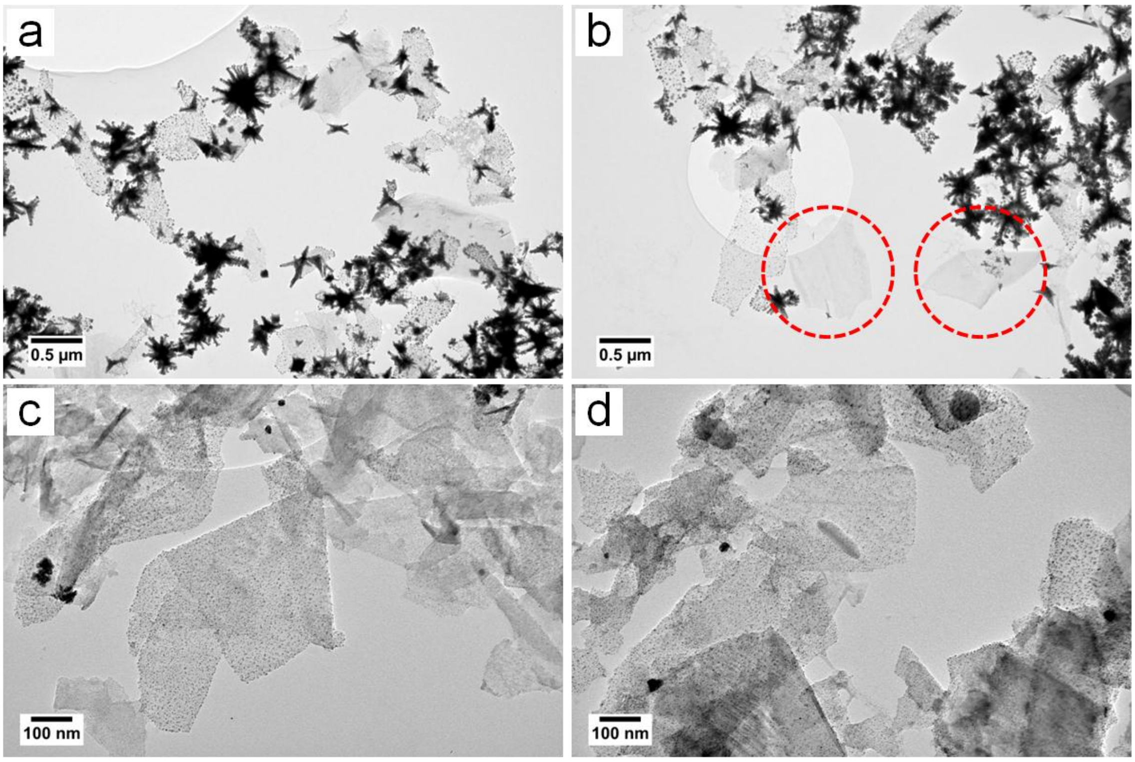

Figure S2. TEM images of Pd-NPs decorated graphene sheets with excess calixarene (a and b) and (c and d) after removing excess *p*-H_2O_3P-calix[8]arene.

S3 Additional XPS zoomed-in regions

The zoomed-in XPS P2p and Cl2p regions of Pd(II)/*p*-H_2O_3P-calix[8]arene/graphene before and after hydrogen reduction are shown in Figure S3. As shown in Figure S3a, the P2p peaks are evident in both of the samples, which indicates the present of *p*-H_2O_3P-calix[8]arene. The Cl2p regions in Figure S3b show that only the Cl2p peak is present in sample 1.

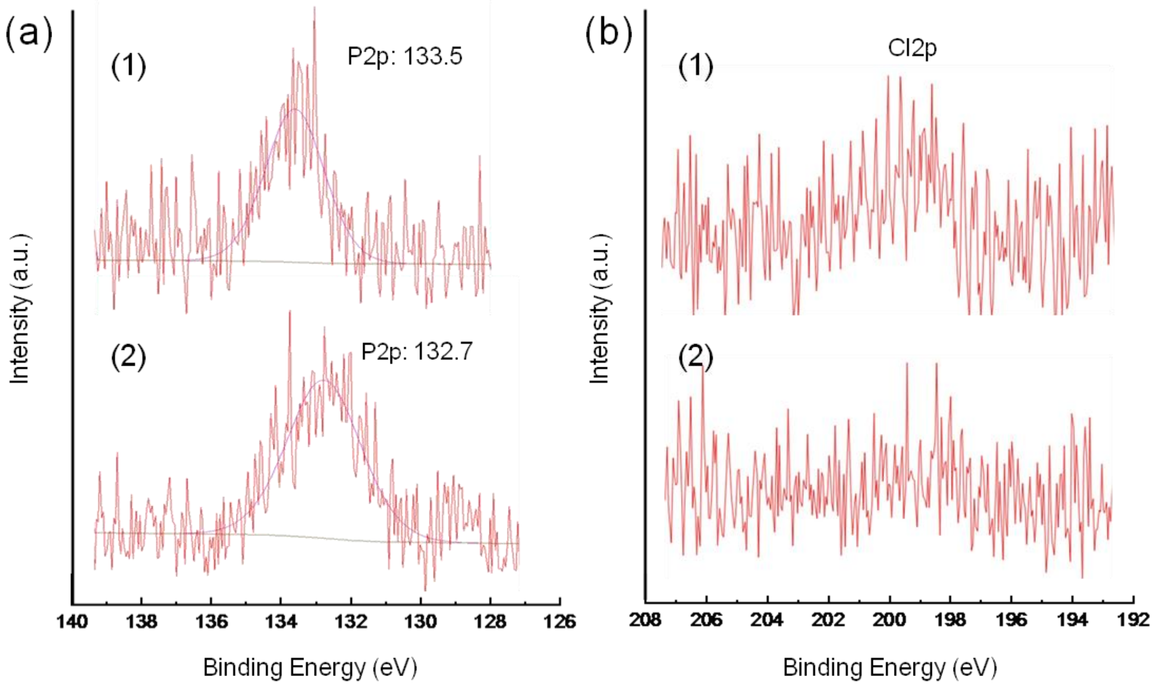

Figure S3. P2p (a) and Cl2p (b) zoomed-in regions of the Pd(II)/*p*-H_2O_3P-calix[8]arene/graphene (1) before and (2) after hydrogen reduction.

S4 Molecular modeling

Materials Studio V6.0 was used for the molecular modelling of solvated *p*-H_2O_3P-calix[8]arene in the presence of H_2PdCl_4 at physiological pH. A periodic water cell with a final density of 1.0 g/ml was setup with 1 *p*-H_2O_3P-calix[8]arene to 4 molecules of H_2PdCl_4 to counter balance the charge for all the phosphonic acid groups with a single deprotonated hydrogen, Figure S4a. The charge on the calix[8]arene was set to -8 as would be the case in pH 7.2. The Discover module was used to optimize the system using the PCFF forcefield and the Conjugate Gradient method with 500,000 iterations using the Polak-Ribiere algorithm and a convergence of 0.1 kcal/mol/Å. A molecular dynamics simulation was carried out to see the distribution of distances between the Pd^{2+} in the presence of the calix[8]arene. The NVT ensemble was used at 298 K with a time step of 1.0 fs and 100,000 steps. The distance distribution between the Pd^{2+} shows the most probable distance around 2 nm, Figure S4b.

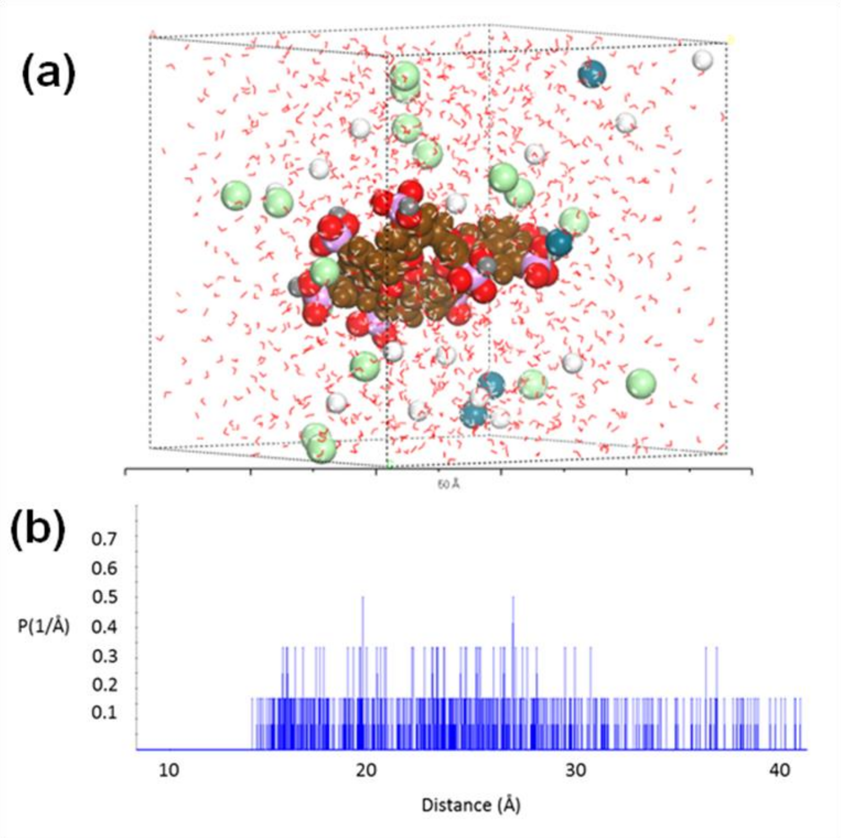

Figure S4. (a) Diagram showing initial system setup. *p*-H_2O_3P-calix[8]arene shown in brown with the phosphonic acid phosphorus in purple, phosphonic acid oxygens in red and phosphonic acid hydrogens in grey. Pd^{2+} is shown in turquoise and Cl^- in green. White balls represent H^+ added onto H_2O to give H_3O^+. (b) Distribution of distances between the Pd^{2+} in the presence of *p*-H_2O_3P-calix[8]arene.

S5 Cyclic voltammogram of the nano-composites

A cyclic voltammogram of the nano-composites on a modified glassy carbon electrode (GCE) in 1 M H_2SO_4 solution is shown in Figure S5a, ESI. The forward anodic sweep has the expected peaks associated with hydrogen desorption, PdOH formation and PdO formation at ~ -0.1 V, 0.5 V and at greater than 0.9 V vs Ag/AgCl respectively. The backward cathodic sweep shows the expected peaks for oxygen desorption and hydrogen adsorption at ~0.4 V and -0.1 V vs Ag/AgCl respectively. All peaks are well defined at 200 mV/s indicating a large exposed Pd surface area and excellent electrical connectivity. Control testings with Pd metal and blank GC electrodes have been carried out, as indicated in Figure S5b. The result shows that the Pd/graphene nano-composites based electrode is electrocatalytically active compared with the blank glassy carbon electrode. It is believed that the potential of Pd/graphene nano-composites electrode will be further discovered and improved for suitable applications.

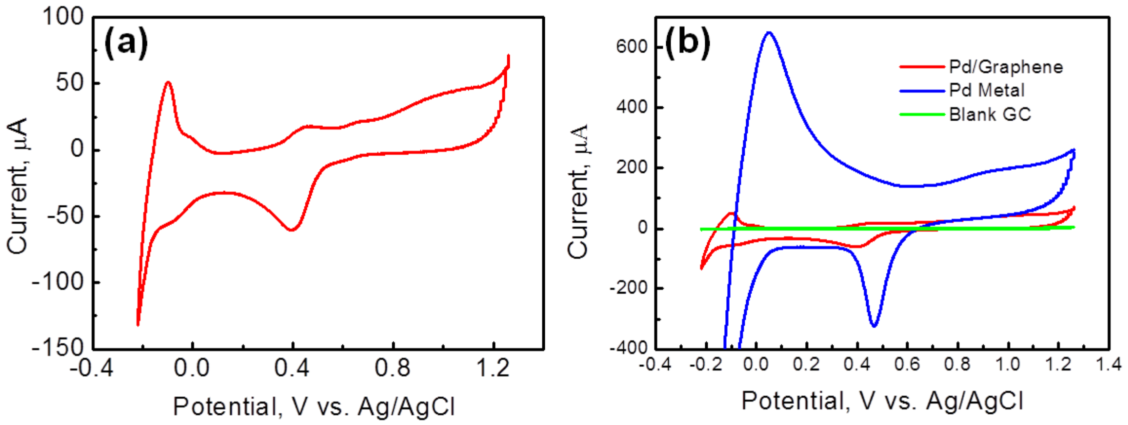

Figure S5. Cyclic voltammogram of (a) electrode coated with Pd-NPs/*p*-H_2O_3P-calix[8]arene/graphene nano-composite, and (b) a combination of Pd/graphene nano-composites, Pd metal, and blank GC electrodes within 1 M H_2SO_4 solution, at a scan rate of 200 mV/s.

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**, 1478-1483.

2 J. Zou, K. S. Iyer and C. L. Raston, *Small*, 2010, **6**, 2358-2361.