

## Supplementary information to

# Size Effects Studies in Catalysis: a Simple Surfactant-Free Synthesis of Sub 3 nm Pd Nanocatalysts Supported on Carbon

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## Experimental Section

**Chemicals:** all chemical were used as received. Pd(OCOCH<sub>3</sub>)<sub>2</sub> (98 %, Aldrich); Pd(NO<sub>3</sub>)<sub>2</sub> (99.8 %, Alfa Aesar); LiOH (anhydrous 98 %, Alfa Aesar); NaOH (98 %, Alfa Aesar); KOH (KOH.xH<sub>2</sub>O, ≥ 99.995 %, Fluka); methanol (≥ 99.8 %, Sigma-Aldrich); ethanol (99.9 %, Kemetyl); water (Milli-Q, Millipore, resistivity > 18.2 MΩ·cm, total organic carbon (TOC) < 5 ppb); carbon support: Vulcan XC72R, Cabot Corporation, BET area: 235 m<sup>2</sup> g<sup>-1</sup> and Ketjen EC-300J, AkzoNobel Polymer Chemistry, BET area: 795 m<sup>2</sup> g<sup>-1</sup>; Ar (99.999 %, Air Liquide).

### **Pd complex reduction**

Pd(OCOCH<sub>3</sub>)<sub>2</sub> and Pd(NO<sub>3</sub>)<sub>2</sub> solutions at 4 mM (or as otherwise indicated) were prepared in methanol. An alkaline solution of methanol (NaOH or LiOH) at 40 mM was alternatively used. The solutions were left under vigorous stirring in sealed glass container and pictures of the solutions taken at regular time intervals.

### **UV-vis measurements**

UV-vis absorption spectra were acquired with a Lambda UV/VIS/NIR absorption spectrometer, Perkin Elmer by diluting the desired solution to a suitable concentration for spectroscopic measurements (typically 0.3 mM) and using the same solvent (e.g methanol or alkaline methanol) for background and measurements.

### **Pd/C synthesis**

To prepare ca. 2 nm Pd catalyst on carbon 4 mg of Pd(NO<sub>3</sub>)<sub>2</sub> were placed in a sealed container. In another container, 1.85 g of carbon Vulcan XC72R (Cabot Corporation) was mixed with 4.35 mL of alkaline methanol NaOH (or LiOH) at 20 mM. The solution containing carbon and the alkaline alcohol was sonicated for 5 minutes (VWR ultrasonic cleaner, 35 kHz, 160 Watt). The content of the second container was then added under vigorous magnetic stirring to the container with Pd(NO<sub>3</sub>)<sub>2</sub>. The container was then closed. The solution of Pd(NO<sub>3</sub>)<sub>2</sub> at 4 mM in alkaline methanol with a nominal Pd/C weigh ratio of ca. 50 wt. % was then left to stir for 3 hours (or as indicated).

To prepare 5-25 nm Pd catalyst on carbon 4 mg of Pd(NO<sub>3</sub>)<sub>2</sub> were placed in a glass container. In another container, 1.85 g of carbon Vulcan XC72R (or Cabot Corporation) was mixed with 4.35 mL of methanol. The solution containing carbon and the alkaline alcohol was sonicated for 5 minutes. The content of the second container was then added under vigorous stirring to the container with Pd(NO<sub>3</sub>)<sub>2</sub>. The container was then closed. The solution of Pd(NO<sub>3</sub>)<sub>2</sub> at 4 mM with a nominal Pd/C weigh ratio of ca. 50 wt. % in methanol was then left to stir for 3 hours (or as indicated).

### ***TEM characterisation***

For TEM analysis a JEOL 2100 microscope operated at 200 kV was used. Size and morphologies were estimated by recording images at three different magnification (at least x100 000, x200 000, x300 000) in at least three randomly selected areas. The samples were prepared for TEM analysis by dropping the solutions containing the Pd/C ink diluted by a factor 50 in methanol on carbon coated copper TEM grids (Quantifoil). The size analysis was performed by measuring the size at least 100 nanoparticles using the *ImageJ* software.

For characterisation of the nanoparticles after electrochemical treatment Pd nanoparticles supported on carbon were collected from the glassy carbon tip and redispersed in ethanol prior to deposition on a TEM grid.

### ***Influence of the base and nature of the carbon support***

No effect of the base (NaOH vs. LiOH) or the carbon support (Vulcan XC72R or Ketjen EC-300J) could be observed on the size of the nanoparticles. A stronger effect of the molar ratio of the base to the Pd metal complex is observed to achieve size control.

### ***Pd loading: atomic absorption spectroscopy***

The actual metal loadings of the different catalysts used for electrochemical testing were analysed by atomic absorption spectroscopy (AAS, Carl Zeiss Technology AAS 5 FL). Samples were prepared by digesting the supported NPs with freshly prepared aqua regia (mixture of 30 % HCl and 65 % HNO<sub>3</sub> in a volume ratio of 1:3).

### ***Pd/C ink preparation***

The as-prepared solutions containing the Pd/C were centrifuged at a 2400 relative centrifugal force (4000 rotations per minute, Sigma 2-5). The methanol was then removed. 15 mL of methanol were added for washing and the step washing/centrifugation repeated 2 times in total. The catalyst so obtained was redispersed in 1.85 mL of ethanol:water (1:3, v:v). 10 µL of a solution of Nafion at 0.1 % and 10 µL of KOH at 0.1 M were added. This solution forms the ink.

### ***Electrode preparation***

10 µL of the ink (6.8 µg of Pd) were deposited on a glassy carbon disc electrode tip (5 mm in diameter) polished to mirror finish using alumina paste (first 1.0 µm, then 0.3 µm), and clean ultrasonically in water. The electrode geometrical surface area of 0.2 cm<sup>2</sup>, therefore the initial loading in Pd is 34 µg cm<sup>-2</sup>.

### ***Electrochemical cell***

A Teflon cell was used. The modified glassy carbon disc electrode, carbon rod, and a saturated calomel electrode were used as working electrode, counter electrode and reference electrode, respectively. All experiments were performed with argon bubbling in the electrolyte.

### **Electrochemical measurements**

The electrochemical surface area of the Pd nanoparticles was estimated by integration of the reduction peak from the 10<sup>th</sup> scans recorded at a scan rate of 50 mV s<sup>-1</sup> in 1 M KOH using 424  $\mu\text{C cm}^{-2}$  as conversion factor.<sup>1</sup>

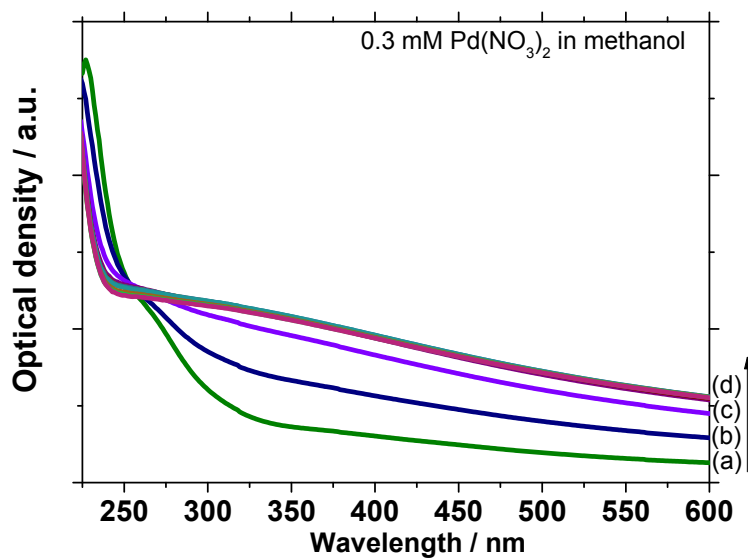
To test the electrochemical properties of the Pd/C catalyst different electrochemical treatments were performed on the same disc electrode tip. For each measurement at least 2 different tips prepared in the same conditions were analysed each time. The sequence of measurements is as follow:

- 1- The electrode is characterised by cycling 10 times between -0.80 and 0.20 V vs. SCE at a scan rate of 50 mV s<sup>-1</sup> in 1 M KOH aqueous electrolyte.
- 2- The electrode is characterised by cycling 50 times between -0.80 and 0.20 V vs. SCE at a scan rate of 50 mV s<sup>-1</sup> in 1 M KOH + 1 M ethanol aqueous electrolyte.
- 3- The electrode is characterised by chronoamperometry for 30 minutes holding the potential at -0.36 V vs. SCE in 1 M KOH + 1 M ethanol aqueous electrolyte.
- 4- The electrode is characterised by cycling 20 times between -0.80 and 0.20 V vs. SCE at a scan rate of 50 mV s<sup>-1</sup> in 1 M KOH + 1 M ethanol aqueous electrolyte.
- 5- The electrode is characterised by chronoamperometry for 30 minutes holding the potential at -0.30 V vs. SCE in 1 M KOH + 1 M ethanol aqueous electrolyte.
- 6- The electrode is characterised by cycling 10 times between -0.80 and 0.20 V vs. SCE at a scan rate of 50 mV s<sup>-1</sup> in 1 M KOH + 1 M ethanol aqueous electrolyte.

All voltages are further expressed vs. the relative hydrogen electrode (RHE) using the formula  $V \text{ vs. RHE} = V \text{ vs. SCE} + 1.07 \text{ V}$ .

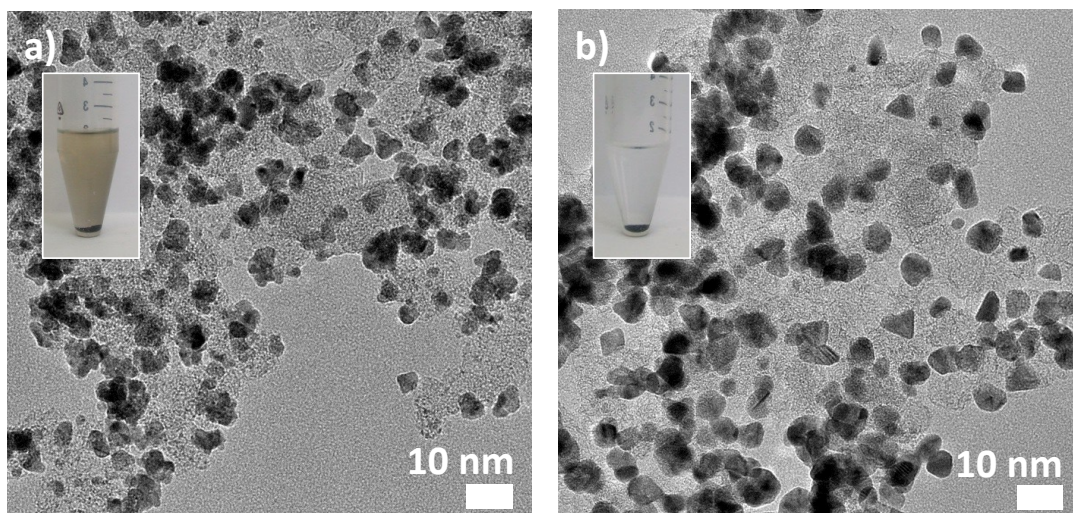
The voltage of 0.71 V vs. RHE (-0.36 V vs. SCE) for chronoamperometry was chosen as a voltage corresponding to the current density intercept of the forward and backward scan. The voltage 0.77 V vs. RHE (-0.30 V vs. SCE) was chosen to reproduce results from Ref [2]. In **Figure 3**, the 2<sup>nd</sup> CV is shown in the figure as the 1<sup>st</sup> CV depends on the starting conditions and is not representative.

## Results



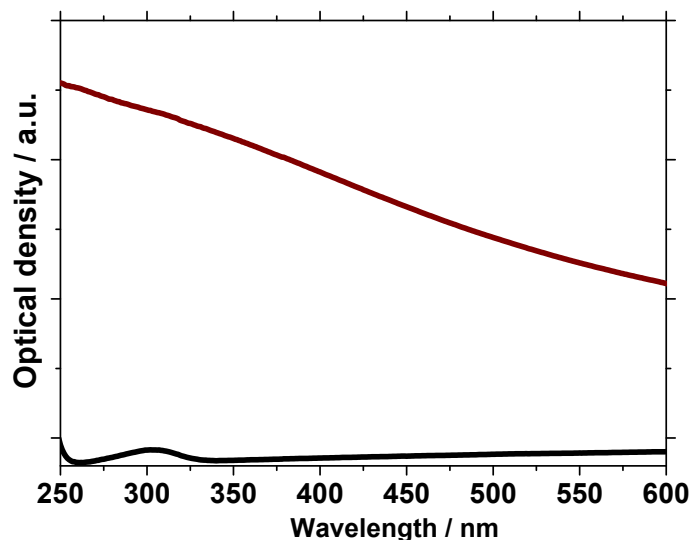
**Figure S1.** *In-situ* UV-vis adsorption spectra of a solution of Pd(NO<sub>3</sub>)<sub>2</sub> at 0.3 mM after (a) mixing the precursor and methanol, (b) after 5 minutes, (c) after 10 minutes, (d) after 15 minutes and the spectra were the same up to 4 hours later.

The characteristic spectra of a sol solution with increasing nanoparticles concentration is observed indicating of the reduction of the Pd complex to Pd nanoparticles. As the reaction proceeds the solution gets browner even if the Pd concentration is relatively low to perform *in-situ* measurements (0.3 mM).



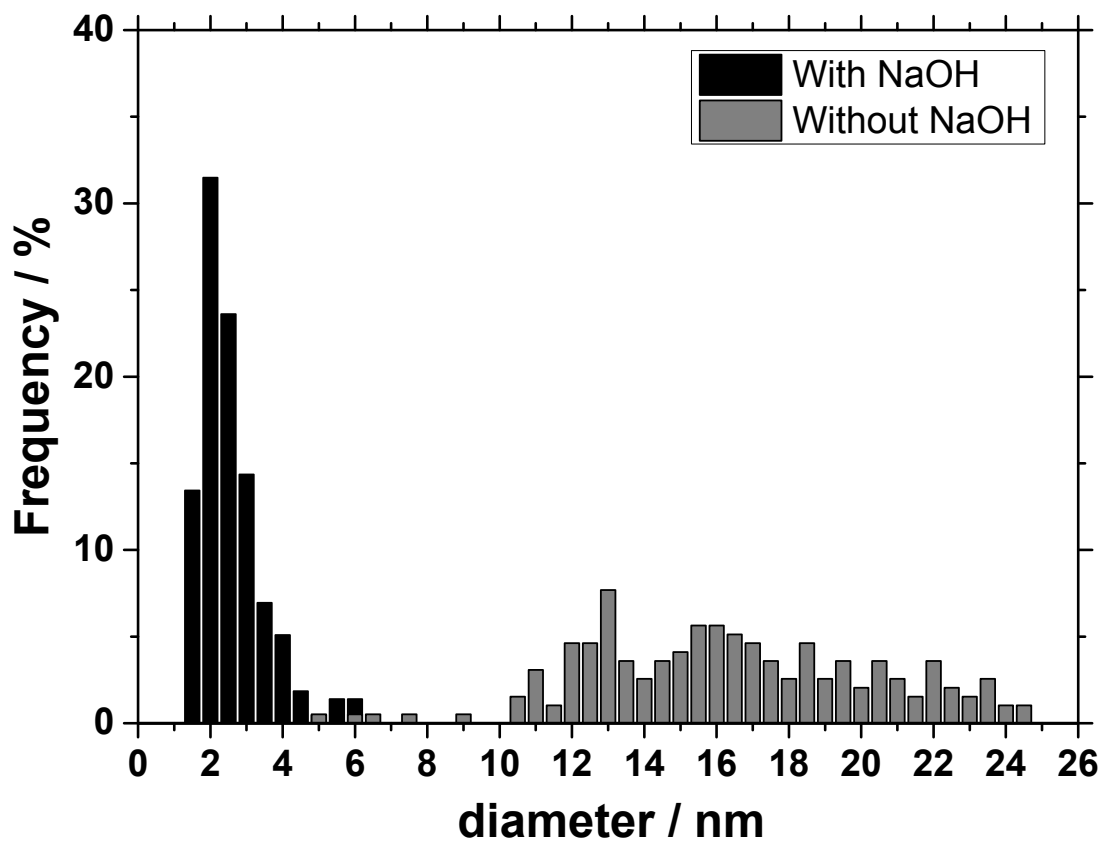
**Figure S2.** TEM micrographs of Pd nanoparticles obtained by mixing 5 mM  $\text{Pd}(\text{NO}_3)_2$  and a carbon support for (a) 10 minutes and (b) 30 minutes. The inset shows the solutions after centrifugation.

A first approach to achieve size control is to stop the reaction before it is completed. When a mixture of  $\text{Pd}(\text{NO}_3)_2$  in presence of a carbon support is left only 10 minutes and the resulting materials collected by centrifugation, a yellow supernatant is observed indicative of residual  $\text{Pd}(\text{NO}_3)_2$  not used during the synthesis, **Figure S2a**. The size of the NPs obtained is larger than 5 nm. If the solution is left 30 minutes the supernatant is transparent indicative of a more complete reaction and the size is also in the range 5-25 nm, **Figure S2b**. Size control by stopping the reaction is therefore challenging due to the fast synthesis method presented here. It is also generating waste: not all the precious metal complex is reduced. Changing the  $\text{Pd}(\text{NO}_3)_2$  concentration also did not lead to a satisfying size control (range investigated: 0.5 mM to 5 mM of  $\text{Pd}(\text{NO}_3)_2$ ).



**Figure S3.** UV-vis adsorption spectra of (brown) a solution of  $\text{Pd}(\text{NO}_3)_2$  at 0.3 mM after a few hours, (dark) the supernatant (non-diluted) obtained after centrifugation of a solution of  $\text{Pd}(\text{NO}_3)_2$  at 5 mM left to react in presence of a support in methanol for 90 minutes.

The UV-vis spectra of the supernatant of a colloidal solution of Pd/C, in dark in **Figure S3**, does not have much colloidal nanoparticles left since the typical UV-vis spectra of a colloidal solution (in brown) is not observed. On the dark curve in **Figure S3**, a small adsorption peak is observed around 300 nm and could be attributed to residual species after reaction (e.g. Pd complex, by-product of the reaction of alkaline methanol in presence of Pd nanoparticles, etc). Furthermore, the produced nanoparticles are expected to be all on the support and not free in the supernatant in a yield of ca. 95 % (otherwise the UV-vis spectra related to the supernatant – dark line in **Figure S3** - would show the same characteristics as the brown line with an optical density equal or slightly lower).



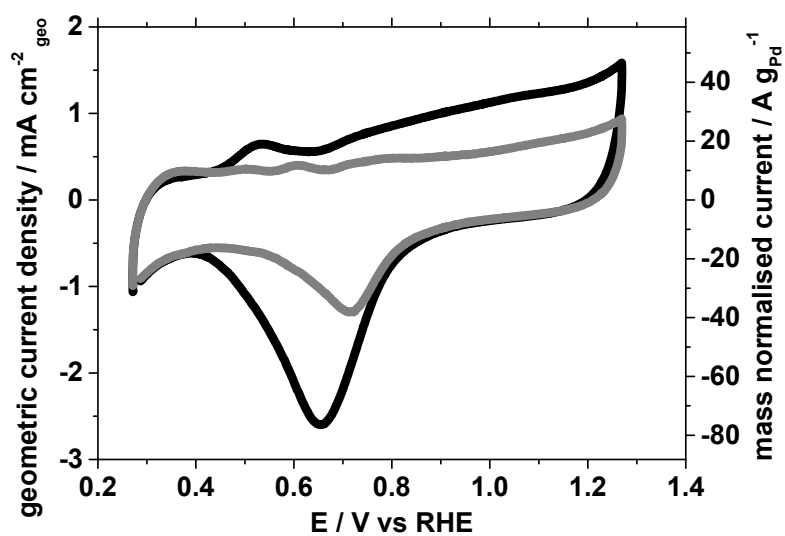
**Figure S4.** Size distribution obtained from TEM analysis for samples prepared without (grey) and in presence (black) of NaOH.

**Table S1.** Comparative properties and performances of Pd-based catalysts estimated from available information in the literature.

Ref	Date	Size <i>nm</i>	Catalyst loading on support <i>wt. %</i>	Pd loading on the electrode <i>mg<sub>(Pd)</sub> cm<sup>-2</sup></i>	ECSA <i>m<sup>2</sup> g<sup>-1</sup></i>	Electrolyte	Tests		Estimated mass activity <i>A g<sup>-1</sup></i>
							Nature	Estimated V vs. SCE*	
This work	2018	< 3	34	0.034	92 48	1 M KOH 1 M ethanol	CV	See below	882
							CA	-0.3 V / 1800 s	145
3	2007	> 7	27	0.10	-	1 M KOH 1 M ethanol	CA	-0.3 V / 960 s	25
4	2010	> 5.5	20	0.02	-	1 M KOH 1 M ethanol	CV	<i>I<sub>f-max</sub></i> at ca. -0.3 V	750
2	2010	> 19	7	0.05	-	1 M KOH 1 M ethanol	CV	<i>I<sub>f-max</sub></i> at ca. -0.25 V	1360
							CA	-0.3 V / 1800 s	37
5	2015	~ 5	-	0.03	-	1 M KOH 1 M ethanol	CV	<i>I<sub>f-max</sub></i> at ca. -0.3 V	333
6	2016	> 3	8	0.008	57.4	0.1 M NaOH 0.5 M ethanol	CV	<i>I<sub>f-max</sub></i> after 250 CVs	556
							CA	-0.35 V / 1500 s	129
7	2016	> 3	-	0.14	1.5	1 M KOH 1 M ethanol	CV	<i>I<sub>f-max</sub></i> at ca. -0.15 V	1260
							CV	<i>I<sub>f-max</sub></i> after 200 CVs	800
							CA	0.2 V / 1000 s	300
8	2017 (commercial benchmark)	-	10	0.02	47.5	1 M NaOH 1 M ethanol	CV	<i>I<sub>f-max</sub></i> at ca. -0.3 V	720
							CA	-0.3 V / 1800 s	50
9	2017	> 5	20	0.10	-	1 M KOH 1 M ethanol	CV	<i>I<sub>f-max</sub></i> at ca. -0.3 V	418
							CA	-0.3 V / 1800 s	180
10	2018	> 20	-	0.02-0.04	5	1 M NaOH 1 M ethanol	CV	<i>I<sub>f-max</sub></i>	682
							CA	-0.3 V / 1800 s	76
11	2018	~ 20	4.5	-	-	0.3 M KOH 1 M ethanol	CV	<i>I<sub>f-max</sub></i>	9.2
12	2018	~ 20	-	-	10.9	1 M KOH 1 M ethanol	CV	<i>I<sub>f-max</sub></i>	288
							CA	-0.33 V / 1800 s	15

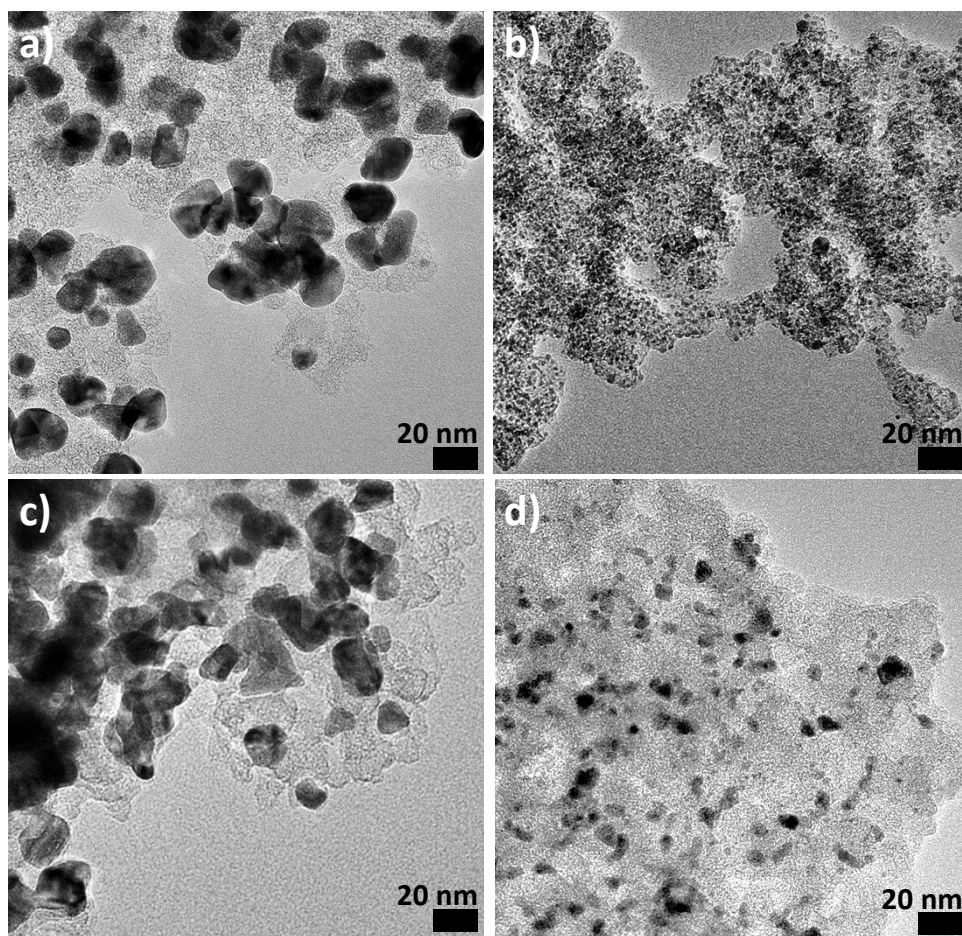
\* Potentials were estimated and converted to be expressed vs. SCE but measurements were made with different reference electrodes and the exact conversion factor is not known. It is a general challenge to compare various reports on Pd nanoparticles since in most cases the nanoparticles are not tested under strictly identical protocols.<sup>6, 13</sup> The overview proposed here does not include Pd-based (e.g. alloys) nanoparticles and focuses on Pd nanoparticles of various size supported on different support materials but also non supported Pd catalysts are included. CV: cyclic voltammetry; CA: chronoamperometry.



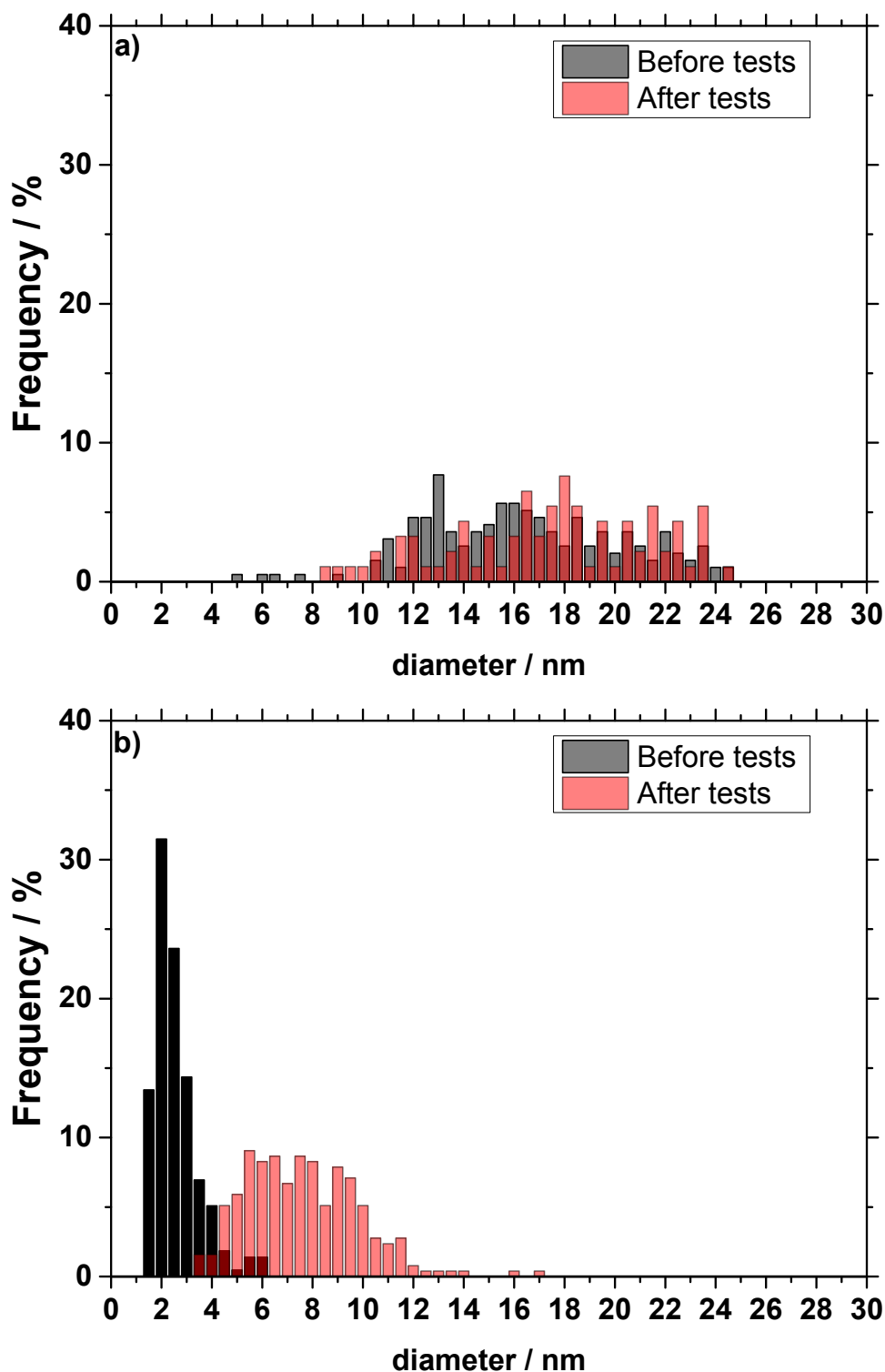


**Figure S5.** Electrochemical characterisation of Pd nanoparticles supported on Vulcan with 5-25 nm (grey) and 2.5 nm (dark) size. The CVs represented correspond to the 10<sup>th</sup> scans at 50 mV s<sup>-1</sup> in 1 M KOH solution with a Pd loading of 34  $\mu\text{g cm}^{-2}$ .

The reduction peak at 0.65 V and 0.71 V vs. SCE for the 5-25 nm and 2.5 nm nanoparticles respectively corresponds to the reduction of Pd<sup>II</sup>O. The lower voltage to observe the reduction peak can be explained by the smaller size of the NPs where oxide species adsorb more strongly.<sup>6</sup>



**Figure S6.** TEM micrographs of Pd nanoparticles obtained by mixing 4 mM Pd(NO<sub>3</sub>)<sub>2</sub> in methanol and a carbon support for 3 hours. (a) Without NaOH. (b) With 20 mM NaOH. The same samples after electrochemical treatments are characterized in (c) and (d) respectively. The loadings estimated by AAS is 34 wt. % in both cases before electrochemical treatments.



**Figure S7.** Size distribution obtained from TEM analysis of carbon supported Pd nanoparticles obtained by mixing 4 mM Pd(NO<sub>3</sub>)<sub>2</sub> in methanol and a carbon support for 3 hours: (a) without NaOH (grey), (b) with (dark) 20 mM NaOH. The same samples after electrochemical treatments are characterised and size distribution reported in red. The loadings estimated by AAS is 34 wt. % in both cases before electrochemical treatments.

## References

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