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Supporting Information

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The Origin of Shape Sensitivity in Palladium-Catalyzed Suzuki–Miyaura Cross Coupling Reactions**

Gillian Collins, Michael Schmidt, Colm O'Dwyer, Justin D. Holmes, and Gerard P. McGlacken**

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Supporting Information

Nanocrystal Synthesis and Immobilization

Shape controlled nanocrystals used in this study were prepared according to literature several procedures.[1] Synthesis of Pd nanocubes: 105 mg of PVP (Mw ~ 55,000), 60 mg of ascorbic acid and 300 mg of KBr were dissolved in 8 ml of water. The mixture was heated for 10 min at 80 °C, under stirring followed by addition of 57 mg Na_2PdCl_4 in 3 ml of water. The solution was heated to 80 °C and aged for 3 h after which the product was collected by centrifugation, washed with water and briefly sonicated. This purification procedure was repeated 3 times. Finally, the nanocubes were re-dispersed in 11 ml of water. Synthesis of 20 nm cubes followed the same procedure with the addition of 600 mg of KBr. Octahedra and cuboctahedra were prepared from cubic Pd seeds. 105 mg of PVP, 100 µl of formaldehyde and 0.3 ml of seed solution were added to 8 ml of water and heated to 60 °C. Varying amounts of Na_2PdCl_4 dissolved in 3 ml of water were added to obtain cuboctahedra (8.7 mg) or octahedral (29 mg). The reaction was kept at 60 °C for 3 h and the products were collected and purified by the procedure previously described. The nanocrystals were immobilized on carbon by stirring the solution in the presence of activated carbon at room temperature, which has been previously dried in a vacuum oven at 120 °C. The product was collected by filtration and dried under vacuum. Similar Pd loadings, as determined by ICP, were used in the reaction. The average Pd loading was 3.6 wt%, with not more the 0.2 wt% difference between each catalyst sample.

Suzuki-Miyaura Cross Coupling Reactions

In a typical experiment 0.268 g of phenylboronic acid (2.2 mmol). 0.468 g of 4-methoxyiodobenzene or 0.25 ml of 4-methoxybromobenezene (2 mmol), 0.553 g (4 mmol) of K_2CO_3 were added to 30 ml of ethanol/water (3:1). The reactions were initiated by addition

of the catalyst (0.5 mol %). Reactions were conducted at room temperature and sampled at regular intervals for GC analysis. Samples were analyzed using an Agilent 7890A GC system, equip with a flame ionisation detector (FID). Products were identified against authenticated standards and quantified by calibration to obtain response factors (RF) against the known internal standard (dodecane).

Materials Characterization:

Electron Microscopy.

Scanning electron microscopy (SEM) images were obtained using a FEI DualBeam Helios NanoLab 600i high resolution SEM. Transmission electron microscopy (TEM) analysis was performed using a Jeol 2100 transmission electron microscope at an operating voltage of 200 kV.

X-ray Photoelectron Spectroscopy.

XPS data was acquired using a KRATOS AXIS 165 monochromatized (Al Kα = 1486.6 eV) x-ray photoelectron spectrometer. Spectral fitting was carried out on using CASA software. All spectra were referenced to the C 1s spectrum at a binding energy (BE) of 284.6 eV. The photoemission data was processed using a Shirley background correction. The high resolution Pd 3d core level spectra were fit to asymmetric Gaussian-Lorentzian profiles. The Pd(0) peak was fixed at a binding energy of 335.4 eV with a FWHM of 0.9.

Table S1. Statistics of surface atoms and surface sites on cubic, cuboctahedral and octahedral Pd NCs.

Nanocrystal	**N_{tot} [a]**	**N_{surf} [b]**	**N_{e+c} [c]**	**% surf**	**% e+c**	**yield [d] %**	**TOF_{tot} [e]**	**TOF_{surf} [f]**
cubes	515151	30002	596	5.82	0.16	94	6.2	106
octahedra	316394	23718	918	7.5	0.29	58	3.8	52
cuboctahedra	702219	42012	1404	6.0	0.2	79	5.3	88

Calculations for cubic and octahedral nanocrystals are based on equations derived by Hartog and van Hardeveld assuming a perfect face centred cubic lattice.[2] Calculations for the cuboctahedra nanocrystals were based on the work of Benfield for a cuboctahedron consisting of 6 square and 8 triangular faces.[3] [a] m is the number of atoms lying on an equivalent edge including the corner atoms. [b] N_{tot} is the total number of atoms in each nanocrystal (cubic: $N_{tot} = 4m^3 - 6m^2 + 3m$; octahedral, $N_{tot} = 1/3m(2m^2 + 1)$ and cuboctahedral $N_{tot} = 1/3(2m - 1)(5m^2 - 5m + 3)$. [c] N_{surf} is the number of surface atoms (cubic $N_{surf} = 12m^2 - 24m + 14$; octahedral $N_{surf} = 4m^2 - 8m + 6$ and cuboctahedral $N_{surf} = 10m^2 - 20m + 12$). N_{e+c} is the number of edge and corner atoms. Cubic: $N_{e+c} = 12(m - 2) + 8$; octahedral $N_{e+c} = 12(m - 2) + 6$; cuboctahedral $N_{e+c} = 24(m - 2) + 12$. [d] Percentage yield after 30 h (determined by GC). [e] TOF_{tot} is the turnover frequency calculated from molar equivalents of Pd (0.5 mol%). [f] TOF_{surf} are the turnover frequencies normalized to the total number of surface atoms on each polyhedron.

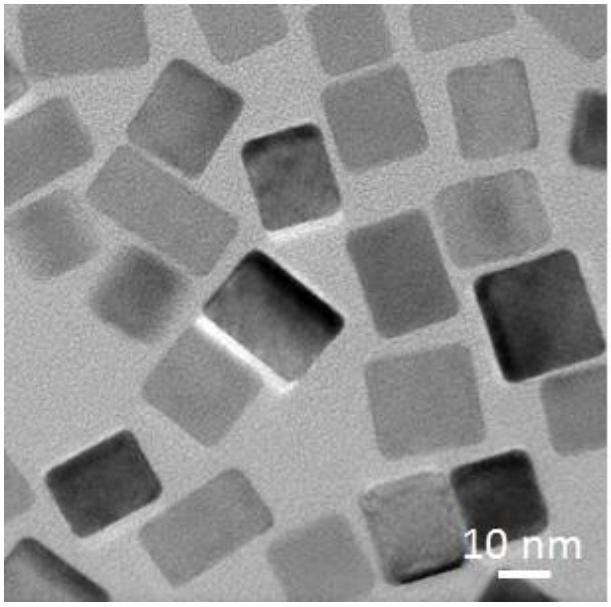


Fig. S1 TEM of (a) as-synthesized unsupported Pd cubic NCs.

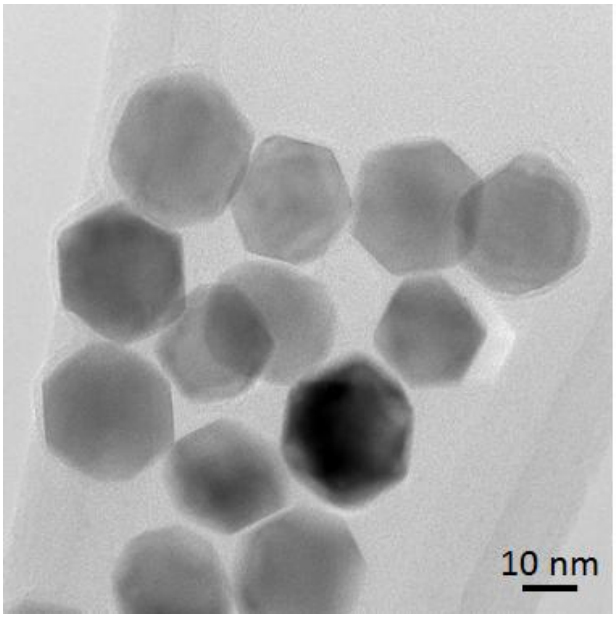


Fig. S2. TEM of (a) as-synthesized unsupported Pd cuboctahedra NCs.

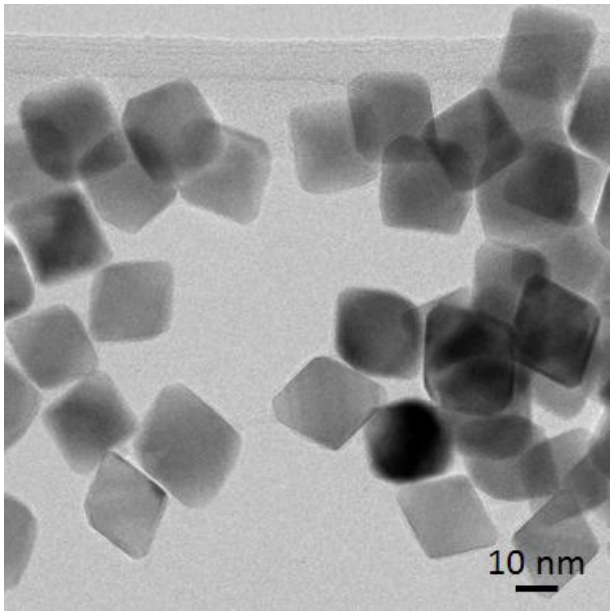


Fig. S3. TEM of (a) as-synthesized unsupported Pd octahedral NCs.

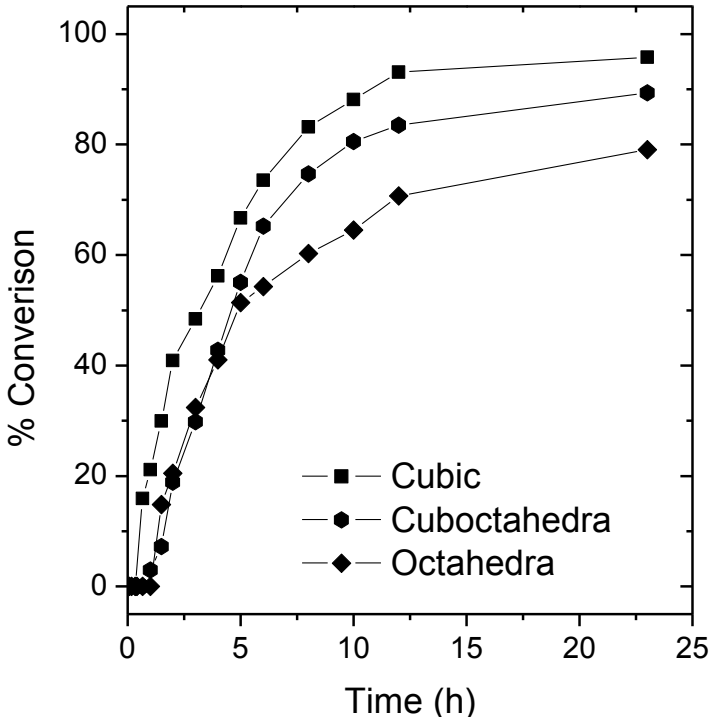


Figure S4. Reaction profile of Suzuki coupling of 4-iodoanisole and phenyl boronic acid catalysed by cubic, cuboctahedral and octahedral Pd NCs.

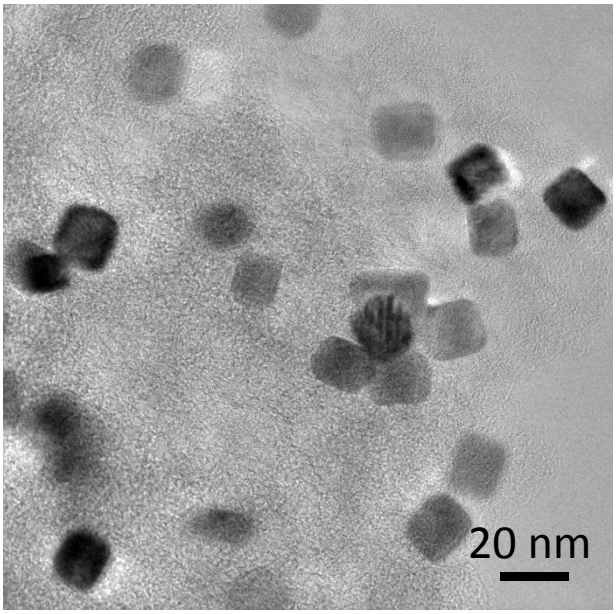


Figure S5. Cubic Pd NCs after Suzuki coupling reaction.

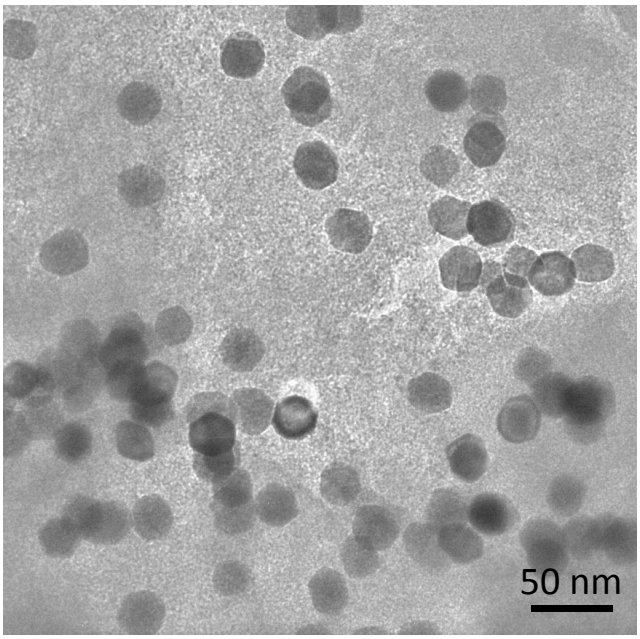


Figure S6. Cuboctahedral Pd NCs after Suzuki coupling reaction.

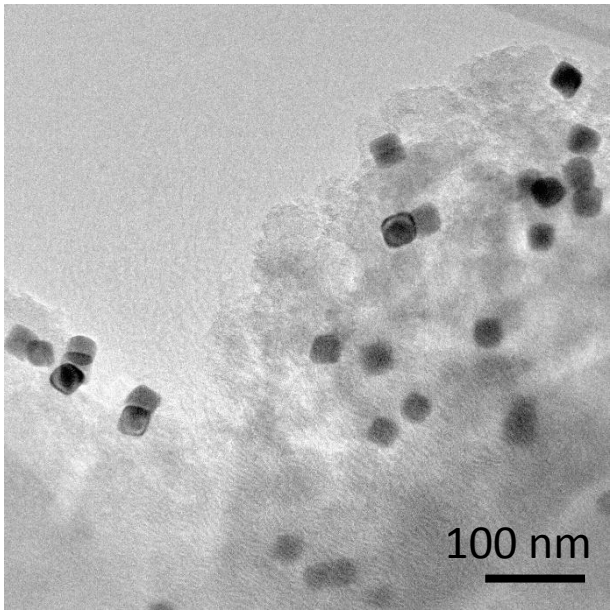


Figure S7. Octahedral Pd NCs after Suzuki coupling reaction.

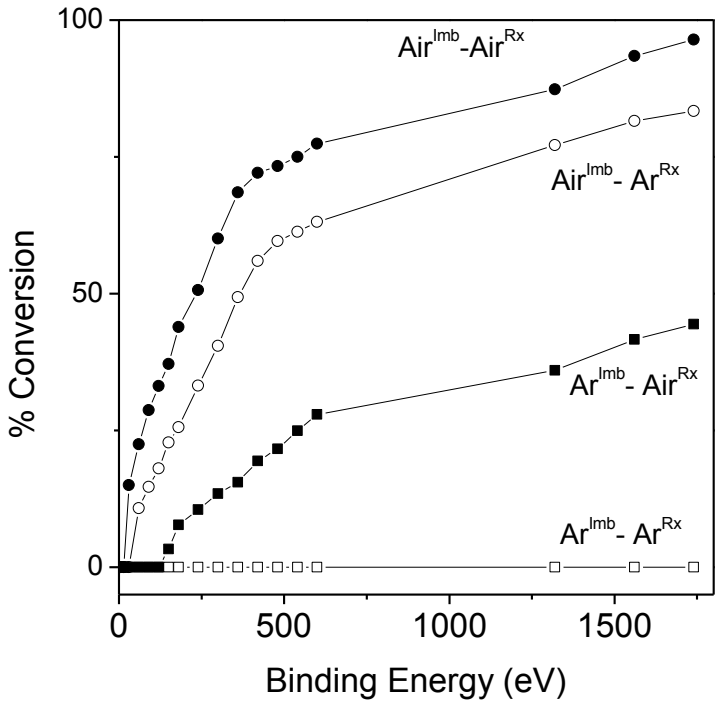


Figure S8. Reaction profile of 4-iodoanisole and phenylboronic acid using cubic Pd NCs.

Table S2. ICP analysis of reaction filtrates using cubic Pd NCs immobilized and reacted under air or Ar.

Reaction	[Pd]/ ppm
Air^{Imb}-Air^{Rx}	1.22
Air^{Imb}-Ar^{Rx}	0.63
Ar^{Imb}-Air^{Rx}	0.61
Ar^{Imb}-Ar^{Rx}	0.12

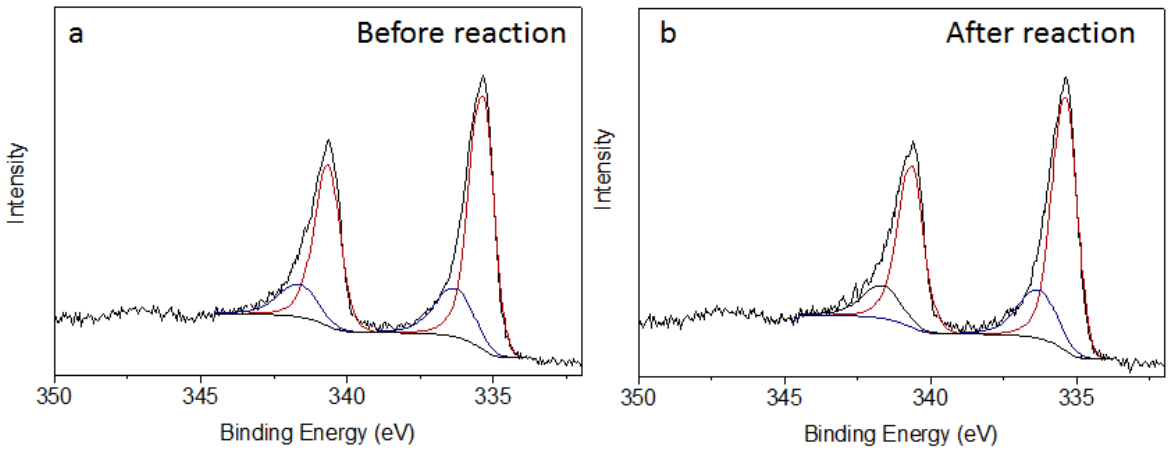


Figure S9. Pd 3d core level spectra of Pd NCs immobilized under Ar (a) before reaction and (b) after reaction under Ar.

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[1] a) M. Jin, H. Zhang, Z. Xie, Y. Xia, *Energy Environ. Sci.* **2012**, *5*, 6352; b) M. Jin, H. Zhang, Z. Xie, Y. Xia, *Angew. Chem. Int. Ed.* **2011**, *50*, 7850.

[2] R. Vanharde, F. Hartog, *Surf. Sci.* **1969**, *15*, 189.

[3] R. E. Benfield, *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 1107.