

Electronic Supplementary Information (ESI)

**Nanoparticles in a Box: A Concept to Isolate, Store and Re-use
Colloidal Surfactant-Free Precious Metal Nanoparticles**

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1. Experimental Section

1.1. Material Synthesis and Preparation

1.1.1 Synthesis of “Unprotected” Pt Nanoparticles (NPs)

Colloidal „unprotected“ Pt NPs were prepared by a slightly modified recipe of Wang et al.¹: 0.25 g of $\text{H}_2\text{PtCl}_6 \cdot \text{H}_2\text{O}$ (40% Pt, ChemPur) was dissolved in 25 mL ethylene glycol (EG, 99.8%, Sigma-Aldrich) in a 250 mL glass flask. After adding a solution of 25 mL 0.5 M NaOH (98.9%, Fisher Chemical) in EG, the mixture was vigorously stirred at 500 rpm. The flask was equipped with a reflux condenser and the precursor solution was heated to 160°C using a preheated oil bath. Thereby the stirring was kept at a speed of 500 rpm. The formation of Pt NPs is indicated by colour change from yellow to black after about 5 min. The reaction mixture was kept at 160°C for 1.5 h to ensure complete reduction of the Pt precursor. Then the particle dispersion was cooled down to ambient temperature.

1.1.2 Synthesis of “Unprotected” Ru Nanoparticles (NPs)

Colloidal „unprotected“ Ru NPs were also prepared by a slightly modified recipe of Wang et al.¹ and almost analogue to “unprotected” Pt NPs. Therefore 0.104 g $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ (38-42% Ru, Sigma-Aldrich) was dissolved in 25 mL EG and a solution of 25 mL 0.5 M NaOH in EG was added. The mixture was vigorously stirred at 500 rpm. The flask was equipped with a reflux condenser and the precursor solution was heated to 160°C using a preheated oil bath while maintaining the stirring of 500 rpm. After 5 min the brown solution turned black, indicating the formation of Ru NPs. The reaction mixture was kept at 160°C for 1.5 h to ensure complete reduction of the Ru precursor followed by cooling to ambient temperature.

1.1.3 Purification of “Unprotected” Pt and Ru Nanoparticles (NPs)

“Unprotected” Pt NPs were precipitated by adding one equivalent of 1 M HCl (VWR), while eight equivalents of 1 M HCl were used to precipitate “unprotected” Ru NPs. The precipitated NPs were isolated by centrifugation and removing the supernatant. Afterwards, the particles were again washed with 1 M HCl to remove residual EG. For further investigations the cleaned particles were redispersed in the desired organic solvent (cyclohexanone, $\geq 99.0\%$, Sigma Aldrich or acetone, 99.9 %, VWR).

1.1.4 Preparation of “OH⁻ Stabilized” Pt and Ru Nanoparticles (NPs)

The purified Pt or Ru NP were redispersed in two equivalents (with respect to EG) of cyclohexanone ($\geq 99.0\%$, Sigma-Aldrich) and then added to eight equivalents (with respect to EG) of a 12.5 mM aqueous NaOH solution. The resulting emulsion was vigorously stirred for 45 min. During mixing the

particles are transferred from the organic phase into the aqueous alkaline phase as indicated by a colour change of the two phases. The organic phase turns clear and the aqueous phase becomes dark. The two phases were filled in a separation funnel and the "OH⁻ stabilized" NPs in H₂O separated from the organic phase after proper phase separation was achieved.

1.1.5 Isolation of "OH⁻ stabilized" Pt and Ru Nanoparticles as Solid Powders and Redispersing

For isolation of "OH⁻ stabilized" Pt and Ru NPs as solid powders, H₂O was completely removed from the aqueous particle dispersion by using a rotary evaporator (P = 20 mbar; T = 50°C) to give a brown-grey solid.

For redispersing H₂O or EG was added to the solid "OH⁻ stabilized" NPs so that the same metal concentration was achieved as used for the synthesis of "unprotected" NPs (compare 1.1.1). While redispersing in H₂O occurs immediately, the same process takes about 10 min in EG, which can be accelerated by sonicating and heating.

1.2 Characterization

1.2.1 IR-Spectroscopic Measurements

All IR spectra were recorded in ATR mode on a Thermo-Nicolet Avatar 370 FT-IR spectrometer. A smart performer ATR unit with a ZnSe crystal plate was applied. All spectra were recorded with a resolution of 4 cm⁻¹ and taking 48 scans.

1.2.2 IR-Spectroscopy of Colloidal "Unprotected" Nanoparticles in Organic Solvent

The precipitated and washed particles were redispersed in 0.5 equivalents (with respect to EG) of pure EG or cyclohexanone. In order to record IR spectra of these colloids the resulting dispersion was simply dropped onto the ATR crystal and the pure solvent was used as reference.

1.2.3 IR-Spectroscopy of Nanoparticle Films Exposed to Aqueous Solutions of Different pH Values

Precipitated and washed particles were redispersed in acetone and dropped onto ZnSe ATR crystal. Solvent removal was achieved by evaporation at ambient conditions which led to solid film of aggregated particles. An IR spectrum of the dried particle film was recorded and used as reference. Then 12.5 mM aqueous NaOH, pure H₂O, or 1 M HCl was dropped onto the particle film and the resulting changes were recorded.

1.2.4 IR-Spectroscopy of "OH⁻ Stabilized" Pt Nanoparticles Redispersed in EG

Isolated "OH⁻ stabilized" Pt NP (see 1.1.5) were redispersed in 0.5 equivalents (with respect to the amount of EG used for synthesis) of pure EG. Spectra of these colloids were recorded in ATR mode directly after redispersion in EG and 3h, 16 h, 24 h, and 48 h after redispersion in EG. Pure EG was used as a reference.

1.2.5 Transmission Electron Microscopic (TEM) Investigations

The as-prepared Pt and Ru NPs were purified and cleaned as described above (1.1), redispersed in acetone and a drop of each dispersion was placed onto TEM grids (ultrathin carbon film, Quantifoil, Cu 200 mesh). The grids were dried at ambient conditions for 30 min.

The "OH⁻ stabilized" NP powders were redispersed in H₂O and dropped onto a TEM grid. Particles that had been stored in alkaline H₂O were directly dropped onto a TEM grid. Samples that were stored as solid powders by applying the chemical cycle shown in Figure 5 were redispersed in acetone when performing the step 5 to 1 (see Fig. 5). Then a drop of this dispersion was placed onto a TEM grid. All samples were dried at ambient conditions for 30 min.

A FEI Tecnai F20 S-TWIN microscope was used at an acceleration voltage of 200 kV and a magnification of 230k. Particle size distributions were determined using ImageJ and counting at least 200 particles.

1.2.6 X-ray Absorption Spectroscopic (XAS) Characterization of Colloidal "Unprotected" Nanoparticles in EG and alkaline H₂O

XAS investigations on Pt NPs dispersions were carried out at the Diamond Light Source (DLS), Didcot (England), using the quick EXAFS beam line, B18. The storage ring of the DLS was operated at a beam current of 300 mA and the storage ring energy was 3.0 GeV. In order to probe the electronic properties Pt NPs two samples were prepared: i) particles dispersed in EG representative for the CO covered state they exhibit in organic solvents and ii) particles dispersed in alkaline H₂O. The samples were firstly frozen in liquid nitrogen and during the XAS measurements the samples were kept cold. Si(111) double crystal monochromators were used in combination with a Ge 9 element detector for fluorescence acquisition of the Pt L₃ edge spectra. The averaged XAS spectra (obtained from three scans) were analysed by using the IFEFFIT software suite.² Preliminary data processing included the background subtraction and edge-step normalization. The energy units (eV) were converted to photoelectron wave vector k units (\AA^{-1}) by assigning the photoelectron energy origin, E_0 , corresponding to $k = 0$, to the first inflection point of the absorption edge. The resulting $\chi(k)$ functions were weighted with k^2 to compensate for the dampening of the XAFS amplitude with increasing k . Subsequently, the EXAFS spectra were Fourier-transformed to obtain pseudo radial structure functions (RSFs). The amplitude reduction factor (S_0^2) was obtained from the fit of the EXAFS spectra of the Pt foil to be 0.84. Using the

Artemis software² the coordination number (N), interatomic bond length (R), mean squared bond length disorder (σ^2) and correction to the energy origin (ΔE_0), together with its error bars were established for the Pt-Pt and Pt-O scattering pairs by fitting theoretical EXAFS signal to the data in r-space.

1.3 Catalysis Experiments

1.3.1 Catalyst Preparation

For catalytic investigations two different preparation routes were tested:

First, as-prepared “unprotected” Pt NPs were precipitated, rinsed, and redispersed in cyclohexanone (see Fig. 1 and section 1.1 in SI). Next, the particles were deposited onto Al₂O₃ (Puralox SCCa 150/200; Sasol, grain size = 200-500 μ m) from cyclohexanone by adding Al₂O₃ to give a nominal metal loading of 2 wt% (with respect to the amount of Pt precursor initially used for synthesis) and by removing the solvent with a rotary evaporator (P = 20 mbar; T = 60°C). The supported catalyst was rinsed twice with acetone and subsequently dried 10 min in a desiccator at reduced pressure and ambient temperature. Second, NPs redispersed in cyclohexanone were transferred into alkaline H₂O, the solvent was removed by using a rotary evaporator, and the NPs stored as solid powders (see Fig. 5 and section 1.1 in SI). Particles were redispersed in EG for 24 h or 48 h prior to precipitation by adding HCl and redispersing in cyclohexanone (see Fig. 1 and section 1.1 in SI). From cyclohexanone the particles were deposited onto Al₂O₃ (Puralox SCCa 150/200; Sasol, grain size = 200-500 μ m) by adding Al₂O₃ to give a nominal metal loading of 2 wt% (with respect to the amount of Pt precursor initially used for synthesis) and by removing the solvent with a rotary evaporator (P = 20 mbar; T = 60°C). The supported catalyst was rinsed twice with acetone and subsequently dried 10 min in a desiccator at reduced pressure and ambient temperature.

The actual metal loadings of the different catalysts 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.

1.3.2 Catalytic Hydrogenation of 2-Butanone

Five in-house designed stainless steel autoclaves were used for catalytic investigations. The autoclaves were placed on a fivefold stir plate and connected to the same H₂ gas line in order to perform five experiments in parallel under identical conditions. In all experiments each autoclave was loaded with 10 mL 2-Butanone (>99%, Sigma-Aldrich) and 0.2 g catalyst. After purging three times with H₂ (Linde 5.0) the pressure was set to 20 bar. Experiments were performed at a temperature of 293 K and a

stirring rate of 800 rpm. In order to determine reaction rates, the conversion was kept below 10% (reaction time = 1 h). This enables to assume differential operation conditions and to determine reaction rates directly from conversions.³ After reaction the catalyst was removed by centrifugation and the product was analysed by gas chromatography (see 1.3.3). The experimental errors of the activities were determined by performing five experiments and estimating the resulting standard deviation.

1.3.3 Product Analysis of Catalytic Experiments

The reaction mixtures of the catalytic experiments were analysed by a gas chromatography (Shimadzu GC-2010plus AF IVD) using a Zebron (ZB-WAXplus, 30 m length, 0.25 mm inner diameter, 0.25 μm film thickness) column and a flame ionization detector (FID). A column flow of 0.86 mL min^{-1} was applied with He (Line, 5.0) as carrier gas and a linear velocity of 25.1 cm s^{-1} . The oven was held at 50°C for 1 min, then heated to 75 °C at a rate of 5 °C min^{-1} and kept for 1 min. After further heating to 180°C at a rate of 30 °C min^{-1} the temperature program was stopped.

2. Supporting Data

2.1. Supporting Data of Phase Transfer Experiments

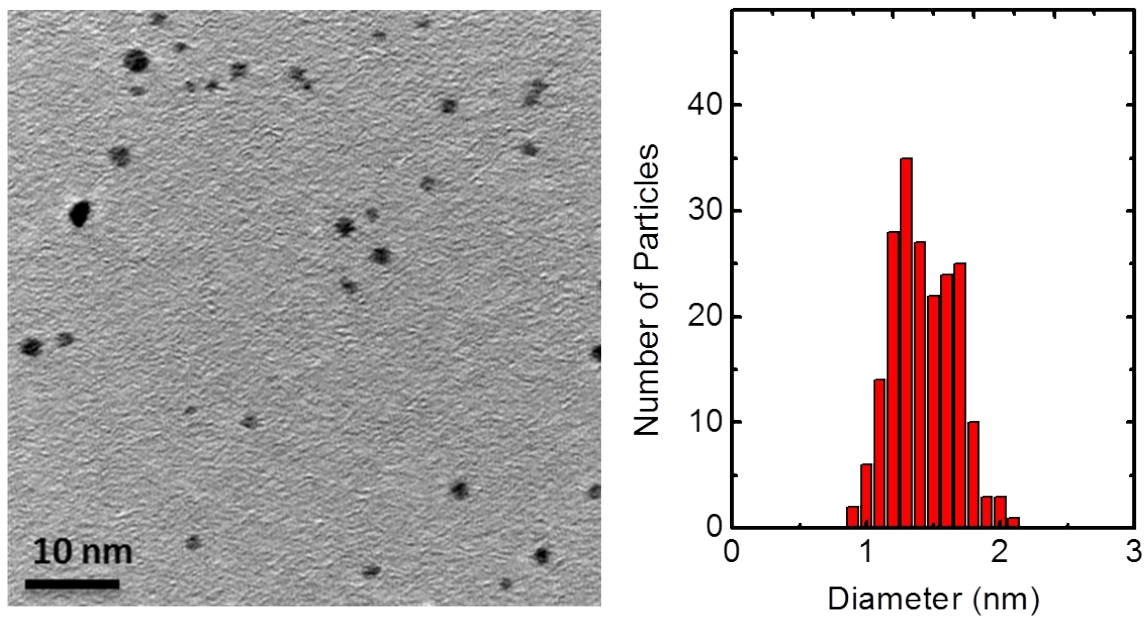


Fig. S1 Representative TEM image (left) and particle size distribution (right) of Pt as-prepared NPs. The mean particle size is $d = 1.4 \pm 0.4$ nm.

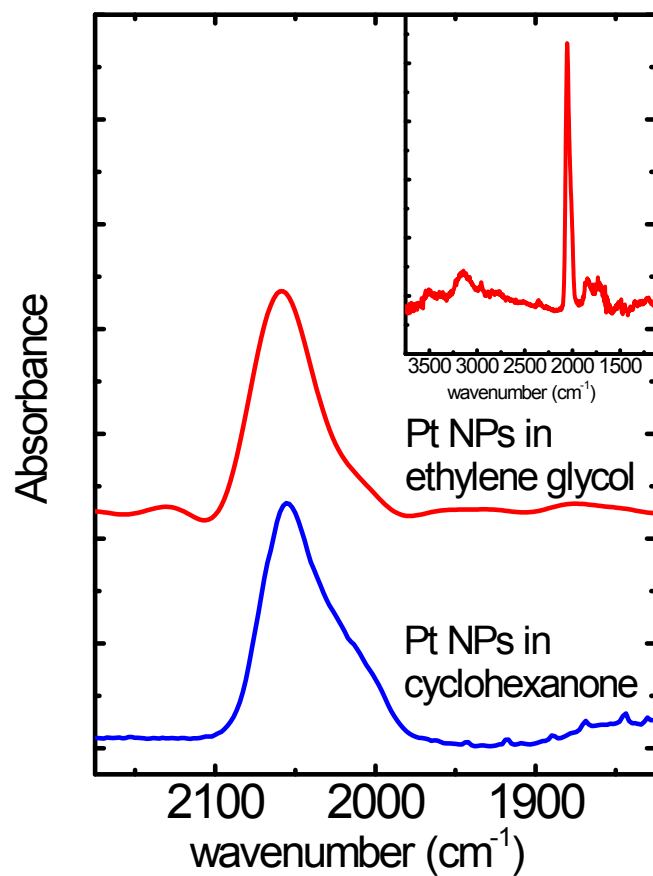


Fig. S2 „Unprotected“ Pt NPs handled as illustrated in Fig. 1 and then redispersed in EG (red) or cyclohexanone (blue). A pronounced band appears between 2055 cm^{-1} and 2060 cm^{-1} , related to linearly bound CO and revealing a CO-saturated surface. The inset shows a full spectrum of particles redispersed in EG. Bands below 2000 to 1700 cm^{-1} (see inset) are associated to two- and threefold bound CO. Bands around 3000 are related to small deviations in the background, but not to surface bound solvent species as previously demonstrated by NMR spectroscopy.

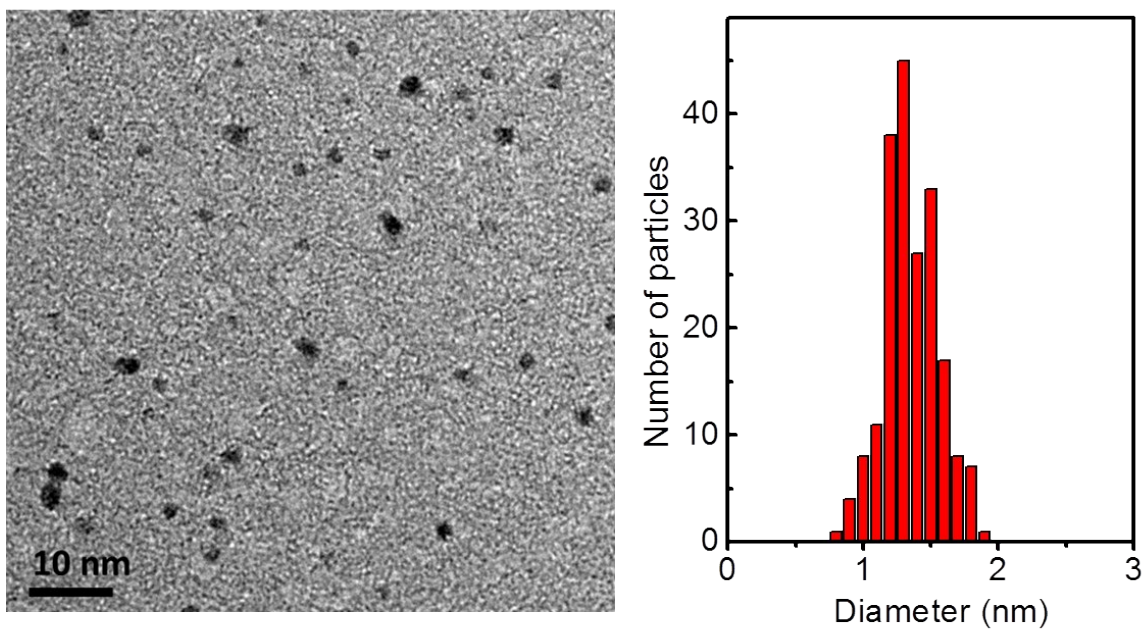


Fig. S3 Representative TEM image (left) and particle size distribution (right) of Pt NPs redispersed in cyclohexanone that were exposed to phase transfer conditions using 1M HCl (see Fig. 2, experiment show on the right). The mean particle size is $d = 1.3 \pm 0.3$ nm.

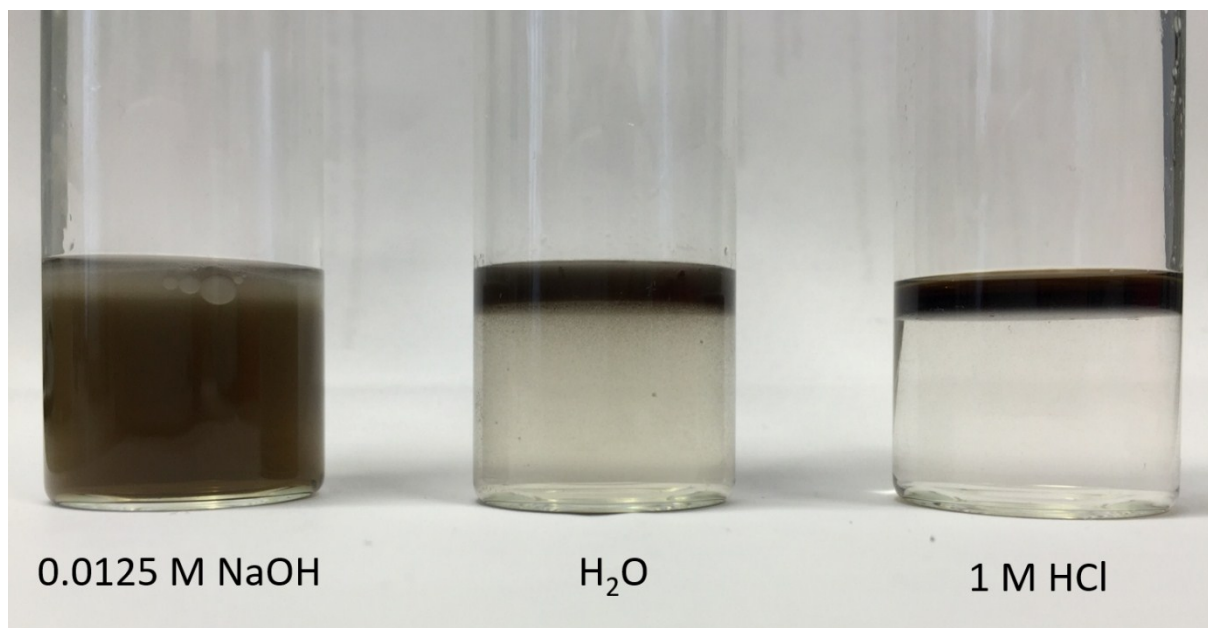


Fig. S4 Phase transfer experiments performed with “unprotected” Ru nanoparticles dispersed in cyclohexanone (upper phase) and aqueous solutions of different pH values (lower phase). No changes were obtained at high proton concentrations (right). Neutral H₂O leads to flocculation (middle). Under alkaline conditions the particles are transferred (left), when the OH⁻ concentration in the aqueous phase is high enough so that the final pH after transfer is alkaline (pH > 7).

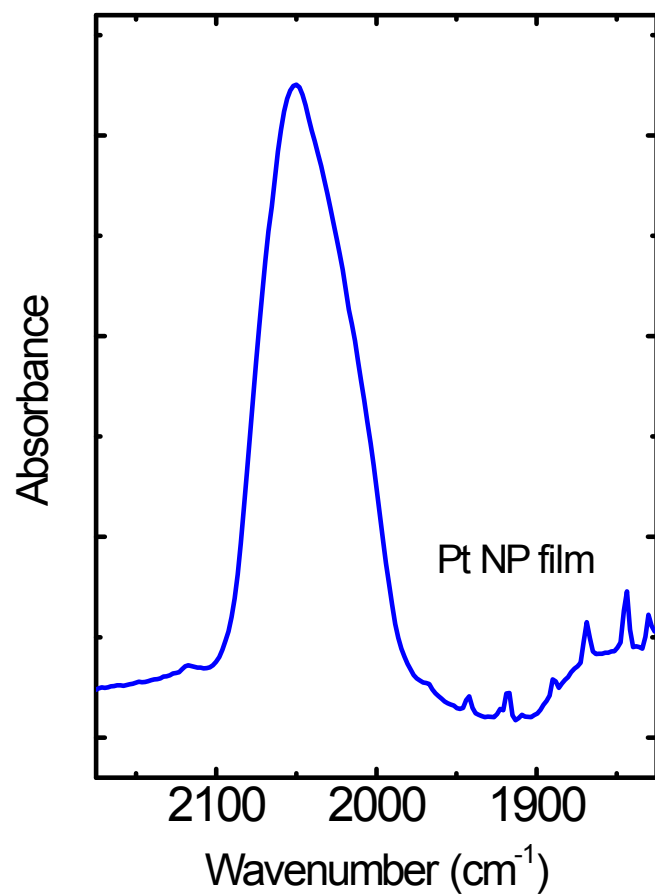


Fig. S5 IR spectrum of a Pt NP film prepared on ATR crystal. The pronounced band at around 2055 cm⁻¹ is related to linearly bound CO. The small shoulder at 1840 cm⁻¹ indicates the presence of bridge-bonded CO.

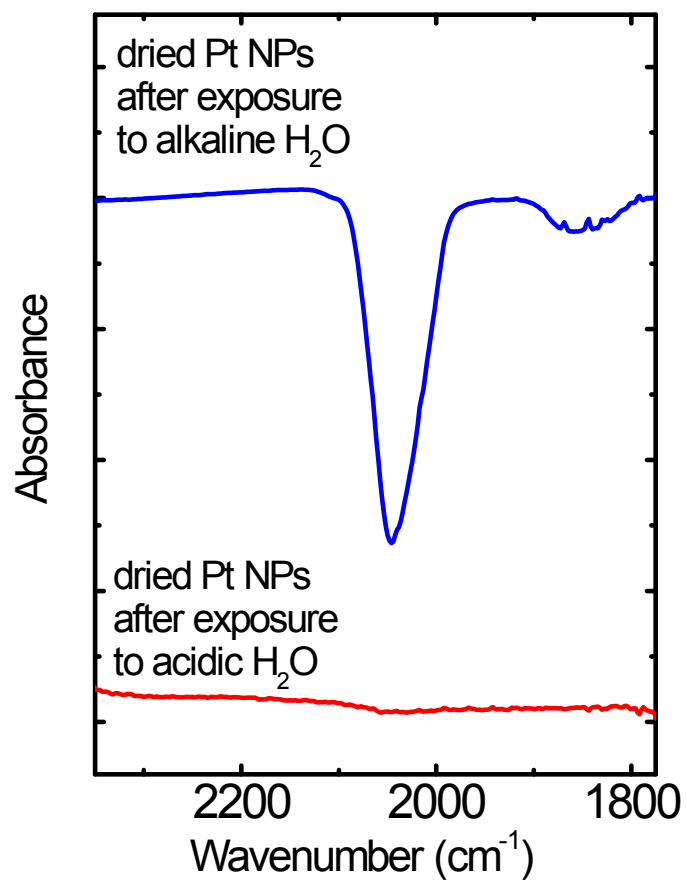


Fig. S6 „Unprotected“ Pt NPs deposited onto an ATR crystal after exposed to acidic (red) and alkaline (blue) H₂O. Exposure of dried Pt NPs to neutral H₂O led to the same spectral changes as observed for alkaline solutions (blue).

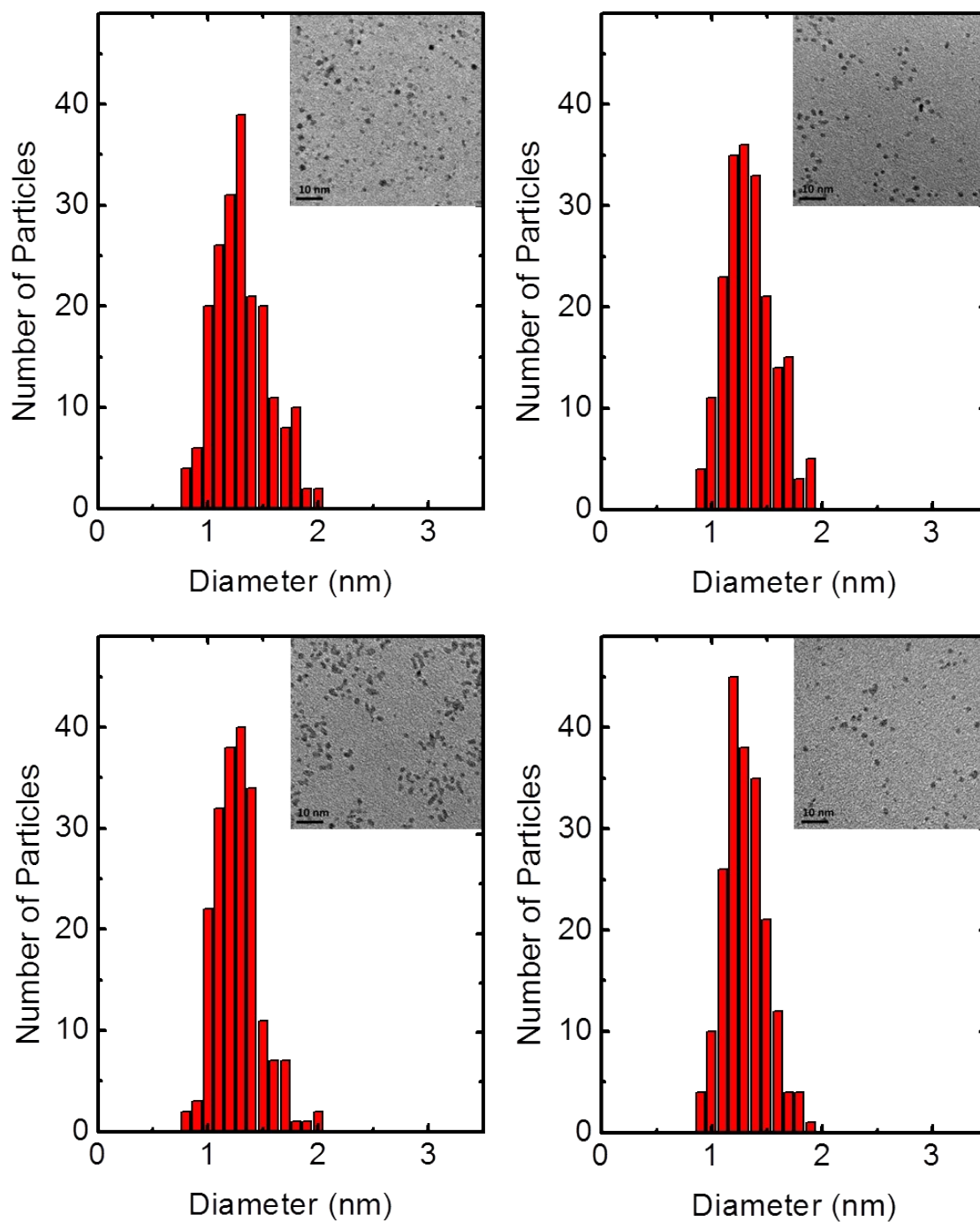


Fig. S7 Particle size distributions and representative TEM images of as-prepared “unprotected” Ru NPs (a), particles stored in alkaline H₂O for two weeks (b), particles stored as solid powder for two weeks (c), and (d) particles that passed the complete chemical cycle shown in Figure 5. The mean particle diameters of these four samples are $d = 1.3 \pm 0.4$ nm (a), $d = 1.3 \pm 0.4$ nm (b), $d = 1.3 \pm 0.3$ nm (c), and $d = 1.3 \pm 0.3$ nm (d). No change in particle size is obtained within the accuracy of the size analysis.

2.2. Results and Discussion of X-ray Absorption Spectroscopic (XAS) Characterization of Colloidal "Unprotected" Nanoparticles in EG and alkaline H₂O

In Figure S8 the Pt L₃-edge XANES spectra of the dispersed Pt nanoparticles in EG and alkaline H₂O show the characteristic behaviour of the white line intensities. The white line intensity (2p → 5d transition) reflects the degree of the vacancy of Pt 5d orbitals near the Fermi level and allows determination of the oxidation state of the Pt from these samples. As a reference, the XANES spectra of the Pt foil is also shown in Figure S8. The heights of the white line intensities for these samples are clearly different. The Pt NPs dispersed in alkaline H₂O exhibit a higher white line intensity than those of the Pt nanoparticles in EG and of the Pt foil. This observation reveals that the Pt nanoparticles in alkaline H₂O are strongly oxidized compared the Pt nanoparticles in EG.

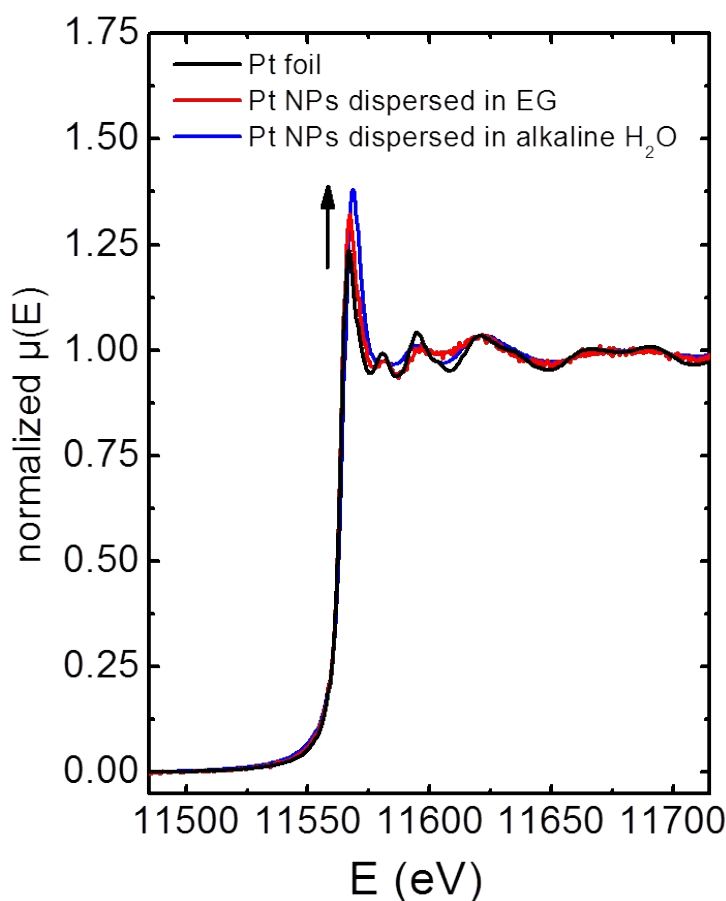


Fig. S8 Pt L₃-edge XANES spectra for the Pt nanoparticles dispersed in EG and alkaline H₂O and for the Pt foil as reference.

Figure S9 shows the k²-weighted Fourier-transformed EXAFS spectra and the corresponding fits for the Pt NPs dispersed in EG (a, left) and alkaline H₂O (b, right). Comparison reveals an additional signal at

around 2 Å in the EXAFS spectra for the Pt NPs in alkaline H₂O, indicating that these NPs are oxidized. Table S1 summarizes the best fit parameters from the EXAFS analysis of both samples. The EXAFS spectra for the Pt nanoparticles dispersed in alkaline H₂O clearly evidence a contribution of the Pt-O scattering pair. As the partial coordination number of the Pt-O is smaller than that of the Pt-Pt, the Pt-O bond appears as a surface oxide.

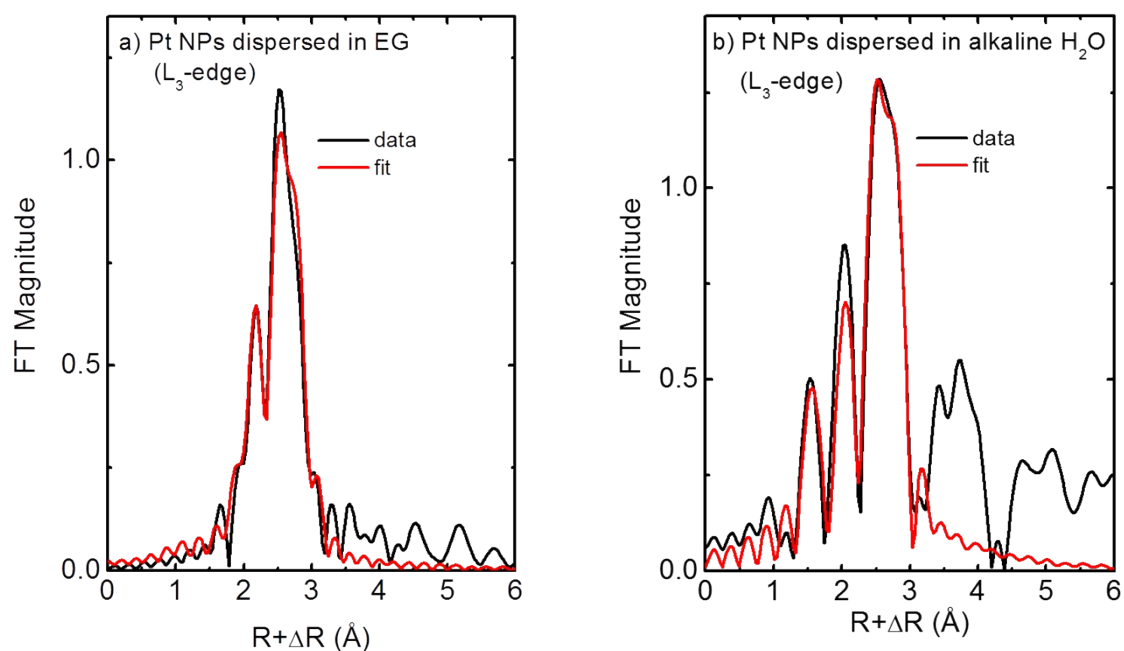


Figure S9. Fourier-transform (FT) magnitudes of the k^2 -weighted EXAFS spectra (black line) and of the corresponding fits (red line) at the Pt L_3 -edge for the Pt nanoparticles dispersed in EG (a) and alkaline H₂O (b). The k -ranges for the FT spectra were from 2 to 14 Å⁻¹, while the ranges for the fits were from (a) 1.8 to 3.1 Å and (b) 1.3 to 3.1 Å, respectively.

Table S1. First nearest neighbor coordination shell (N), atomic distance (R), mean square disorder parameter (σ^2), shift of energy (E_0) at the corresponding edges, R_f -factor (closeness of the fit as quality parameter) for the Pt NPs dispersed in alkaline H_2O and EG.

Pt NPs	bond	N	R / Å	$\sigma^2 \times 10^{-4} / \text{Å}^2$	$\Delta E_0 / \text{eV}$	R_f
EG	Pt – Pt ₁	6.6 ± 0.7	2.755 ± 0.005	56 ± 5	4.8 ± 0.7	0.015
H ₂ O/NaOH	Pt – Pt ₁	5.6 ± 1.0	2.740 ± 0.007	33 ± 8	5.2 ± 1.6	0.024
	Pt – O ₁	0.3 ± 0.2	1.923 ± 0.011	71 ± 25		
	Pt – M	5.9 ± 0.7				

2.3. TEM Images and Particle Size Distributions of the Different Stages of the Chemical Cycle shown in Figure 5

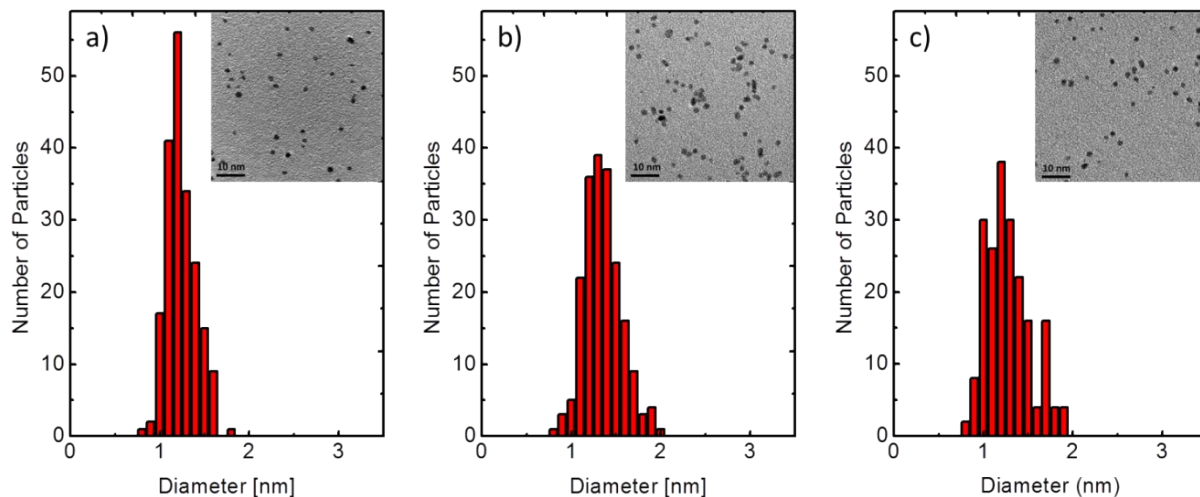


Figure S10. Particle size distributions and representative TEM images of Pt NPs at the different stages of the chemical cycle shown in Figure 5. (a) corresponds to as-prepared particles in cyclohexanone which represents step 1 of the chemical cycle. (b) shows a TEM image and the according particle size distribution of a TEM sample prepared from an alkaline Pt NP dispersion. This represents step 2 and 3 of the chemical cycle. For step 4 and 5 no images can be provided as EG does not allow for preparing TEM samples. Due to the low vapour pressure of EG samples dry not properly but the EG evaporates under the ultra-high vacuum conditions (UHV) in a TEM. As a result, the clean conditions needed for TEM studies cannot be fulfilled for such samples. (c) shows a sample prepared from NPs in cyclohexanone after they passed step 4 and 5 which furthermore corresponds to a sample that passed the entire chemical cycle shown in Figure 5. The particle sizes of (a), (b), and (c) are $d = 1.3 \pm 0.2$ nm, $d = 1.4 \pm 0.3$ nm, and $d = 1.2 \pm 0.2$ nm, respectively. This demonstrates that no significant change in particle size is obtained at any stage of the chemical cycle shown in Figure 5.

2.4. Metal Loadings of Supported Catalysts Prepared with “Fresh” and “Stored” Pt NPs

Table S2 Metal contents of Al₂O₃ supported Pt NPs prepared with i) NPs immediately after synthesis and ii) NPs that were stored as solid powders. The experimental errors of the metal loading were determined from the standard deviation of measurements performed on four individually prepared catalysts. The experiments show that within the limits of accuracy of the method no significant change of the metal loading is obtained. It is hence concluded that particle storage and reuse can be achieved without significant loss of the precious metal.

Sample	Pt content
Al ₂ O ₃ supported Pt NPs prepared with “fresh” NPs	1.59 ± 0.07 wt%
Al ₂ O ₃ supported Pt NPs prepared with “stored” NPs	1.57 ± 0.09 wt%

3. References

1. Y. Wang, J. W. Ren, K. Deng, L. L. Gui and Y. Q. Tang, *Chem. Mater.*, 2000, **12**, 1622-1627.
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