Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Seeded Growth and Catalytic Properties of Highly Branched Palladium Nanostructures.

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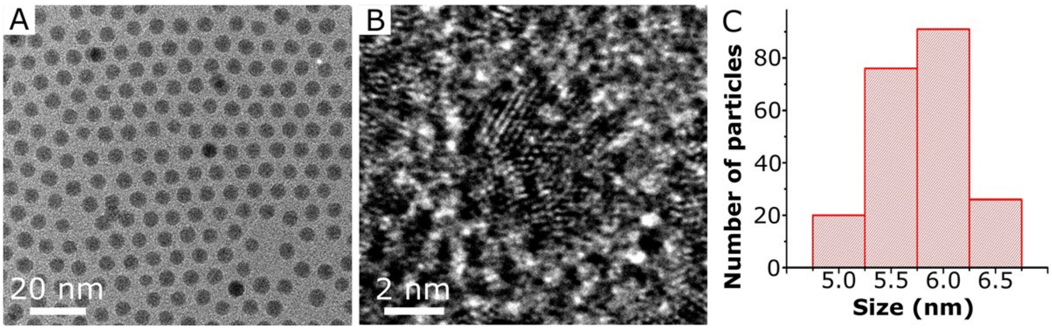


Figure S1: Palladium nanocrystals with an average size 5.8 ± 0.4 nm were used as seeds for the subsequent growth of palladium nanocrystals. a) Low magnification TEM image of Pd seeds. b) High-resolution TEM image of a single Pd seed showing their polycrystalline nature. c) Histogram showing the size distribution of the Pd seeds, with an average size of 5.8 ±0.4 nm.

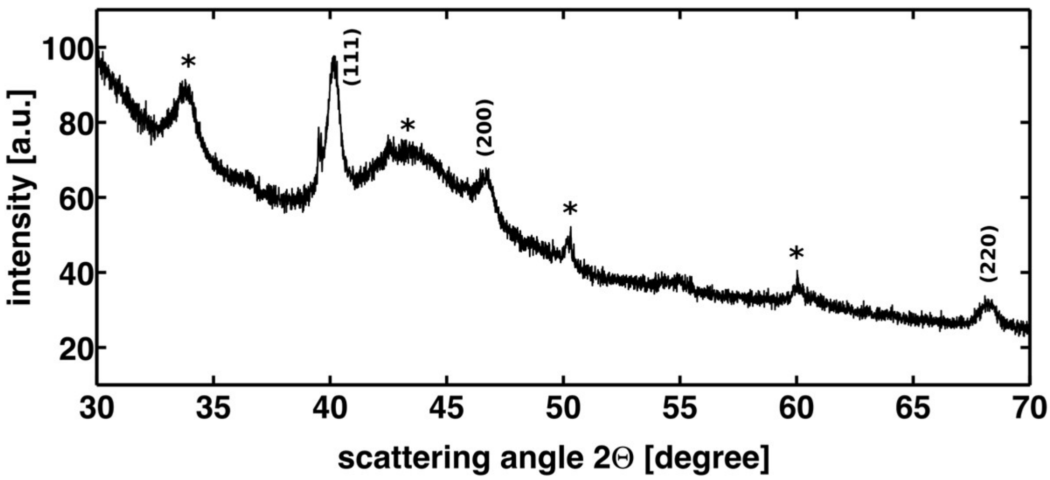


Figure S2: XRD plot of the branched Pd nanostructures loaded onto a carbon support. The high background is from the presence of the carbon support. The peaks labeled with * are due to graphitized carbon. The peaks located at 40.1°, 46.6° and 68.1° are assigned to the (111), (200) and (220) crystal facets of fcc Pd respectively.

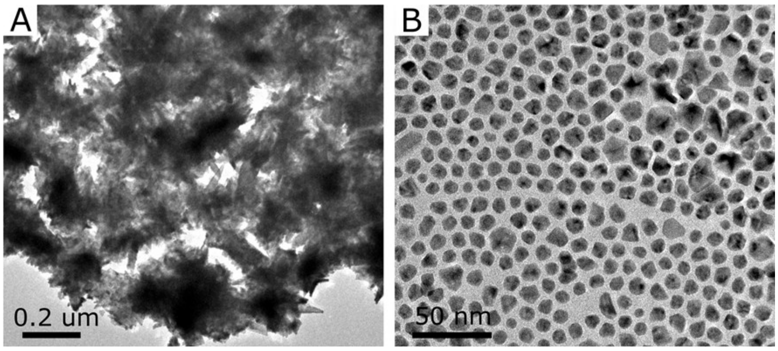


Figure S3: Effect of changing the capping agent. a) Nanoparticles obtained from only oleic acid (10 eq.) as the capping ligand. NC's are branched and extremely large, >0.2 um. b) Particles produced from using only oleylamine (10 eq.) as the capping agent. NC's appear to be well faceted and small (around 10 nm).

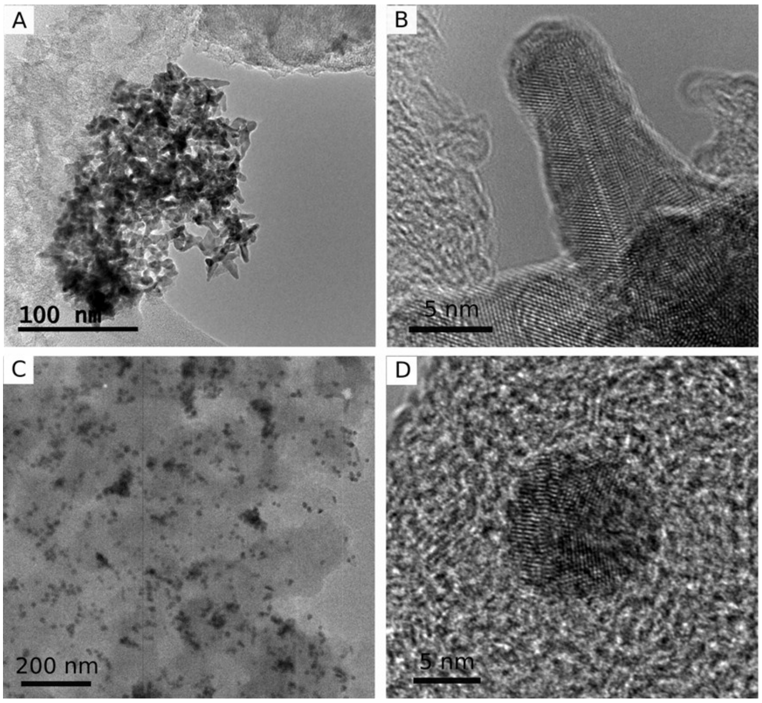


Figure S4: Nanocrystals loaded on carbon. a) Low-resolution TEM image of branched NC's loaded on carbon support, b) high-resolution TEM image of a single branched NC loaded on carbon support, showing that the structure has been retained, c) Low-res TEM image of Pd Icosahedra loaded on carbon support, d) High-resolution TEM image of a single Pd Icosahedra loaded on carbon support, showing that structure has been retained.

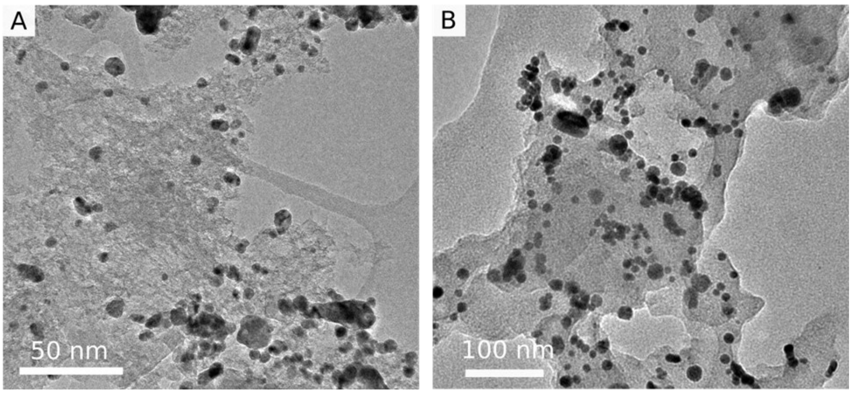


Figure S5: TEM images of Nanocrystals loaded on carbon after heat treatment (In air, at 200°C for 3 hrs). a) Low-resolution TEM image of branched NC's loaded on carbon support after HT. NC's have not retained their shape, b) Low-resolution TEM image of Pd icosahedra NC's loaded on carbon support after HT. NC's have not retained their shape, and there is evidence of NC sintering.

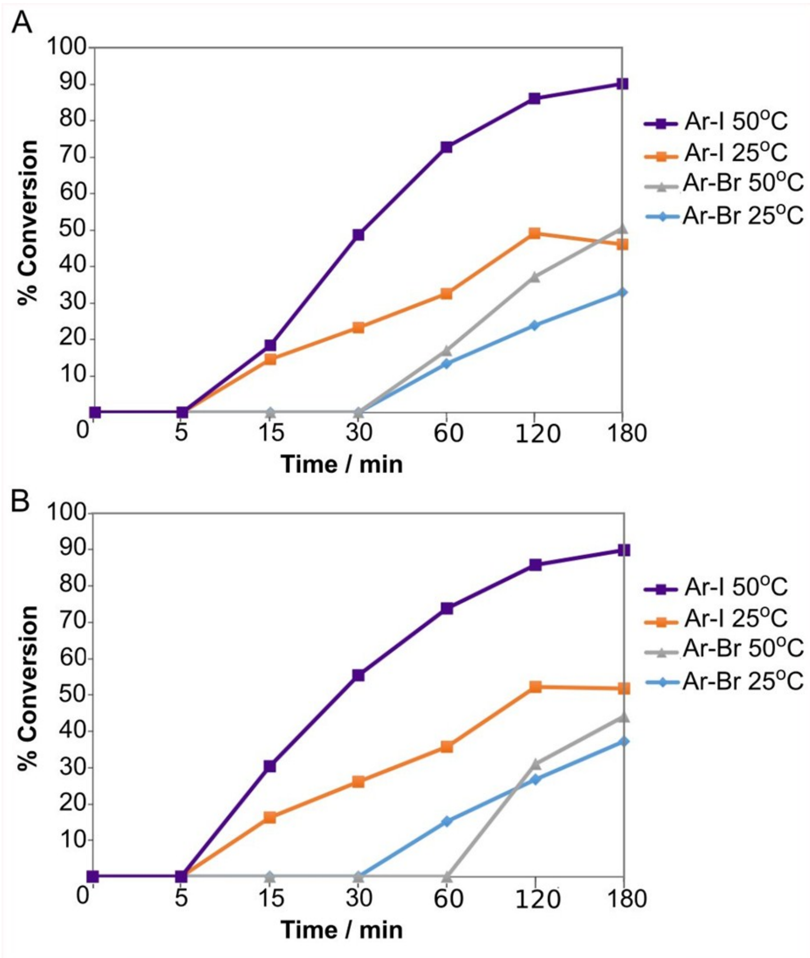
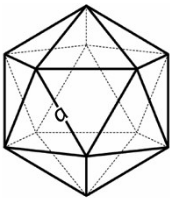


Figure S6: % Conversion vs. Reaction time, indicating the lag times for the Suzuki coupling of 4-methoxyiodobenzene and 4-methoxybromobenzene with phenylbornic acid at 25 and 50°C. for a) Branched Pd Nanostructures and b) Pd Icosahedra.

Turn-Over-Frequency (TOF) Calculations

Calculation of the TON_{surf} and TOF_{surf} for the Pd icosahedra nanocatalysts



The Pd icosahedra synthesized here have an average size of 12.9 nm.
Therefore, the edge length, a, is:

$$r = \frac{a}{4}\sqrt{10 + \sqrt[2]{5}}$$

$$\frac{r}{0.951} \quad \frac{6.45}{0.951}$$

a) <u>Total number of Pd atoms in one Pd icosahedron, TNA_{ico}, is:</u>

Palladium has a face-centered-cubic structure and a lattice constant of 0.389 nm. Each volumetric unit cell contains the equivalent of 4 Pd atoms.

The volume of a single Pd icosahedron is:

$$V_{ico} = \frac{5(3+\sqrt{5})}{12} a^3 = \frac{5(3+\sqrt{5})}{12} (6.78 \text{ nm})^3 = 680.7 \text{ nm}^3$$

The volume of the Pd unit cell, is:

$$V_{cell} = (0.389 \text{ nm})^3 = 0.0589 \text{ nm}^3$$

Therefore, the number of atoms in a single Pd icosahedron is:

$$TNA_{ico} = \frac{V_{ico}}{V_{cell}} \text{ x No. Pd atoms in unit cell} = \frac{680.7\ nm^3}{0.0589\ nm^3} \text{ x } 4 = 46228.3$$

b) <u>Number of Pd atoms on the surface of a single Pd icosahedron:</u>

An icosahedron is composed of 20 equilateral triangle faces. The smallest repeating unit on a 2-D {111} facet is an equilateral triangle, which contains 2 equivalent Pd atoms.
The lattice parameter for Pd is 0.389 nm. Therefore, the number of atoms at the surface of a single icosahedron is:

$$NSA_{ico} = \frac{A_{ico}}{A_{cell}} \text{ x No. Pd atoms in unit cell} = \frac{398.5\ nm^2}{0.131\ nm^2} \text{ x } 2 = 6079.6$$

Where:

$$A_{ico} = [\frac{\sqrt{3}}{4} a^2] \text{ x } 20 = \frac{5}{\sqrt{3}} a^2 = \frac{5}{\sqrt{3}} (6.78 \text{ nm})^2 = 398.5 \text{ nm}^2\text{, and}$$

$$A_{cell} = \frac{\sqrt{3}}{4} a^2 = \frac{\sqrt{3}}{4} (\sqrt{2} \text{ x } 0.389)^2 = 0.131 \text{ nm}^2$$

c) <u>Total number of surface Pd atoms on the Pd icosahedra in the catalytic reaction solution</u>

Moles of Pd used as a catalyst was calculated based on 0.5mol% of the amount of 4-iodoanisole/4-Bromoanisole (1mmol).

Moles of Pd used as a catalyst = 1 mmol x $\frac{1\,mol}{1000\,mmol}$ x $\frac{0.5}{100}$ = 0.000005 mol

Mass of Pd used in a catalytic reaction, M_{Pd} = 0.000005 mol x 106.42$\frac{g}{mol}$ = 0.0005321 g

Mass of one Pd icosahedron, M_{ico} = $\frac{TNAico\ \times\ MwtPd}{6.022x10^{23}} = \frac{46228.3\ \times\ 106.42\ g/mol}{6.022x10^{23}mol}$ = 8.17x10^{-18} g

Tot. No. icosahedra in a catalytic reaction, NI_{cat} = $\frac{M_{Pd}}{M_{ico}} = \frac{0.0005321}{8.17x10^{-18}}$ = 6.51x10^{13}

Therefore, the % atoms on the surface of the Pd icosahedra in the catalytic reaction is:

TNS_{cat} = NI_{cat} x NSA_{ico} = 6.51x10^{13} x 6079.6 = $3.96x10^{17}$

TNA_{cat} = NI_{cat} x TNA_{ico} = 6.51x10^{13} x 46228.3 = $3.01x10^{18}$

% Surface atoms = $\frac{TNS_{cat}}{TNA_{cat}}$ × 100 = $\frac{3.96x10^{17}}{3.01x10^{18}} \times 100 = 13.2$ %

d) Calculating the TON and TOF for Pd Icosahedra

Example: For the catalytic reaction of 4-Iodoanisole at 50°C, The yield is 89.7% at 180min reaction time.
Therefore, the TON normalized to the number of surface Pd atoms, TON_{surf} is:

TON_{surf} = $\frac{Moles\ of\ 4-Iodoanisole\ converted}{Mole\ of\ Surface\ Pd\ atoms\ in\ Cat.rxn.} = \frac{0.001mol\ x\ 0.897}{6.58x10^{-07}}$ = 1364

Where:

Mole of surface atoms of Pd icosahedra = $\frac{No.\ Pd\ atoms\ on\ the\ surface\ of\ the\ icosahedra}{No.Pd\ atoms\ in\ the\ icosahedra}$ x $mole\ of\ Pd\ icosahedra$

= $\frac{3.96x10^{17}}{3.01x10^{18}}$ x 0.000005mol = 6.58x10^{-07} mol

Therefore, the Turnover Frequency normalized to the number of surface Pd atoms, TOF_{surf} is:

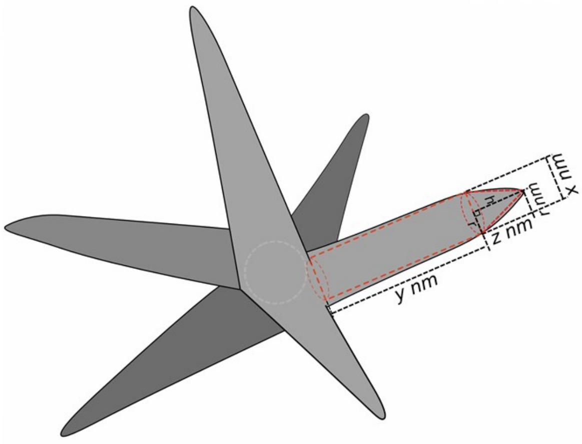
TOF_{surf} = $\frac{TON_{surf}}{180\ min} = \frac{1364}{180}$ = 7.58 min^{-1}

e) Summary table of TON_{surf} and TOF_{surf} for the Pd Icosahedra:

All TOF_{surf} are calculated for 180min.

Reaction	Reaction Temp. (°C)	Yield (%)	TON	TON_{surf}	TOF_{surf} (min^{-1})
Ar-Br	25°C	37.1	74	564	3.13
Ar-I	25°C	44.0	88	669	3.72
Ar-Br	50°C	51.8	104	788	4.38
Ar-I	50°C	89.7	179	1364	7.58

Calculation of the TON_{surf} and TOF_{surf} for the Pd branched nanocatalysts



Measurements obtained from HRTEM
r = 4 nm
x = 8 nm
y = 24 nm
z = h = 5 nm

To complete the geometric calculations of the highly branched Pd nanocrystals, a few assumptions were made, as follows:

- Each particle consists of 6 branches
- Each branch is modelled as a cylinder with a cone on the top
- Each branch radiates from a central point (seed)
- The seed does not contribute to the available surface area, but does contribute to the total volume of the nanoparticle
- Volume of Pd seed (diameter = 5.8 nm) calculated as a sphere

a) Total number of Pd atoms in one branched Pd NP , TNA_{BNC}, is:

Palladium has a face-centered-cubic structure and a lattice constant of 0.389 nm. Each volumetric unit cell contains the equivalent of 4 Pd atoms.

The volume of a single branch is:

$$V_{branch} = V_{cyl} + V_{cone} = (\pi \times 7^2 \times 24) + (\pi \times 7^2 \times 8/3) = 4105 \text{ nm}^3$$

$$V_{BNC} = 6(V_{branch}) + V_{seed} = (6 \times 4105) + (102.2) = 24732.2 \text{ nm}^3$$

Where:

$$V_{seed} = \frac{4}{3}\pi (5.8/2)^3 = 102.2 \text{ nm}^3$$

Therefore, the number of atoms in a single Pd branched nanocrystal is:

$$TNA_{BNC} = \frac{V_{BNC}}{V_{cell}} \text{ x No. Pd atoms in unit cell} = \frac{24732.2\ nm^3}{0.0589\ nm^3} \text{ x } 4 = 1679733.3$$

Where:

$V_{cell} = (0.389\ nm)^3 = 0.0589\ nm^3$

b) Number of Pd atoms on the surface of a single branched Pd NC:

The {115}, {113} and {220} HI facets present on the surface of the branched nanostructures consist of a combination of {111} and {002} facets. To calculate the number of atoms on the surface of these branched nanostructures, we have assumed that the surface consists of ¾ {111} facets and ¼ {001} facets. This has been incorporated into the calculation for the 2-D unit cell area. The smallest repeating unit on a 2-D {111} facet is an equilateral triangle, which contains the equivalent of 2 Pd atoms. The smallest repeating unit on a 2-D {001} facet is a square, which contains the equivalent of 2 Pd atoms. The lattice parameter for Pd is 0.389 nm.
The surface area of a single branch is calculated as a cylinder (less the base and top) and a cone (less the base). We also assume each branched Pd nanostructure has 6 branches, and that the seed doesn't contribute to the surface area of the branched structures.

Based on this, the number of atoms at the surface of a single branched nanocrystal is:

$$NSA_{BNC} = \frac{A_{BNc}}{A_{cell}} \text{ x No. Pd atoms in unit cell} = \frac{7736.1\ nm^2}{0.136\ nm^2} \text{ x } 2 = 113627.7$$

Where:

$$A_{BNC} = 6(A_{cyl} + A_{cone}) = 6[(2\pi \times 7 \times 24) + (\pi \times 7 \times \sqrt{8^2 + 7^2}] = 7736.1\ nm^2$$

$$A_{cell} = \frac{3}{4}(\frac{\sqrt{3}}{4}a^2) + \frac{1}{4}(a^2) = \frac{3}{4}(\frac{\sqrt{3}}{4}(\sqrt{2} \times 0.389)^2 + \frac{1}{4}(0.389^2) = 0.136\ nm^2$$

c) Total number of surface Pd atoms on the Pd icosahedra in the catalytic reaction solution

Moles of Pd used as a catalyst was calculated based on 0.5mol% of the amount of 4-iodoanisole/4-Bromoanisole (1mmol).

$$\text{Moles of Pd used as a catalyst} = 1 \text{ mmol x } \frac{1\ mol}{1000\ mmol} \text{ x } \frac{0.5}{100} = 0.000005 \text{ mol}$$

$$\text{Mass of Pd used in a catalytic reaction, } M_{Pd} = 0.000005 \text{ mol x } 106.42 \frac{g}{mol} = 0.0005321 \text{ g}$$

$$\text{Mass of one branched Pd NP, } M_{BNC} = \frac{TNA_{BNP} \times MwtPd}{6.022x10^{23}} = \frac{1679733 \times 106.42\ g/mol}{6.022x10^{23} mol} = 2.97\text{x}10^{-16} \text{ g}$$

Tot. No. branched Pd NP's in a catalytic reaction, $NBNC_{cat} = \frac{M_{Pd}}{M_{BNP}} = \frac{0.0005321}{2.97x10^{-16}} = 1.79x10^{12}$

Therefore, the % atoms on the surface of the Pd icosahedra in the catalytic reaction is:

$TNS_{cat} = NBNC_{cat} \times NSA_{BNC} = 1.79x10^{12} \times 113627.7 = 2.04x10^{17}$

$TNA_{cat} = NBNC_{cat} \times TNA_{BNC} = 1.79x10^{12} \times 167933.3 = 3.01x10^{18}$

$$\% \text{ Surface atoms} = \frac{TNS_{cat}}{TNA_{cat}} \times 100 = \frac{1.59x10^{17}}{3.01x10^{18}} x\ 100 = 6.8\ \%$$

<u>d) Calculating the TON and TOF for Pd Icosahedra</u>

Example: For the catalytic reaction of 4-Iodoanisole at 50°C, The yield is 90% at 180min reaction time.
Therefore, the TON normalized to the number of surface Pd atoms, TON_{surf} is:

$$TON_{surf} = \frac{Moles\ of\ 4 - Iodoanisole\ converted}{Mole\ of\ Surface\ Pd\ atoms\ in\ Cat.rxn.} = \frac{0.001mol\ x\ 0.90}{3.38x10^{-07}} = 2661$$

Where:

$$\text{Mole of surface atoms of Pd icosahedra} = \frac{No.\ Pd\ atoms\ on\ the\ surface\ of\ the\ BNC}{No.Pd\ atoms\ in\ the\ BNC} \times mole\ of\ Pd\ BNC$$

$$= \frac{2.04x10^{17}}{3.01x10^{18}} \times 0.000005\text{mol} = 3.38x10^{-07} \text{ mol}$$

Therefore, the Turnover Frequency normalized to the number of surface Pd atoms, TOF_{surf} is:

$$TOF_{surf} = \frac{TON_{surf}}{180\ min} = \frac{2661}{180} = 14.78\ \text{min}^{-1}$$

<u>e) Summary table of TON_{surf} and TOF_{surf} for the branched Pd nanocrystals:</u>

All TOF_{surf} are calculated for 180min.

Reaction	Reaction Temp. (°C)	Yield (%)	TON	TON_{surf}	TOF_{surf} (min^{-1})
Ar-Br	25°C	33.0	66	976	5.42
Ar-I	25°C	50.4	101	1490	8.28
Ar-Br	50°C	46.0	92	1360	7.56
Ar-I	50°C	90.0	180	2661	14.78