Supporting information for Investigating Particle Size Effects in Catalysis by Applying a Size Controlled and Surfactant-Free Synthesis of Colloidal Nanoparticles in Alkaline Ethylene Glycol – the Case Study of the Oxygen Reduction Reaction on Pt

Jonathan Quinson,[†,‡,*] *Masanori Inaba,*[†,‡] *Sarah Neumann,*[±] *Andreas A. Swane,*[†] *J. Bucher,*[※] *Søren B. Simonsen,*[⁑] *Luise Theil Kuhn,* [⁑] *Jacob. J. K. Kirkensgaard,*[ǂ] *Kirsten M. Ø. Jensen,*[†] *Mehtap Oezaslan*[├] *Sebastian Kunz*[±] *and Matthias Arenz*[†,※,*]

[†] Nano-Science Center, Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark

[※] Department of Chemistry and Biochemistry, University of Bern, Freiestrasse 3, CH-3012 Bern, Switzerland

[⁑] Department of Energy Conversion and Storage, Technical University of Denmark, Frederiksborgvej 399, 4000 Roskilde, Denmark

ǂ Niels Bohr Institute, University of Copenhagen, Universitetsparken 5, 2100 Copenhagen Ø, Denmark

├ Carl von Ossietzky Universität Oldenburg, School of Mathematics and Science Department of Chemistry, 26111 Oldenburg, Germany

± Institute of Applied and Physical Chemistry, University of Bremen, Leobenerstraße, 28359 Bremen, Germany

Corresponding Authors

* E-mails: matthias.arenz@dcb.unibe.ch, jonathan.quinson@chem.ku.dk

Table S1. Examples from literature focusing on the surfactant-free polyol process.

Reference	Date	Platinum concentration / mM	NaOH concentration range / mM	Range of Base/Pt molar ratio	Different Platinum concentrations studied
1	2000	0.37-51	The pH was adjusted to 12, probably involuntarily keeping the NaOH/Pt ratio constant		**YES**
2	2006	28	200 -100	7.1 - 3.6	**NO**
3	2012	5.4	453 - 10	84 - 2	**NO**
4	2015	10	500 - 62.5	50 - 6.25	**NO**
5	2016	6	42 - 12	7 - 2	**NO**
6	2017	2	250 - 0	125 - 0	**NO**

Different metal complexes, different synthesis parameters (volume, time synthesis, mode of synthesis, etc.) were used. The summary focused on colloidal synthesis of monometallic platinum nanoparticles and excludes one-pot synthesis directly on a support except for [5].

Table S2. Experimental synthesis conditions for the data presented in Figure 2 and the size estimated from SAXS measurements.

Volume / mL	**Platinum concentration / mM**	**NaOH concentration / mM**	**NaOH/Pt molar ratio**	**Diameter (nm)**
4	10	250	25	1.10 ± 0.23
4	10	125	12.5	1.37 ± 0.32
4	10	109	6.3	2.52 ± 0.29
4	10	63	3.1	5.07 ± 0.18
4	5	125	25	1.05 ± 0.27
4	2.5	63	25	0.97 ± 0.34
4	1.25	31	25	1.09 ± 0.27

SAXS Analysis

Small-angle X-ray scattering (SAXS) was performed at the Niels Bohr Institute SAXSLab instrument at University of Copenhagen. This instrument is equipped with a 100XL + micro-focus sealed X-ray tube from Rigaku producing a photon beam with a wavelength of 1.54 Å. The scattering patterns were recorded with a 2D 300 K Pilatus detector from Dectris. The two-dimensional scattering data were azimuthally averaged, normalized by the incident radiation intensity, the sample exposure time and the transmission and corrected for background and detector inhomogeneities using standard reduction software. The background measurement was on a pure ethylene glycol sample. The radially averaged intensity I(q) is given as a function of the scattering vector $q = 4\pi.\sin(\theta)/\lambda$, where λ is the wavelength and 2θ is the scattering angle.

The background corrected scattering data was fitted with a model of polydisperse spheres described by a volume-weighted log-normal distribution. The model expression for the intensity is:

$$\mathrm{I}(q) = C \int P_s^2\,(q,R) V(R) D(R) dR \quad (1)$$

where C is an overall scaling constant, P_s is the sphere form factor, V the particle volume and D the log-normal size distribution. The sphere form factor is given by:

$$P_s(q,R) = 4\pi R^3 \frac{\sin(qR) - qR\cos(qR)}{(qR)^3} \quad (2)$$

and the log-normal distribution by:

$$D(R) = \frac{1}{R\sigma\sqrt{2\pi}} \exp\left(\frac{-\left[\ln\left(\frac{R}{R0}\right)\right]^2}{2\sigma^2}\right) \quad (3)$$

In one case it was necessary to include a structure factor contribution to model the data properly. We employed a hard-sphere structure factor as described in Reference [**7**]. Basically, this depends on the sphere radius and the sphere volume fraction. The fitting was done using home written MATLAB code invoking a least-squares χ^2-minimisation to optimise agreement between data and model. Thus, the free parameters in the model are the radius and variance of the polydisperse size distribution as reported in the paper. The scattering data and corresponding fits can be seen in **Figure S1**.

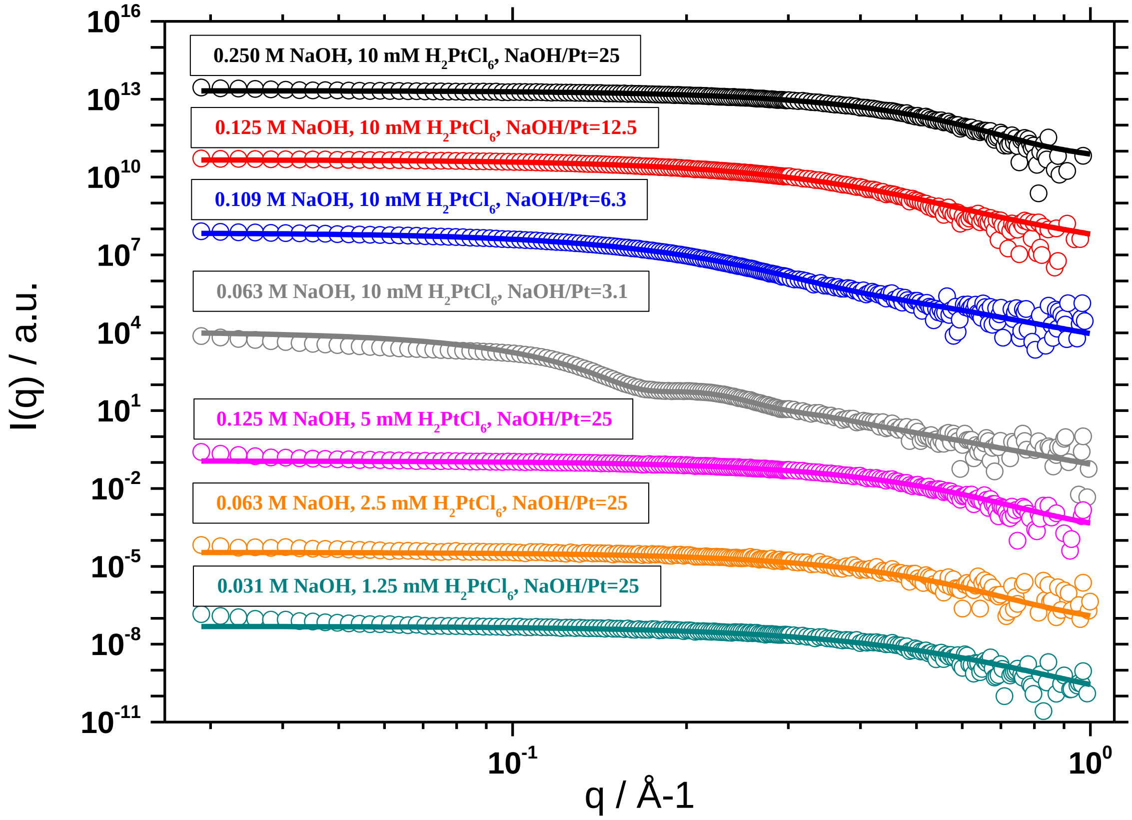

Figure S1. SAXS data (circles) and corresponding fits (plain line) related to **Figure 2** in the manuscript.

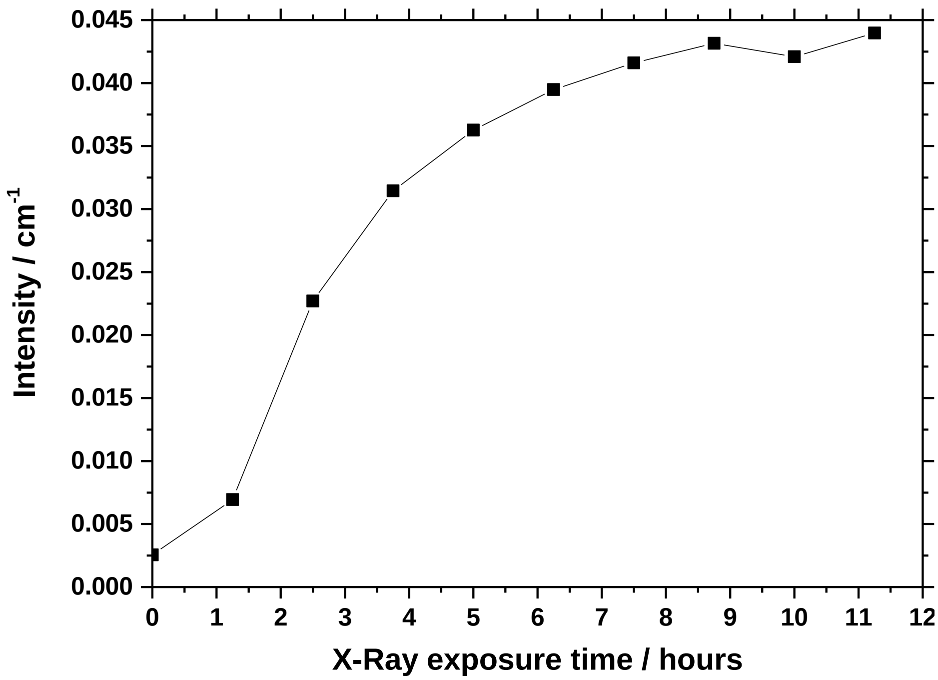

Figure S2. Time evolution of SAXS intensity for q = 0.086 $Å^{-1}$ indicating that the X-ray beam induces particle growth (2 mM H_2PtCl_6 and 250 mM NaOH).

Hypothesis for the size control by the NaOH/Pt molar ratio

A model to explain why the NaOH/Pt ratio controls the size is proposed. The hypothesis is that the nanoparticles will grow until a certain OH^- surface coverage is reached. As a result, the ratio between NaOH concentration and Pt surface atoms should be constant. This hypothesis is tested below by a rough estimation of the ratio of OH^- ions to Pt surface atoms (here called Ω) based on the obtained size of the nanoparticles (NPs) determined from the SAXS and TEM data:

$$\frac{\#(OH)}{\#(Pt\ surface\ atoms)} = \Omega \qquad \text{eq. (1)}$$

Where # corresponds to the ‘number of’ and Ω is the ratio of OH to Pt surface atoms.

The total number of Pt atoms in a NP is estimated by:

$$\#\,(Pt\ atoms\ per\ NP) = 0.75\,\frac{V\,(Pt\ NP)}{V\,(Pt\ atom)} \quad \text{eq. (2)}$$

Where V corresponds to ‘volume of’.

The total number of Pt surface atoms of a NP is given by:

$$\#\,(Pt\ surface\ atoms\ per\ NP) = 0.785\,\frac{A\,(Pt\ NP)}{A\,(Pt\ atom)} \quad \text{eq. (3)}$$

Where A corresponds to ‘external surface area of’.

Experimentally given are the molar ratio between NaOH and Pt as well as the obtained NP size.

Assuming that $\#(NaOH\ per\ NP) \sim \#(OH\ per\ NP)$, the molar ratio between NaOH and Pt is:

$$\frac{NaOH}{Pt} \sim \frac{\#(NaOH\ per\ NP) * \#\,(NPs)}{\#\,(Pt\ atoms\ per\ NP) * \#\,(NPs)} \sim \frac{\#(OH\ per\ NP)}{\#(Pt\ atoms\ per\ NP)} \quad \text{eq. (4)}$$

Inserting eq.1 into eq.4, we obtain:

$$\frac{NaOH}{Pt} \sim \frac{\Omega * \#\,(Pt\ surface\ atoms\ per\ NP)}{\#\,(Pt\ atoms\ per\ NP)} \quad \text{eq. (5)}$$

And with eq.2 and eq.3:

$$\frac{NaOH}{Pt} \sim \Omega * \frac{A\,(Pt\ NP)}{V\,(Pt\ NP)} * \frac{V\,(Pt\ atom)}{A\,(Pt\ atom)} * \frac{0.785}{0.75} \sim \Omega * \frac{Pt\ atom\ diameter}{NP\ diameter} \quad \text{eq. (6)}$$

Where the Pt atom diameter corresponds to the covalent diameter of a Pt atom taken as 0.27 nm.

$$\Omega \sim \frac{NaOH}{Pt} * \frac{NP\ diameter}{Pt\ atom\ diameter} \quad \text{eq. (7)}$$

Under our hypothesis, Ω should be a constant.

Using the experimental results to estimate Ω we obtain the following values:

NaOH/Pt	NP diameter (nm)	# atoms in a NP	# atoms at the surface of a NP	% or surface atoms	Ω
25	1.1	52	53*	100*	104*
13	1.4	95	20	84	63
10	2.1	341	187	55	78
6	2.5	581	67	46	59
5.5	2.9	897	357	40	59
5	4.0	2353	679	29	74
4.5	5.5	6118	1284	21	92

*naturally the model needs to break down at extremely small particles

Despite using a very simplistic model, the value of Ω is rather constant and thus supports the hypothesis that the OH^- surface concentration is not only responsible for the stabilization of the particles, but also the stop of the growth process.

Table S3. Properties of Pt nanoparticles obtained with different NaOH/Pt ratio from different characterization methods.

Characterization		NaOH/Pt	
		10	4.5
TEM	Diameter / nm	2.0 ± 0.6	3.6 ± 0.8 5.5 ± 1.6
FTIR	CO peak / cm^{-1}	2020	2045
XAS (EXAFS)	N(Pt-Pt_1)	6.6 ± 0.7	8.7 ± 1.4
	R(Pt-Pt1) / Å	2.755 ± 0.005	2.758 ± 0.008
	R_f	0.015	0.013

	ΔE_0 / eV	4.8 ± 0.7	6.4 ± 1.4 eV
	σ^2 x 10^{-4} / $Å^2$	56 ± 5	57 ± 6
PDF	R_W / %	16.3	15.1
	Unit cell / Å	3.930	3.941
	B_{iso} / $Å^{-2}$	1.03	0.92
	delta2 / Å	3.98	3.75
	Crystallite size / nm	2.2	3.8

Diameter analysis: when the NaOH/Pt molar ratio decreases the reproducibility of the size control decreases, the two values quoted for NaOH/Pt of 4.5 are the extreme values obtained for different samples prepared. It can be concluded that the NaOH/Pt ratio of 4.5 lead to nanoparticles in the size range 3-5 nm. In contrast good reproducibility is obtained for NaOH/Pt molar ratio of 10.

XAS analysis: N is the coordination number (indicative of the average number of neighboring atoms). R is the interatomic bond length. R_f indicates the closeness of the fit to the data as quality parameter. σ^2 is the mean squared bond length disorder. ΔE_0 is the correction to the energy origin.

PDF analysis: R_w is a measure of the fit quality (lower value corresponds to better fit). B_{iso} describes atomic motion of the Pt nanoparticles. delta2 relates to correlated motion between neighboring atoms.

XAS. From X-ray absorption near edge structure XANES data (not shown), it is confirmed that while the initial precursor consists in the form of Pt(IV), after synthesis mainly Pt(0) can be detected. From EXAFS data, no fit could be obtained for the nanoparticles after synthesis that could be assigned to Pt-Cl. These results suggest the total consumption of the initial H_2PtCl_6 precursor.

PDF. The unit cell parameter decreases with decreasing size, as expected for Pt nanoparticles.[8] The B_{iso} values increase with size, which may account for structural disorder possible arising from bond softening and disorder.[9]

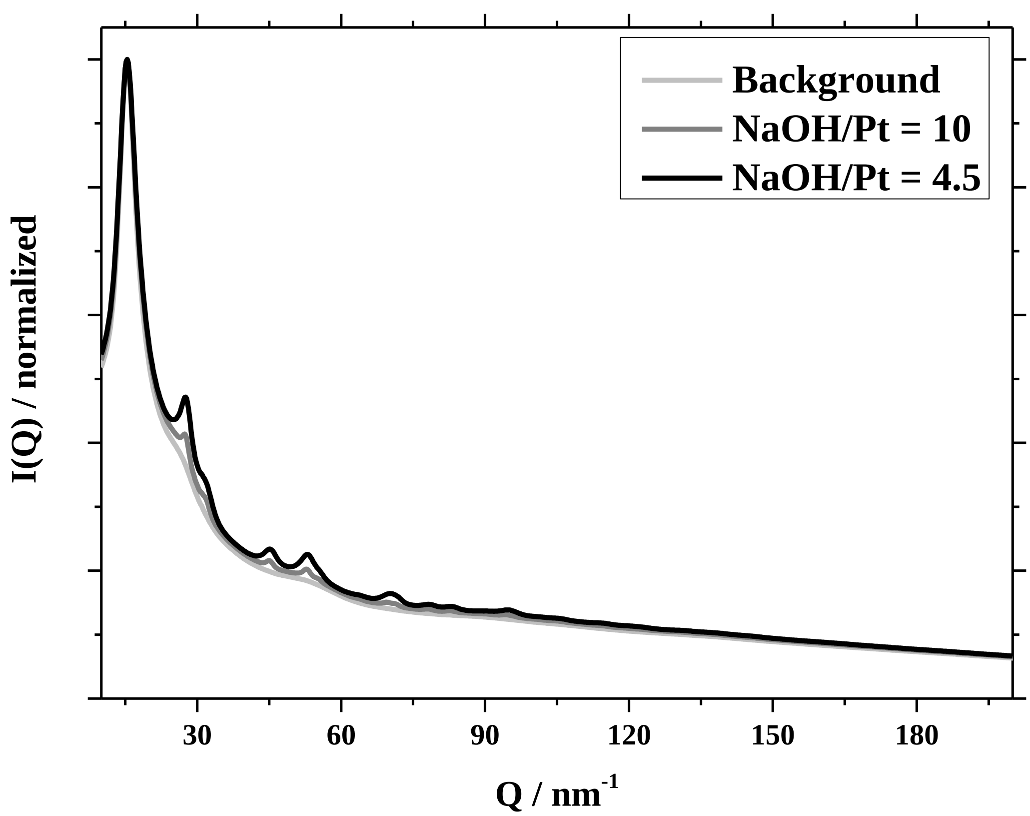

Figure S3. Normalized intensity of X-ray total scattering for PDF analysis of Pt nanoparticle obtained with different NaOH/Pt molar ratio as indicated.

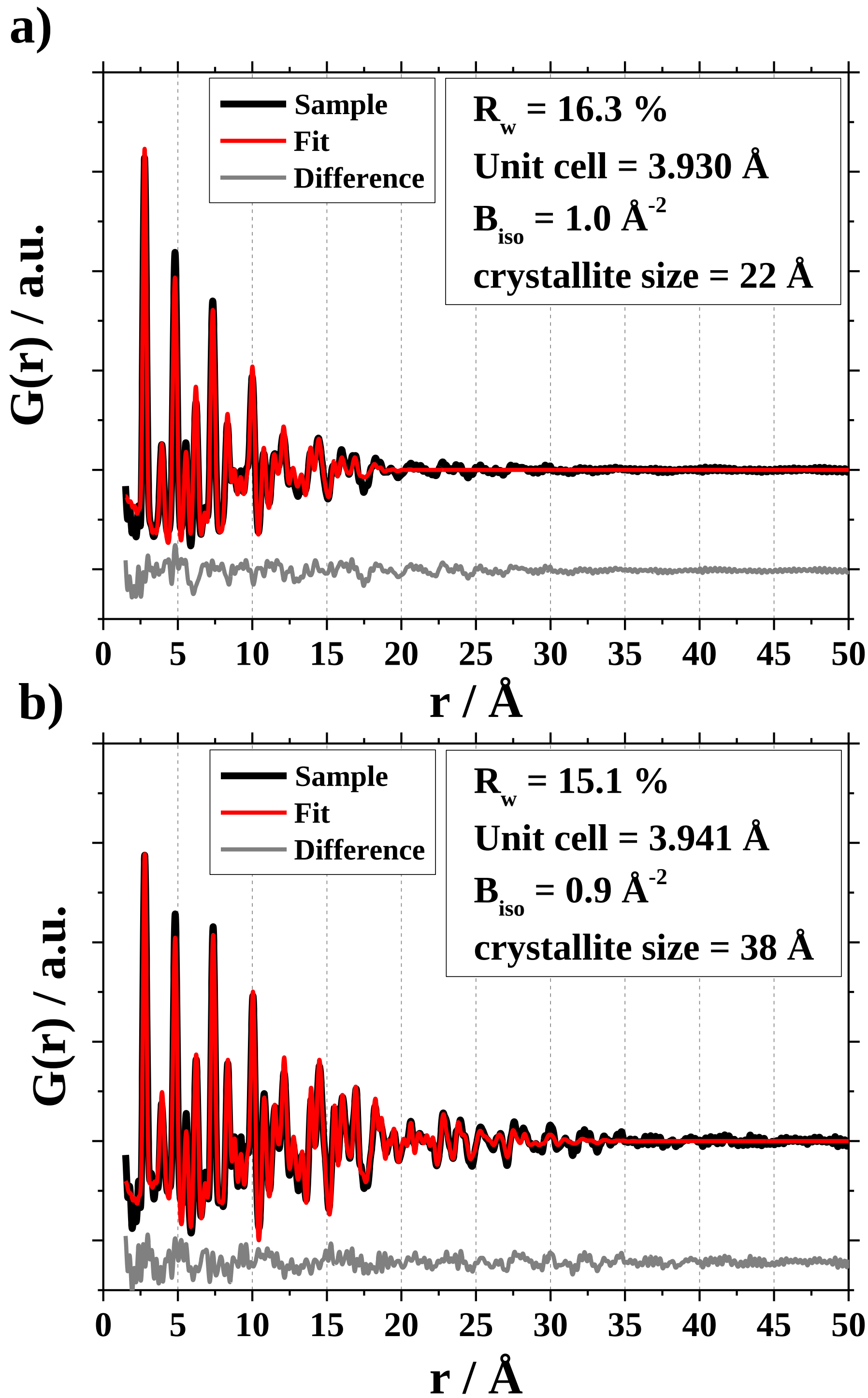

Figure S4. PDF characterization of the obtained Pt nanoparticles prepared with a NaOH/Pt molar ration of (a) 10 and (b) 4.5.

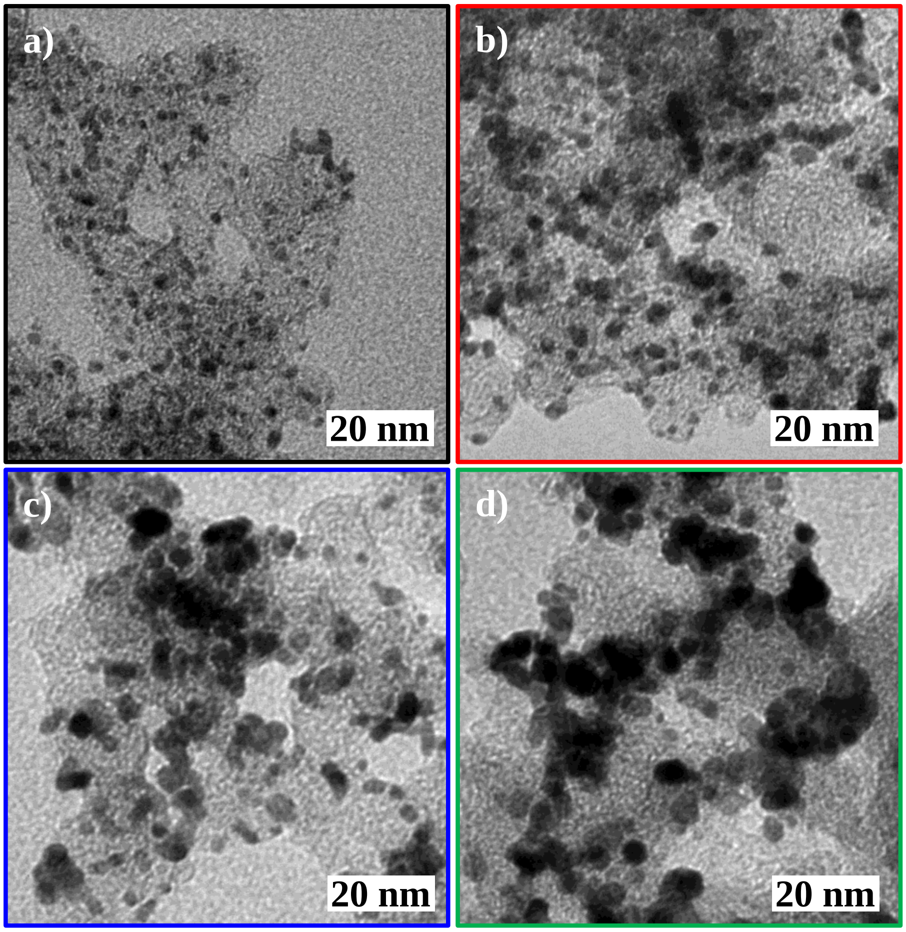

Figure S5. TEM micrographs of catalysts with a nominal 50 wt. % Pt on carbon (Vulcan XC72R) obtained using nanoparticles synthesized using NaOH/Pt molar ratio of: (a) 10, (b) 5.5, (c) 5 and (d) 4.5.

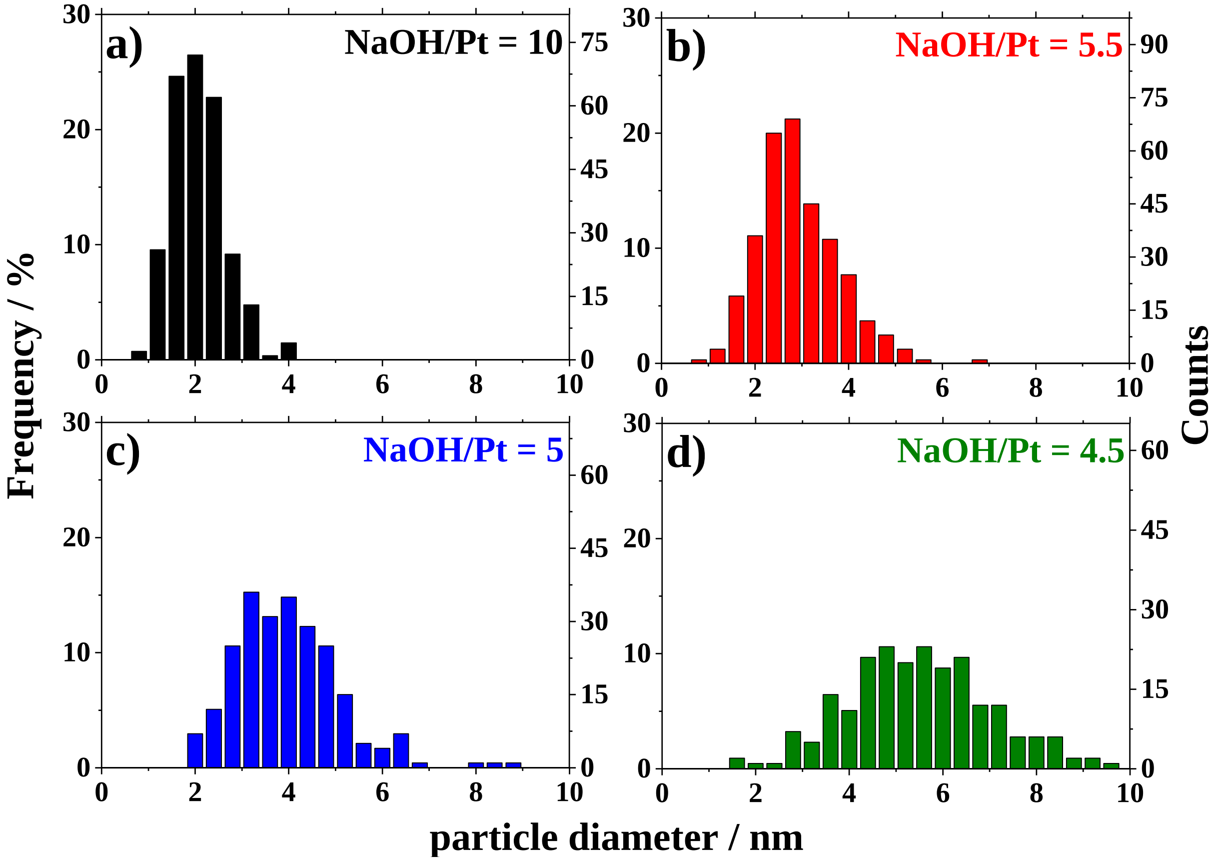

Figure S6. Particle size distribution estimated from TEM micrographs for Pt nanoparticles prepared with different NaOH/Pt molar ratio as indicated: (a) 10, (b) 5.5, (c) 5 and (d) 4.5.

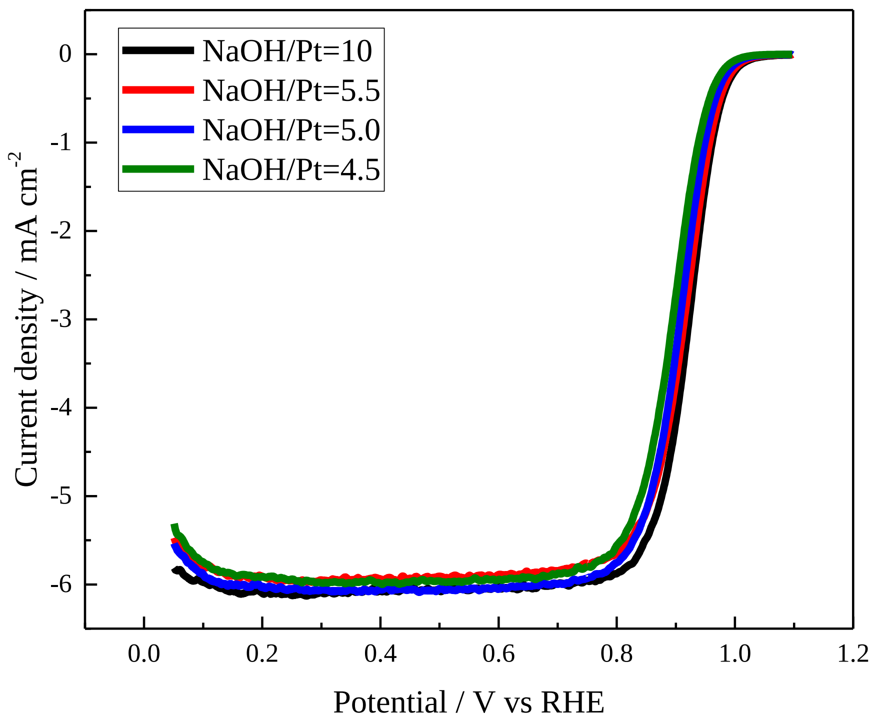

Figure S7. Linear sweep voltammograms (positive scans) for Pt/C catalysts prepared from different colloidal Pt particle suspensions. The nominal Pt loading on the high surface area carbon support and the glassy were kept constant at 50 wt. % and 14 $\mu g_{(Pt)}$ cm^{-2}, respectively. The measurements were conducted in O_2-saturated 0.1 M $HClO_4$ at scan rate of 50 mV s^{-1} with 1600 rpm.

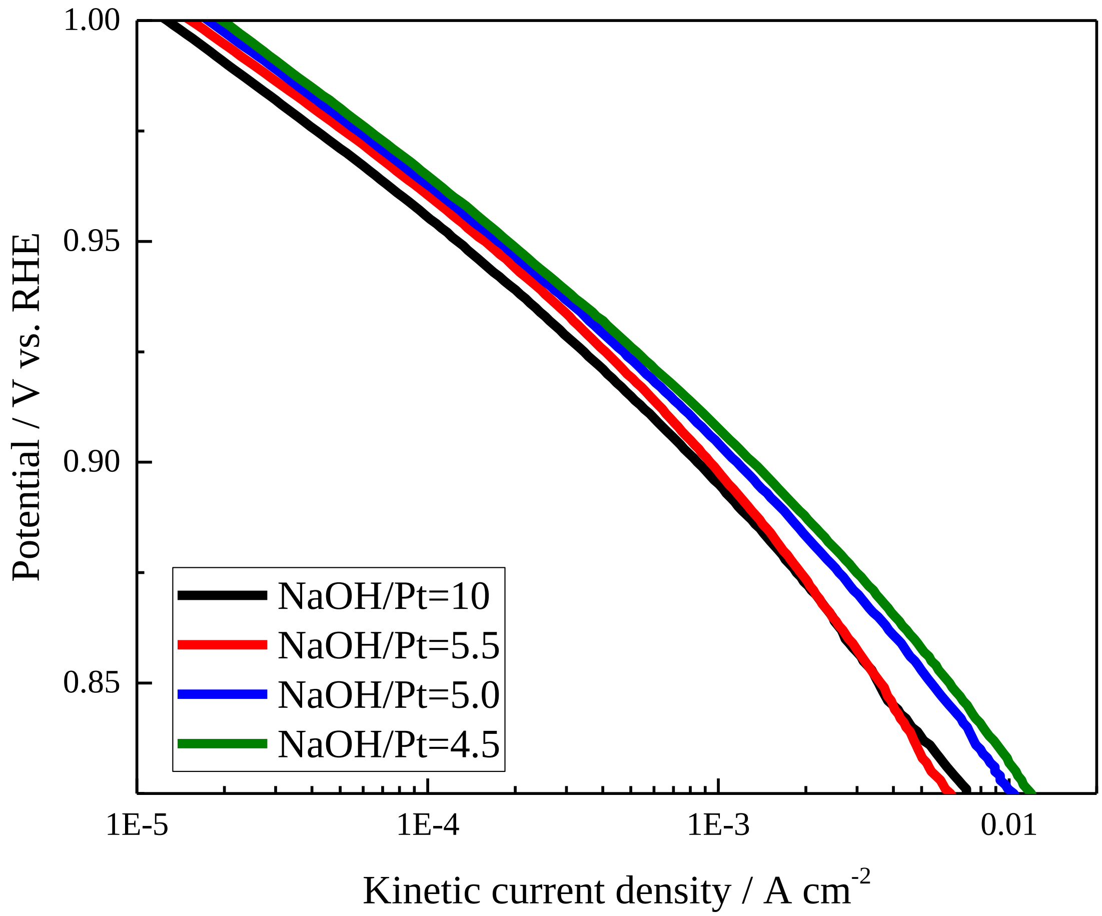

Figure S8. Tafel plots obtained by extrapolating the linear sweep voltammograms in Figure S3 with the Koutecky-Levich equation.

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