

Supporting Information

Green chemistry and first-principles theory enhance catalysis: Synthesis and 6-fold catalytic activity increase of sub-5 nm Pd and Pt@Pd nanocubes

Valentina Mastronardi^{1,2,⊥}, Junseok Kim^{3,⊥}, Marina Veronesi^{4,5}, Tania Pomili^{1,2}, Francesco Berti⁴, Gayatri Udayan^{6,7}, Rosaria Brescia⁸, Justus S. Diercks⁹, Juan Herranz⁹, Tiziano Bandiera⁴, Kristen A. Fichthorn^{3,*}, Pier Paolo Pompa¹, Mauro Moglianetti^{1,7, •,*}

1. *Nanobiointeractions&Nanodiagnostics, Istituto Italiano di Tecnologia, Via Morego 30 – 16163 Genova, Italy*

2. *Department of Chemistry and Industrial Chemistry, University of Genova, Via Dodecaneso 31, 16146 Genova, Italy*

3. *Department of Chemical Engineering, The Pennsylvania State University, University Park, Pennsylvania 16802, United States*

4. *D3-PharmaChemistry, Istituto Italiano di Tecnologia, 16163 Genoa, Italy*

5. *Structural Biophysics And Translational Pharmacology Facility, Istituto Italiano di Tecnologia, 16163 Genoa, Italy*

6. *Department of Engineering for Innovation, University of Salento, Via per Monteroni, 73100 Lecce, Italy*

7. *Center for Bio-Molecular Nanotechnologies, Istituto Italiano di Tecnologia, Via Barsanti 14 – 73010 Arnesano (Lecce), Italy*

8. *Electron Microscopy Facility, Fondazione Istituto Italiano di Tecnologia, Via Morego 30, 16163 Genova, Italy*

9. *Electrochemistry Laboratory, Paul Scherrer Institut, Forschungsstrasse 111, 5232 Villigen-PSI, Switzerland*

⊥ Equally Contributing Authors

• Current address: *Institute for the Study on Nanostructured Materials (ISMN), National Research Council (CNR), Via Gobetti 101, 40129 Bologna, Italy*

* mauro.moglianetti@hiqnano.com, fichthorn@psu.edu

Table of Contents

1.	Synthetic methods and TEM characterization	3
1.1.	Pd Seed Synthetic Procedure	3
1.2.	Pt Seed Synthetic Procedure	3
1.3.	Synthesis procedure of 3 nm, 5 nm and 20 nm Nanocubes.	4
1.3.1.	3 nm Nanocubes	4
1.3.2.	5 nm Nanocubes	5
1.3.3.	17 nm Nanocubes	6
1.4.	Role of seeds morphology	7
1.5.	Synthetic methods at different concentration of KBr	7
1.6.	Synthetic methods at different concentrations of KBr	9
1.6.1.	Shapes modulation at increasing KBr concentration	9
1.6.2.	40 mM KBr	10
1.6.3.	54mM KBr	10
1.7.	Open vessel	11
1.8.	Role of ascorbic acid in the growth of nanocubes	11
1.9.	Shape modulation by increasing the concentration of formic acid	11
2.	Synthetic Procedure for the scale-up using Flexiwave Microwave Reactor	12
2.1.	5 nm Pd citrate-capped Nanocrystal Scale-Up method	12
2.2.	3 nm Pt citrate-capped Nanocrystal Scale-Up method	12
3.	DFT Calculations	13
4.	Electrochemical characterization	16
5.	NMR	18

1. Synthetic methods and TEM characterization

1.1. Pd Seed Synthetic Procedure

Pd seeds were synthesized by adding 80 μL of PdCl_2 acidic solution (56.4mM) (Sigma-Aldrich) to 130 mL of MilliQ water at room temperature, immediately followed by a quick addition of 8.8 mL solution containing 0.03 M sodium citrate and 2 mM citric acid and 550 μL of freshly prepared NaBH_4 (0.02 M). The vessel was placed in glycerol bath already at 105 $^\circ\text{C}$ to obtain a quick reduction of the Pd ions. The reaction was kept at these conditions for 10 minutes under magnetic stirring at moderate rate. The vessel was then removed from the glycerol bath and left to cool under stirring for another hour.

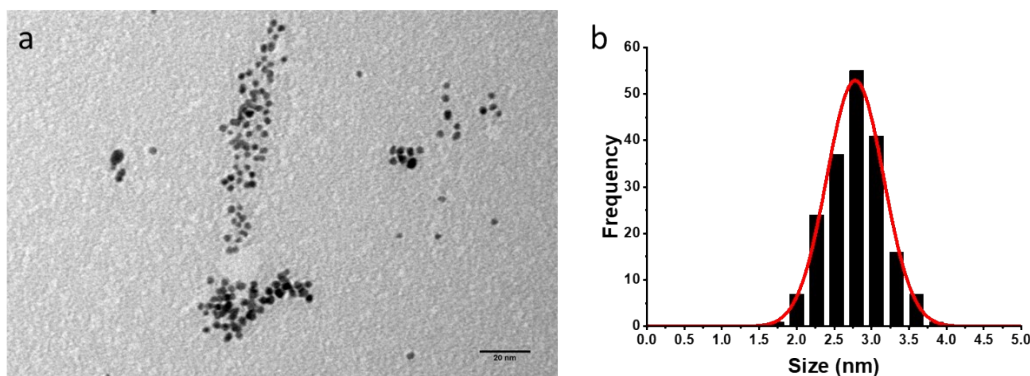


Figure S1. TEM images of Palladium seeds (a) and size distribution analysis (b).

1.2. Pt Seed Synthetic Procedure

The procedure for the Pt seeds is by adding 35 μL hexachloroplatinic acid aqueous solution at 0.5 M to 90mL of MilliQ water at 90 $^\circ\text{C}$. After 1 min, 2mL of solution containing sodium citrate 1% and citric acid 0.05% was added, immediately followed by a quick addition of 2mL freshly prepared NaBH_4 (0.08%). After 10 minutes, the solution was cooled to room temperature.

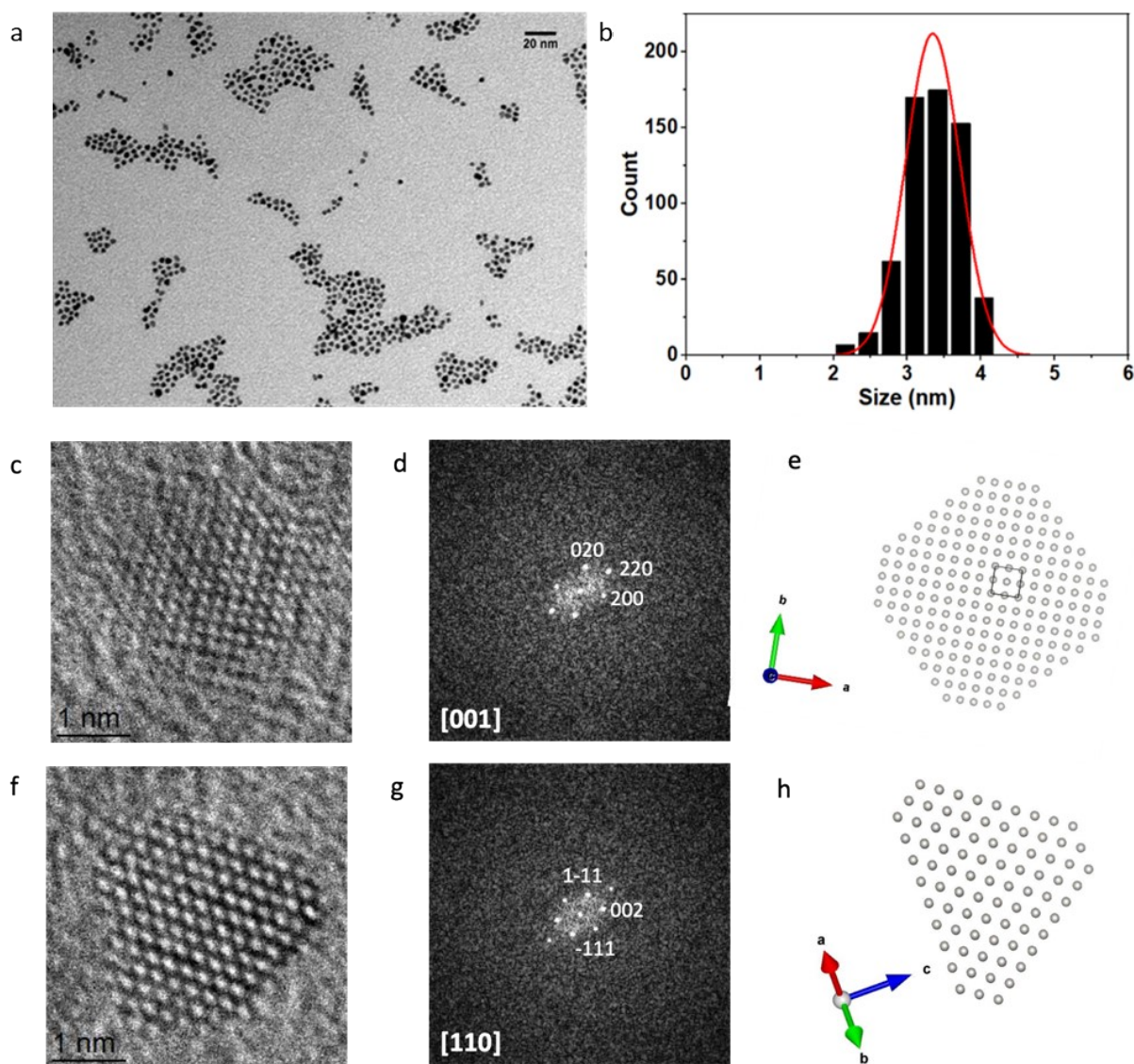


Fig. S2. TEM images of Platinum seeds (a) and size distribution analysis (b). (c, f) HR-TEM images of pyramidal seeds in the sample and (d, g) corresponding FFT patterns, indexed according to cubic Pt (ICSD 41525). (e, h) Projections along zone-axes corresponding to the HRTEM images of the schematic model of a 3.4 nm-base edge slightly truncated pyramidal Pt seed, with a square {001} base and four triangular {111} facets, in agreement with the HR-TEM observations, obtained using VESTA.

1.3. Synthesis procedure of 3 nm, 5 nm and 20 nm Nanocubes.

1.3.1. 3 nm Nanocubes

The synthesis was performed in a sealed glass container (ACE glass pressure reactor with Teflon cap). Platinum nanocrystals seeds (4 mL) were added to 120 mL of MilliQ water at room temperature together with 159 μL of Pd (II) acetate (0.05 M) and 1 mL of a solution containing 0.34 M sodium citrate, 0.2 M formic acid and 0.5 mM L-ascorbic acid. After 1 minute, 1.6 mL of 0.5 M KBr was added in the solution. The vessel was then sealed, placed in a glycerol bath at 105°C for 3 minutes. The reaction was kept for 10 minutes under stirring at moderate rate. After, the solution was cooled to room temperature.

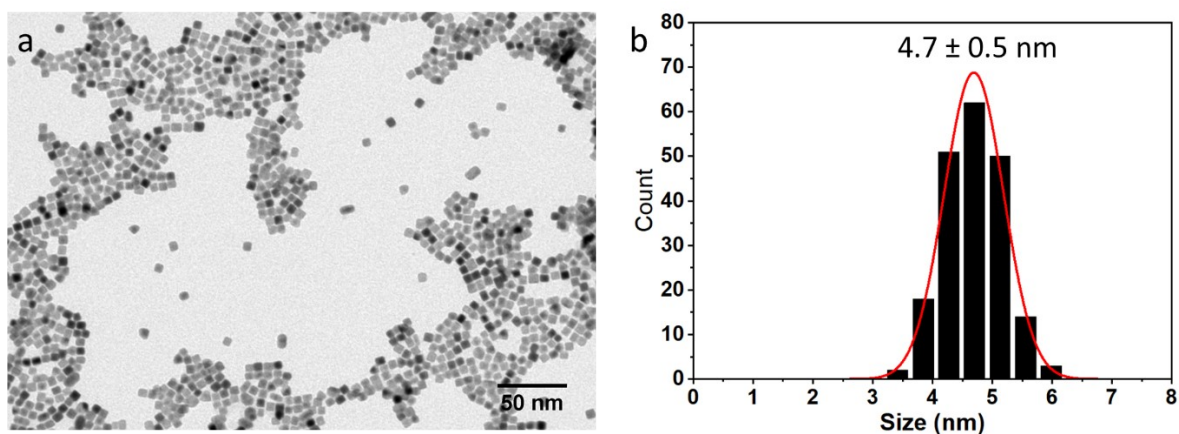


Figure S3. TEM images of 3 nm Pd nanocubes (a) and diagonal size distribution analysis (b).

1.3.2. 5 nm Nanocubes

The synthesis was performed as reported in material and methods of the main text.

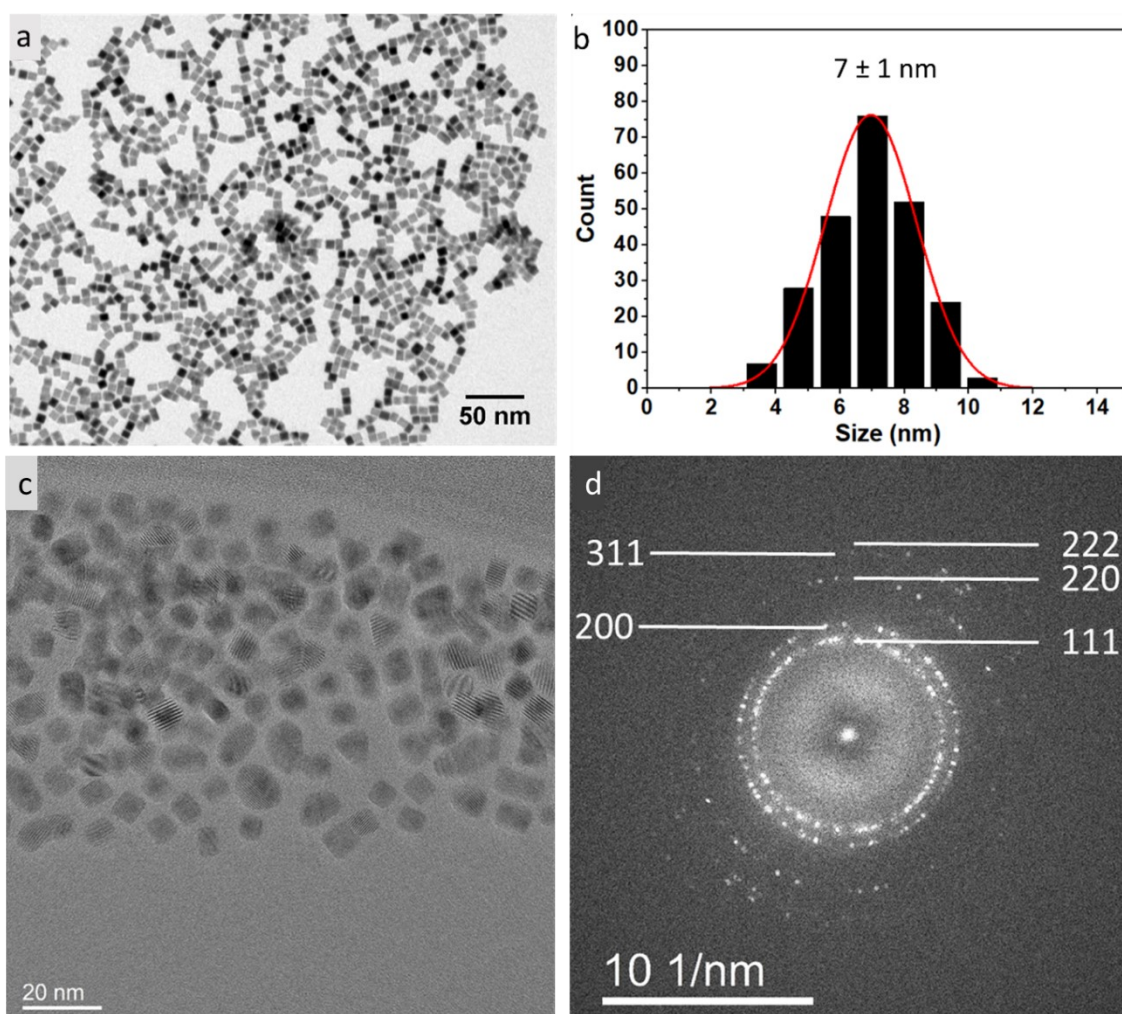


Figure S4. TEM images of 5 nm Pd nanocubes (a) and diagonal size distribution analysis (b). Uv-Vis spectra of the Pd precursors during the synthesis at different times during the 10 minutes reaction. (c) Large field-of view HRTEM image of Pt@Pd nanocubes, acquired using the DED camera, and (d) corresponding FFT. The FFT has been indexed based on fcc Pd crystal structure (ICSD 52251).

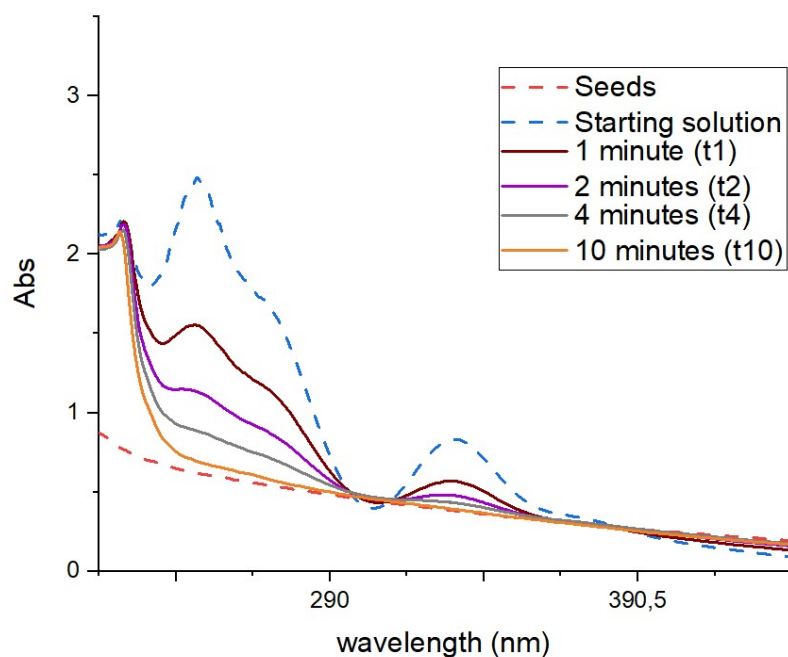


Figure S5. Uv-Vis spectra of the Pd precursors during the synthesis at different time during the 10 minutes reaction. The spectra were recorded on the reaction solution without further purification.

1.3.3. 17 nm Nanocubes

The synthesis was performed in a sealed glass container (ACE glass pressure reactor with Teflon cap). 5nm Nanocubes, used as seeds (4 mL), were added to 60 mL of MilliQ water at room temperature together with 159 μ L of Pd (II) acetate (0.05 M) and 1 mL of a solution containing 0.34 M sodium citrate, 0.2 M formic acid and 0.5 mM L-ascorbic acid. After 1 minute, 1.6 mL of 0.5 M KBr was added to the solution. The vessel was then sealed, placed in a glycerol bath at 105°C for 3 minutes. The reaction was kept for 20 minutes under stirring at moderate rate. After, the solution was cooled to room temperature.

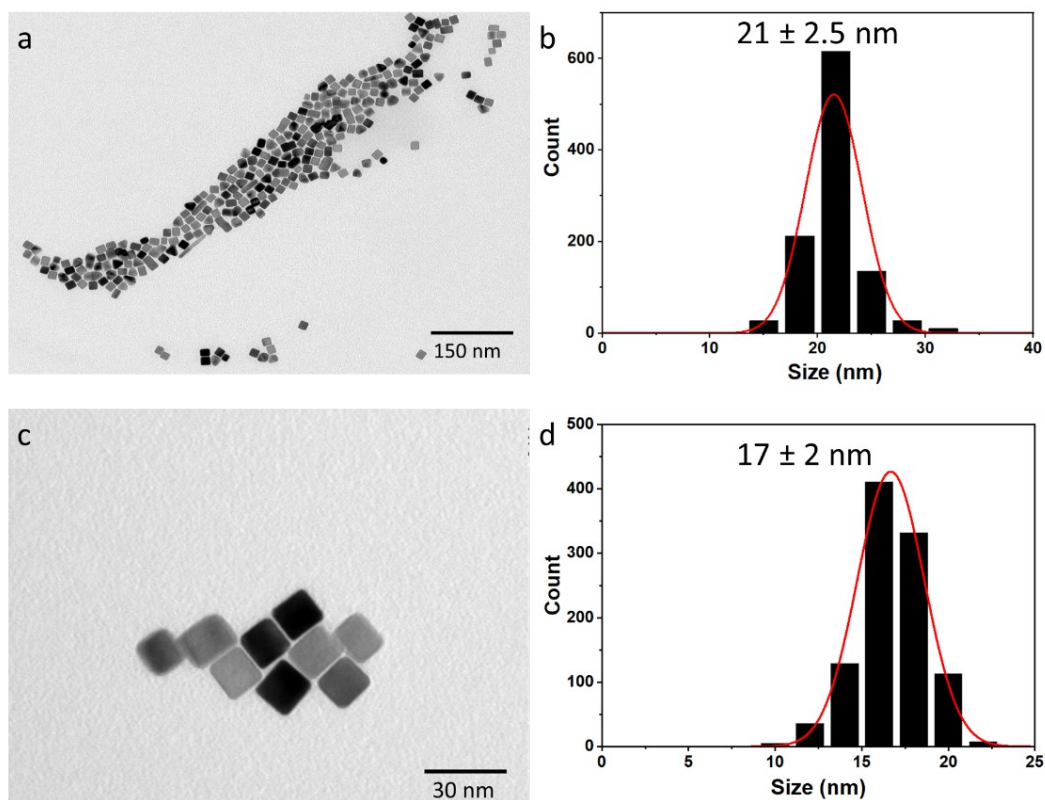


Figure S6. TEM images of 17 nm Pd Nanocubes at two different magnifications (a,c) and size distribution of the diagonal (b) and lateral size (d).

1.4. Role of seeds morphology

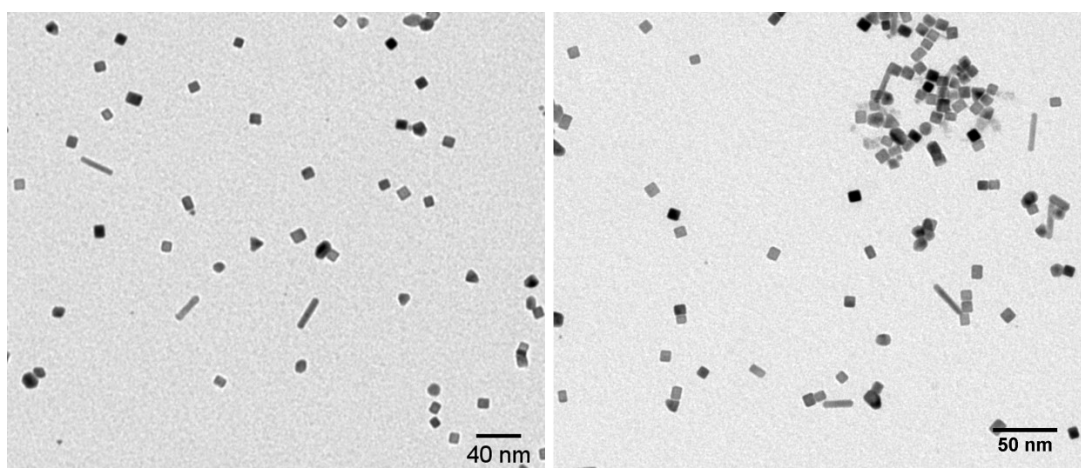


Figure S7. TEM images of Pd Nanocubes obtained using Pd seeds.

1.5. Synthetic methods at different concentrations of KBr

The synthesis was performed in a sealed glass container (ACE glass pressure reactor with Teflon cap). Platinum nanocrystals seeds (4 mL) were added to 60 mL of MilliQ water at room temperature together with 159 μ L of Pd (II) acetate (0.05 M) and 1 mL of a solution containing 0.34 M sodium citrate, 0.2 M formic acid and 0.5 mM L-ascorbic acid at different concentration of KBr.

Table S1. Summary of different experiments conditions to obtain Pd nanocubes at different KBr concentrations within the final reaction solution

Precursor	Reagents	Product
Pd(II) acetate	Pt seeds 0.34Msodium citrate 0.2M formic acid 0.5mM L-ascorbic acid 2.5mM KBr	Polydisperse product with majority of cubes around 8-10 nm (Fig.S8 C).
	Pt seeds 0.34Msodium citrate 0.2M formic acid 0.5mM L-ascorbic acid 6mM KBr	Polydisperse in terms of size; shapes improved with the increase of KBr concentration (Fig.S8 D).
	Pt seeds 0.34Msodium citrate 0.2M formic acid 0.5mM L-ascorbic acid 13mM KBr	Monodisperse Pd nanocubes of around 10 nm (Fig.S8 E).
	2x Pt seeds 0.34Msodium citrate 0.2M formic acid 0.5mM L-ascorbic acid 6mM KBr	Monodisperse 5nm Pd nanocubes were obtained by doubling the amount of seeds used (Fig.S8 F)

1.6. Synthetic methods at different concentrations of KBr

1.6.1. Shapes modulation at increasing KBr concentration

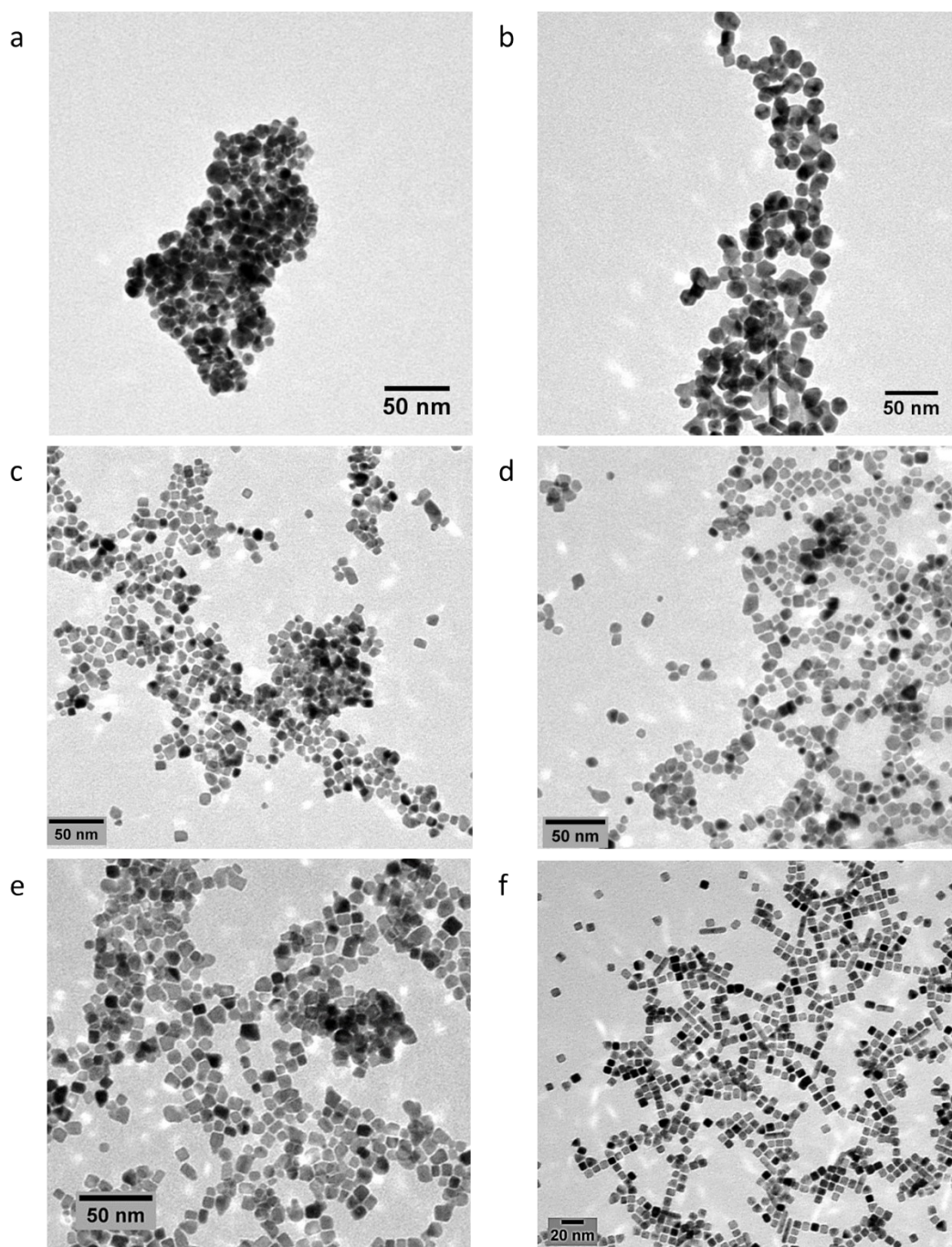


Figure S8. (A, B) TEM micrograph of Pd nanocubes obtained by the seeded growth on single-crystal Pt seeds at different concentrations of KBr. In particular, TEM images in (A) shows the synthesis of aggregated Pd NPs formed by reduction of Pd(II) acetate by a solution containing 0.17 M sodium citrate, 0.1 M formic acid and 0.5 mM L-ascorbic acid without KBr whilst in (B) Pd NPs with a more defined geometry obtained by increasing the concentration of sodium citrate to 0.34 M and formic acid to 0.42 M and 0.5 mM L-ascorbic acid always in the absence of KBr. (C-F) TEM micrograph of Pd

nanocubes obtained by the seeded growth on single-crystal Pt seeds in the presence of 0.34M sodium citrate, 0.2M formic acid, 0.5mM L-ascorbic acid and (C) 2.5 mM KBr; 8-10 nm; polydisperse in terms of shape (D) 6 mM KBr; polydisperse in terms of size; shapes improved (E) 13mM KBr; 8-10nm; well-shaped cubes (F) 13mM KBr; doubled the amount of Pt seeds to obtain nanocubes of around 5-7 nm.

1.6.2. 40 mM KBr

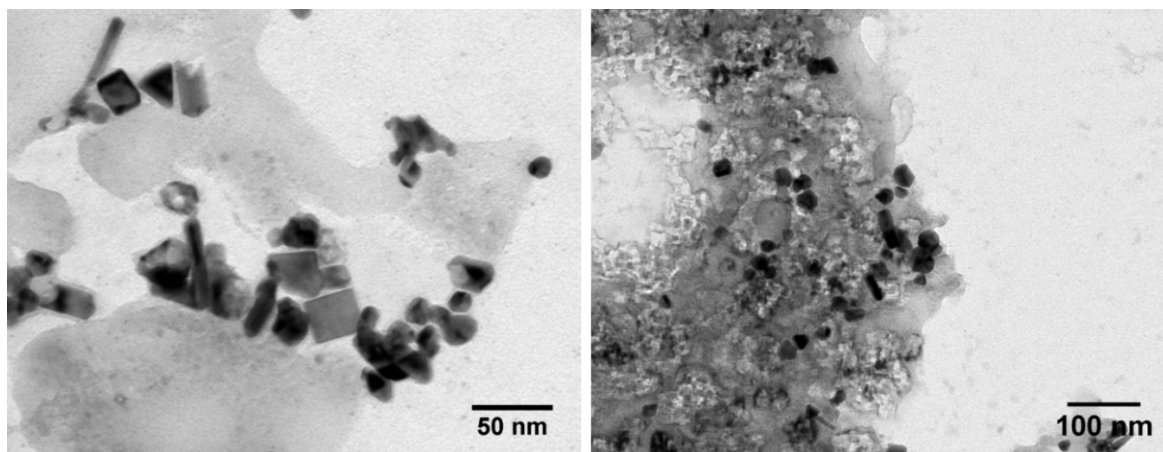


Figure S9. TEM images of polydisperse Pd nanoparticles in term of size and shape.

1.6.3. 54mM KBr

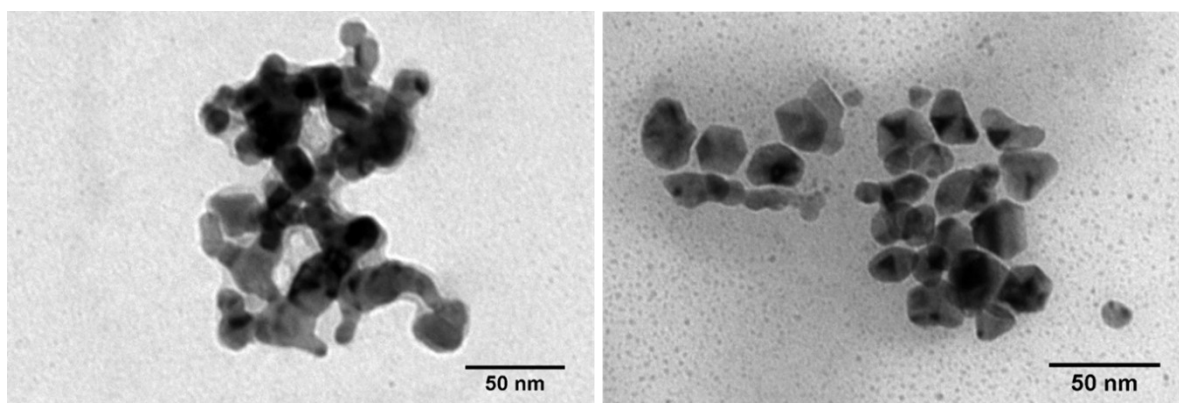


Figure S10. TEM images of unshaped nanoparticles and aggregated nanoparticles obtained with a concentration of 54 mM KBr.

1.7. Open vessel

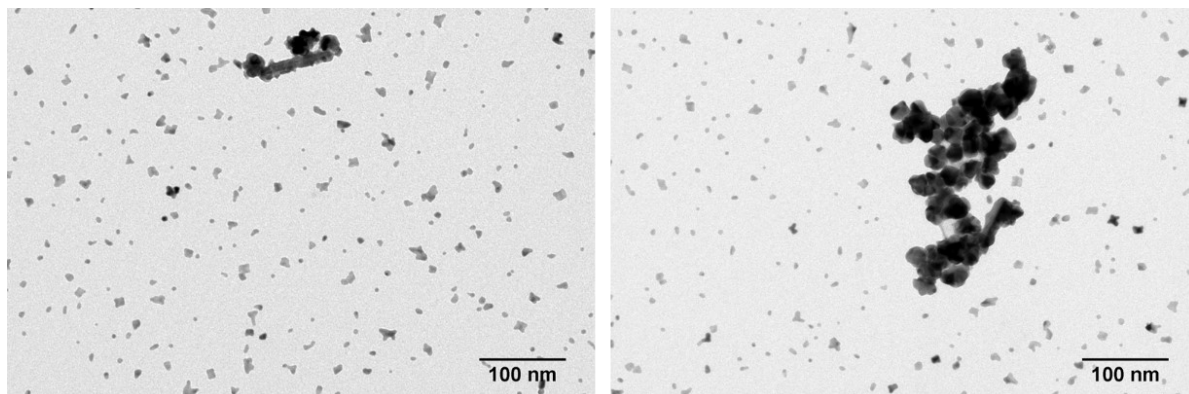


Figure S11. TEM images of unshaped nanoparticles obtained due to an uncontrolled amount of oxygen entering the open vessel.

1.8. Role of ascorbic acid in the growth of nanocubes

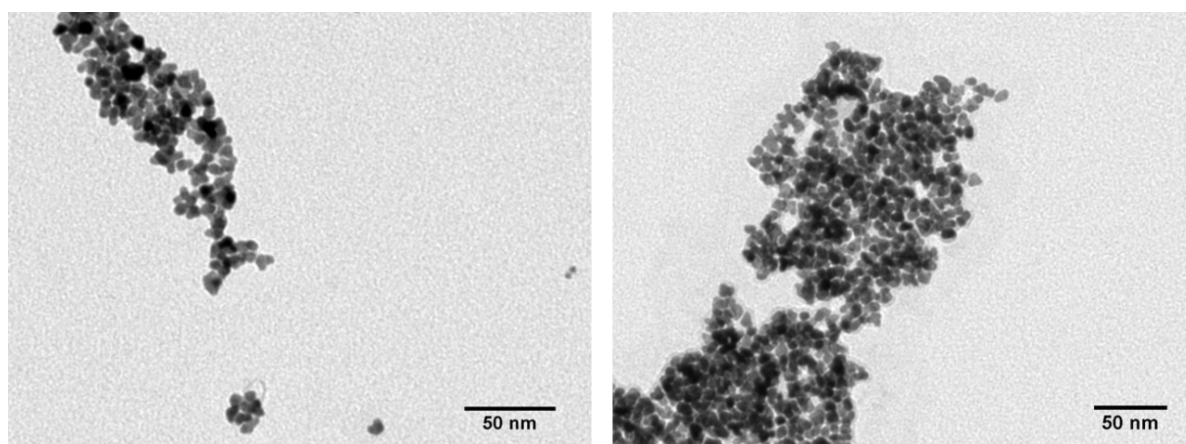


Figure S12. TEM images of unshaped nanoparticles obtained in absence of ascorbic acid.

1.9. Shape modulation by increasing the concentration of formic acid

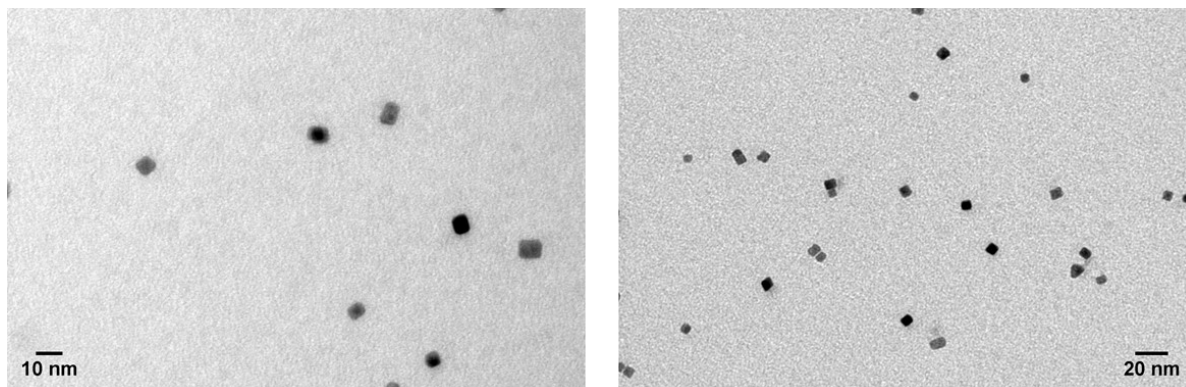


Figure S13. TEM images of Pt@Pd nanocubes at higher concentration of formic acid (0.28 M within 1 ml of mixture added to the reaction vessel).

2. Synthetic Procedure for the synthesis using a Flexiwave Microwave Reactor

All the synthetic processes described in the main text were scaled up in a microwave reactor (Flexiwave Microwave Reactor) using the multi-vessel setup (15 vessels).

2.1. 5 nm Pd citrate-capped Nanocrystal Scale-Up method

Pt seeds (2 mL) were added to 30 mL of MilliQ water together with 79.5 μL of Pd (II) acetate (0.05 M), 800 μL of 0.5 M KBr and 500 μL of a solution containing 0.34 M sodium citrate, 0.2 M formic acid and 0.5 mM L-ascorbic acid. This procedure was quickly repeated for 15 vessels that were then closed, moved in the microwave chamber and brought to 105 $^{\circ}\text{C}$ in 5 minutes. The reaction time was 10 minutes. The containers were then cooled to 20 $^{\circ}\text{C}$.

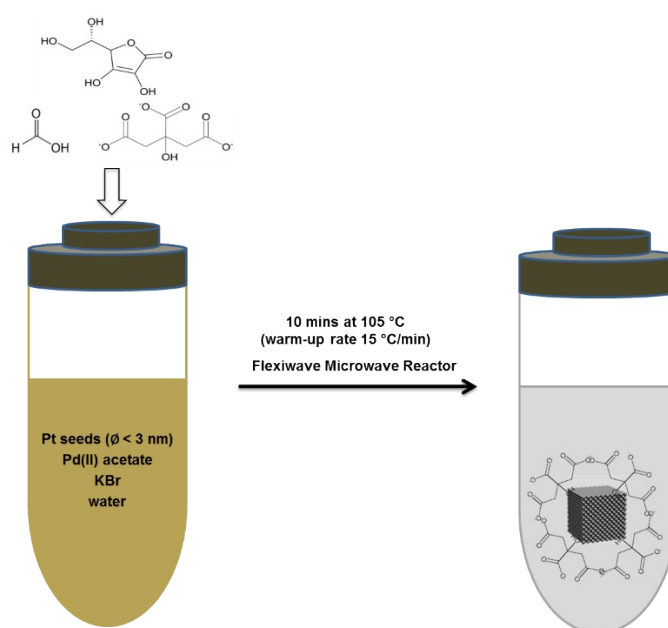


Figure S14. Schematic representation of Pd nanocubes scale-up synthesis in the flexiwave microwave reactor.

2.2. 3 nm Pt citrate-capped Nanocrystal Scale-Up method

Pt seeds (1 mL) were added to 30 mL of MilliQ water together with 79.5 μL of Pd (II) acetate (0.05 M), 400 μL of 0.5 M KBr and 250 μL of a solution containing 0.34 M sodium citrate, 0.2 M formic acid and 0.5 mM L-ascorbic acid. This procedure was quickly repeated for 15 vessels that were then closed, moved in the microwave chamber and brought to 105 $^{\circ}\text{C}$ in 5 minutes. The reaction time was 10 minutes. The containers were then cooled to 20 $^{\circ}\text{C}$.

3. DFT Calculations

Table S2. Convergence test of the surface energy of Pd(100) with 1/4 monolayer (ML) coverage and Br located at the hollow site. The surface energy is taken at a Br⁻ chemical potential of -2.7 eV. Lightly shaded rows represent parameters adopted for our calculations.

Vacuum Spacing (Å)	Surface Energy (eV/Å²)
15	0.0755
18	0.0755
20	0.0755
Plane-Wave Cut-Off Energy (eV)	
400	0.0759
425	0.0753
450	0.0755
500	0.0756
550	0.0755
<i>k</i>-point mesh	
12x12x1	0.0756
13x13x1	0.0755
14x14x1	0.0754
15x15x1	0.0755

Table S3. Unit cells used for Pd surfaces with corresponding *k*-point meshes.

	Pd(111)				
Unit Cell	$(\sqrt{3} \times \sqrt{3})$	$c(2 \times 2)$	(3×3)	(4×4)	(4×6)
<i>k</i>-point mesh	$(10 \times 10 \times 1)$	$(12 \times 10 \times 1)$	$(9 \times 9 \times 1)$	$(5 \times 4 \times 1)$	$(6 \times 4 \times 1)$
	Pd(100)				
Unit Cell	(2×2)	(2×6)	(4×4)	(4×6)	
<i>k</i>-point mesh	$(13 \times 13 \times 1)$	$(10 \times 3 \times 1)$	$(5 \times 5 \times 1)$	$(6 \times 4 \times 1)$	

Table S4. Binding energies of HCOO and COOH on Pd(111).

Br Coverage (ML)	intermediate coverage (ML)	COOH (eV)	HCOO (eV)
0	1/16	-2.87	-2.94
1/4	1/4	-2.13	-1.96
	1/8	-2.80	-2.31
	1/16	-2.50	-2.70
1/3	1/3	-1.52	-1.42
	1/9	-2.31	-1.79
	1/24	-2.39	-2.19

Table S5. Binding energies of HCOO and COOH on Pd(100).

Br coverage (ML)	intermediate coverage (ML)	COOH (eV)	HCOO (eV)
0	1/16	-2.96	-3.05
1/4	1/4	-2.68	-2.47
	1/8	-2.79	-2.32
	1/16	-2.54	-2.40
1/3	1/6	-2.50	-2.08
	1/8	-2.26	-2.01
	1/24	-2.54	-2.04
1/2	1/4	-1.56	-1.21
	1/8	-1.85	-1.27
	1/16	-1.98	-1.19
	1/24	-2.00	-1.69

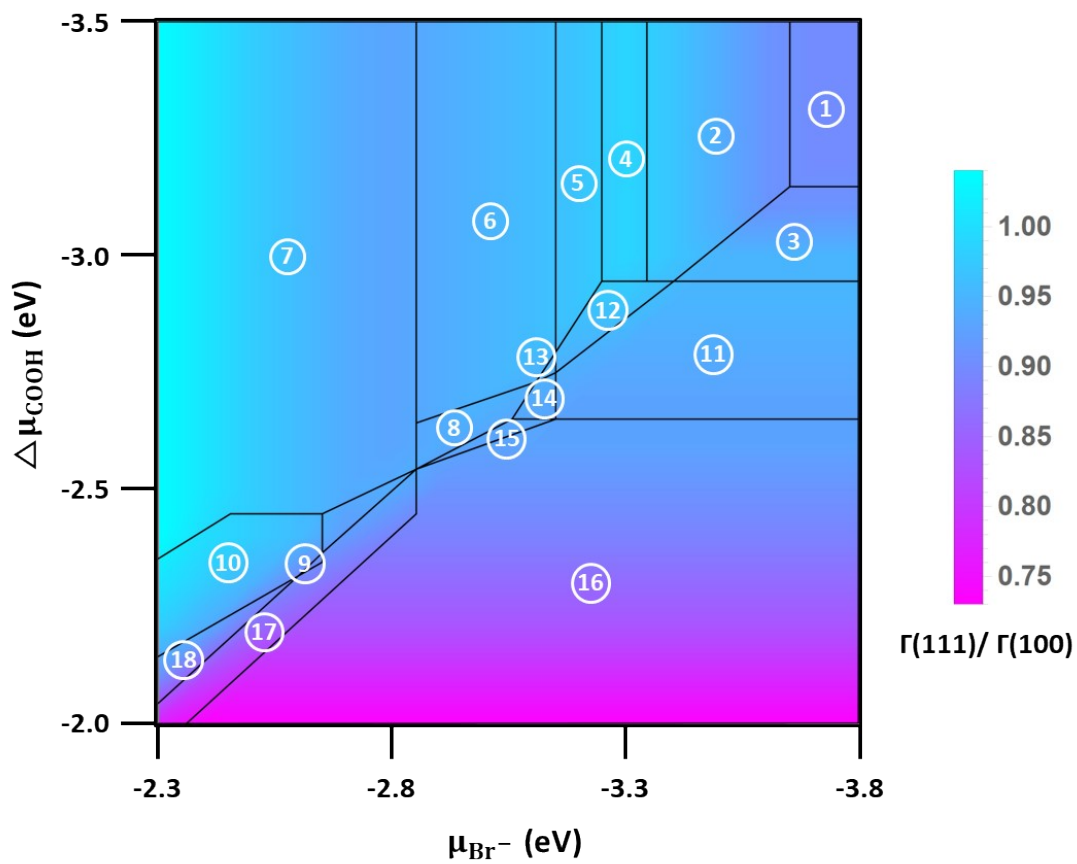


Figure S15. Surface-energy ratio $\gamma(111)/\gamma(100)$ for each of the regions shown in Fig. 3.

4. Electrochemical characterization

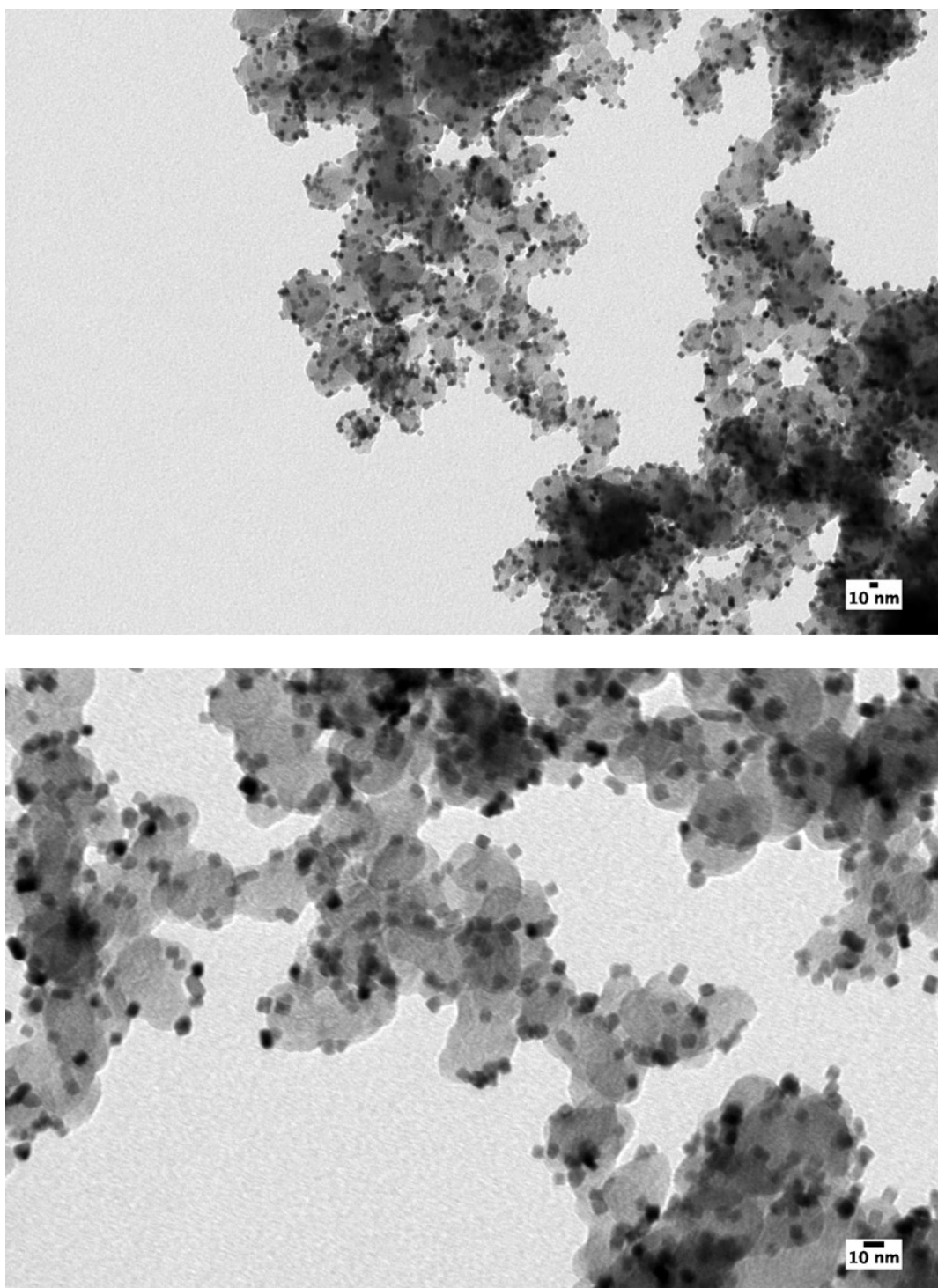


Fig. S16. TEM images of Pd nanocubes supported on amorphous carbon at two different magnifications.

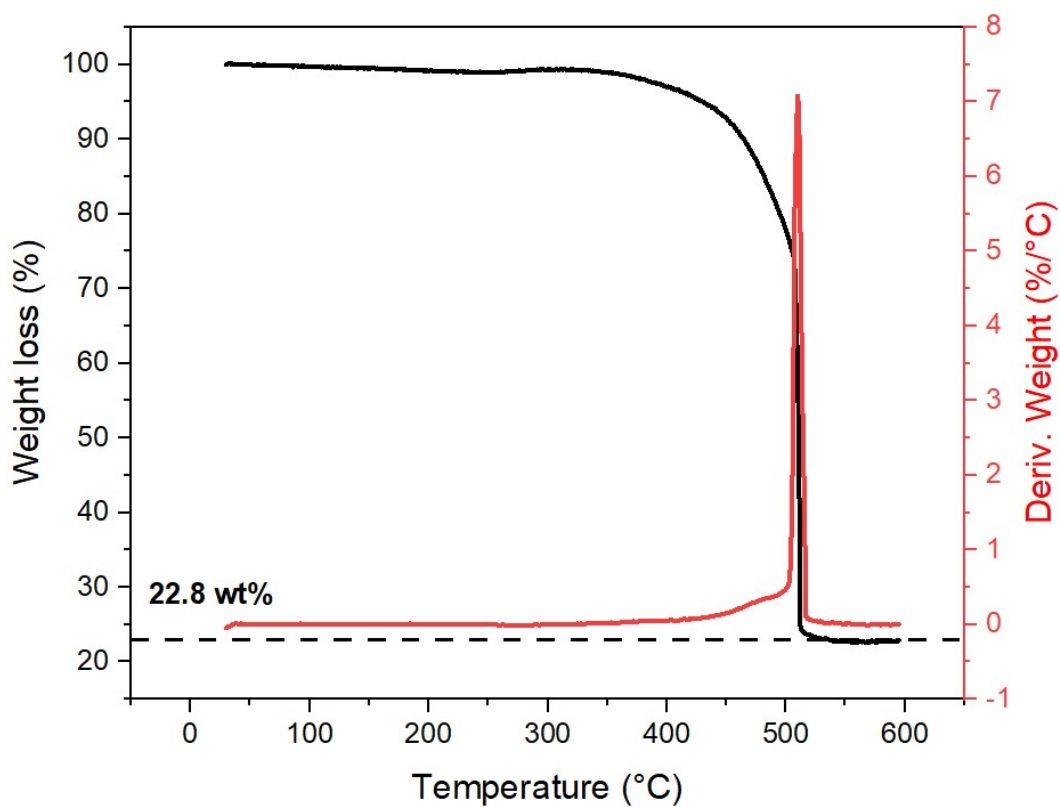


Fig. S17. Thermogravimetric analysis (TGA) in air of the nominally 20 % Pd-nanocubes on Vulcan XC72 carbon.

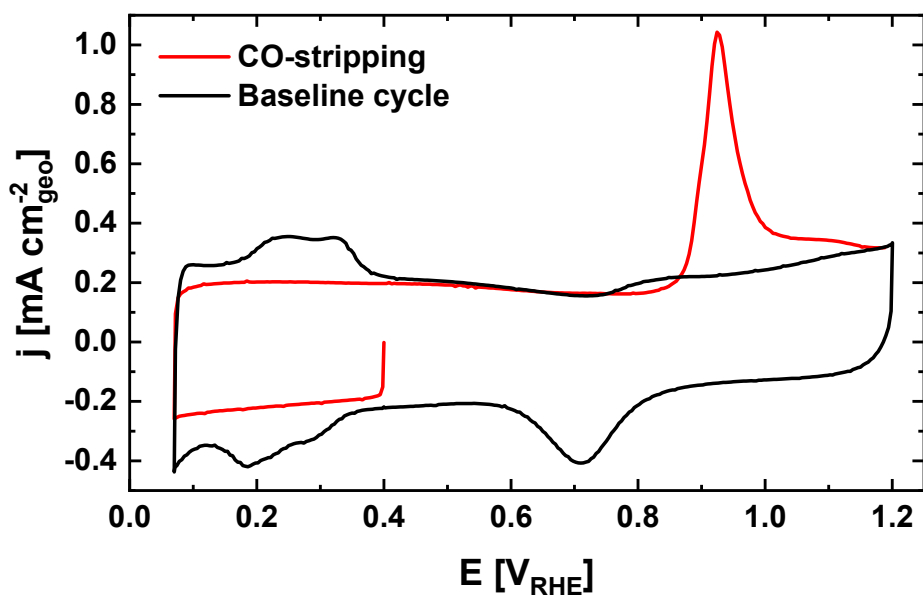


Figure S18. CO-stripping sweep and subsequent baseline CV (recorded at $20 \text{ mV}\cdot\text{s}^{-1}$) recorded in rotating disk electrode (RDE) configuration in N_2 -saturated $0.5 \text{ M K}_2\text{HPO}_4/\text{KH}_2\text{PO}_4$ -buffer on the 10 % Pd/C catalyst with a loading of $10 \mu\text{g}_{\text{Pd}}\cdot\text{cm}^{-2}$.

5. NMR

The reduction in continuous way directly into the NMR tube cannot be followed due to the H_2 liberated from the borohydride consumption and the consequent bubble formation: the bubbles moving in the tube induces inhomogeneity in the NMR sample resulting in a bad water signal suppression and a bad resolution of the signal (Figure S20).

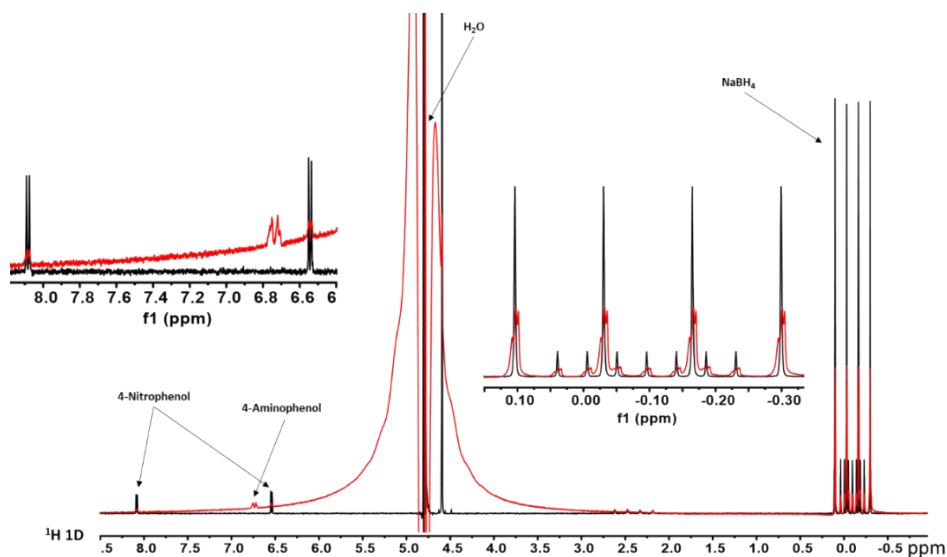


Figure S19. Reduction of 4-nitrophenol: 1D 1H NMR spectra of the reduction of 250 4-Nitrophenol one minute after addition of 0.02 ppm Pd-nanocubes (black) and after 45 minutes (red). The arrows indicate the NMR signals of 4-nitrophenol, 4-aminophenol, water and $NaBH_4$ respectively. As visible in the expanded boxes, bad water suppression 45 minutes after the addition of Pd-nanocubes, compromises the resolution of the NMR spectrum and make impossible an accurate quantification of the compounds.

The reactions were therefore conducted in an end-point format. To do this, we firstly found that 40mM HCl was able to completely quench the $NaBH_4$ and block the reactions. Indeed 1H NMR signals of $NaBH_4$ (Fig 21 black spectrum) disappear completely (Fig 21 red spectrum) after the addition of 40mM HCl.

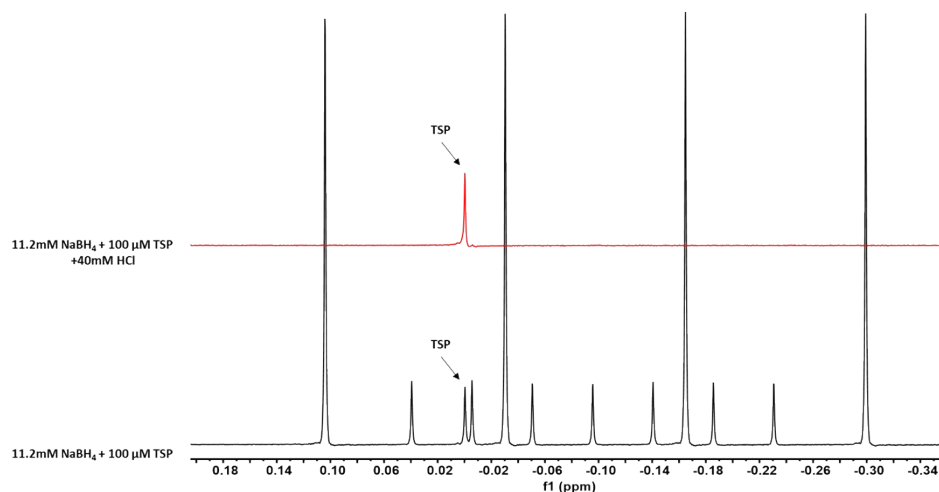


Figure S20. $NaBH_4$ quenching by HCl: 1D 1H NMR spectra of the reduction of 250 4-nitrophenol after one minute from addition of 0.02 ppm Pd-nanocubes (black) and after 45 minutes (red). The arrows indicate the

NMR signals of 4-Nitrophenol, 4-aminophenol, water and NaBH_4 respectively. As visible in the expanded boxes, bad water suppression of water after 45 minutes from Pd-nanocubes addition, compromises resolution of the NMR spectrum and make an accurate quantification of the compounds impossible.

Moreover, in order to avoid false quantification of the different compounds in solution, we further confirmed both the stability of **S** and **P** and the real quench of the reaction in our experimental conditions recording a NMR spectrum immediately after the quench and another spectrum on the same sample after 12 hours (Fig. S22).

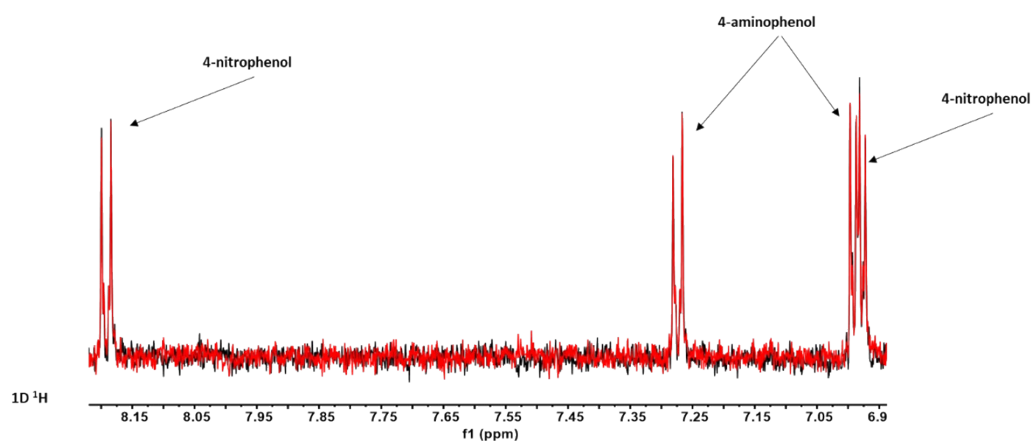


Figure S21. Stability and quench of reduction reaction: expanded region of 1D ^1H NMR spectra of the reduction of 250 μM 4-nitrophenol quenched after 30 minutes adding 40 mM of HCl; spectra recorded immediately after the quench (black) and after 12 hours (red). The arrows indicate the NMR signals of 4-Nitrophenol and 4-aminophenol respectively. No differences are visible between the two spectra, indicating that the addition of 40 mM HCl is enough to quench completely the reaction.