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## ARTICLE

# Reliable Palladium Nanoparticle Syntheses in Aqueous Solution: The Importance of Understanding Precursor Chemistry and Growth Mechanism

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,  
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

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Reliable protocols for the synthesis of palladium nanoparticles (Pd-NPs) in aqueous solution are rarely found and corresponding growth mechanisms often remain unknown. Furthermore, syntheses of Pd-NPs always demand the use of stabilizing agents which are often unfavorable for catalytic applications. In this contribution, the importance of the palladium precursor chemistry as prerequisite for any reliable Pd-NPs synthesis in aqueous solution is shown. This includes a detailed study of the influence of precursor chemistry on the nanoparticle growth mechanism. The findings enable the controlled modification of a common synthetic protocol (*i.e.* the reduction of a palladium precursor with NaBH<sub>4</sub>) for sub 5 nm Pd-NPs without the use of any stabilizing agent. In addition, it is also shown that such mechanistic studies are not only of great importance for the development of novel synthetic procedures. Exemplarily, the successful transfer of the synthesis from lab- to large-scale is demonstrated.

## Introduction

Noble metal nanoparticles (NPs) are widely studied due to their manifold applications in electronics, medicine or catalysis.<sup>1–3</sup> In particular, palladium nanoparticles (Pd-NPs) are of great scientific and commercial interest because of their unique catalytic properties.<sup>4–6</sup>

The catalytic performance of Pd-NPs strongly depends on their size (in particular in the sub 10 nm regime), shape, and surface modification (*i.e.* surfactants, ligands, and coordinating solvents).<sup>7–15</sup> Only few reliable Pd-NP syntheses are described in literature which in general demand the use of stabilizing agents (*i.e.* surface modification).<sup>14</sup> In addition, the syntheses are often carried out in organic solvents, unfavorable for many applications.<sup>10,16</sup> Surface modifications can decrease the catalytic activity of NPs by blocking their active sites. In addition, stabilizing agents can complicate the further use of NPs in catalyst syntheses (*e.g.* immobilization of NPs in porous layers).

Consequently, reliable synthetic protocols for NPs with defined size in aqueous solution without any stabilizing agent are highly demanded.<sup>14,17,18</sup> These solely electrostatically stabilized NPs are free of organic stabilizers or ligands and therefore herein called “naked”. Such “naked” NPs can be used directly for catalytic applications, both in aqueous solution or for solid supports.<sup>17,19,20</sup> Furthermore, “naked” Pd-NPs can be

functionalized with ligands according to the desired application (*e.g.* chiral ligands for enantioselective catalysis<sup>21–23</sup>), without the elaborate removal or exchange of surfactants.<sup>14,18</sup> “Naked” Pd-NPs can also serve as reference system for catalytic properties of NPs.<sup>18</sup>

This contribution addresses: (i) general issues for reliable Pd-NP syntheses in aqueous solution, in particular the precursor chemistry; and (ii) the mechanistic understanding of NP growth. The results enabled the design of a reliable synthetic procedure for “naked” sub 5 nm Pd-NPs in aqueous solution based on the reduction of a metal precursor with NaBH<sub>4</sub>. Furthermore, it is also shown that such mechanistic studies are not only of great importance for the development or improvement of synthetic procedures. Exemplarily, crucial points for a successful upscaling of a lab-scale procedure are deduced for this novel synthesis.

## Experimental section

All chemicals were used as purchased without any purification. Ultrapure water (18.2 MΩ cm) was used as a solvent for all reactions.

Synthesis of Pd-NPs without pH adjustment: 5 ml of a freshly prepared 3 mM NaBH<sub>4</sub> (Sigma Aldrich, 99.99%) solution was mixed 1:1 with 5 ml of a 0.5 mM solution of K<sub>2</sub>PdCl<sub>4</sub> (Alfa Aesar, 99.999%) using Eppendorf pipettes.

Synthesis of Pd-NPs with pH adjustment: The pH value of the precursor solution was adjusted by addition of NaOH (Carl Roth, p.a.) or HClO<sub>4</sub> (Sigma Aldrich, 99.99%). The synthesis was carried out as described above.

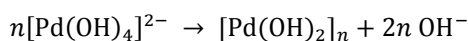
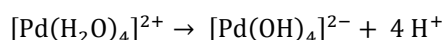
Characterization: UV-Vis spectra of the precursor solutions were measured with a SEC2000 spectrometer (BAS Inc.). SAXS experiments were carried out with a lab-scale setup (SAXSess, Anton Paar) using a flow through quartz cuvette. The SAXS data were evaluated assuming spherical particles with a Schulz-Zimm distribution. Details on the mathematical modeling<sup>24</sup> and the experimental setups can be found in the supplementary information (SI).

## Results and discussion

This contribution consists of four parts. At first, the chemistry of Pd precursors in water is discussed as a key issue for controlled syntheses of Pd-NPs. In the second part, the growth mechanism of Pd-NPs synthesized via the reduction of K<sub>2</sub>PdCl<sub>4</sub> with NaBH<sub>4</sub> is investigated. In the third part, the influence of the precursor chemistry on the NP growth is investigated and a synthetic procedure for “naked” Pd-NPs is deduced. Finally, the upscaling of a lab scale NP synthesis is demonstrated.

### Pd hydrolysis in aqueous solution

Palladium salts such as alkali tetrachloropalladates (X<sub>2</sub>PdCl<sub>4</sub>) or palladium nitrate (Pd(NO<sub>3</sub>)<sub>2</sub>) are typically used as precursors for Pd-NP syntheses.<sup>10,13,14,25–27</sup> In aqueous solution, palladium ions form aqua complexes that are subject to pH dependent hydrolysis.<sup>28</sup> Subsequent olation processes result in the formation of polynuclear hydroxo complexes (following denoted as PHC):<sup>29</sup>



Although hydrolysis of Pd complexes is focus of several publications<sup>29–34</sup>, its influence on syntheses of Pd-NPs in aqueous solution is to the best of our knowledge not described in the literature. In this section the hydrolysis of Pd complexes in aqueous solution and its influence on Pd-NP syntheses are discussed exemplarily for K<sub>2</sub>PdCl<sub>4</sub>. A detailed study that includes other common Pd precursors can be found in S2 of the SI.

Fresh solutions of K<sub>2</sub>PdCl<sub>4</sub> in a typical concentration for NP syntheses (e.g. 0.25–3 mM) are transparent and yellow. Within minutes, the color of the precursor solutions changes to brown due to the formation of PHC. The PHC precipitate within hours (see Fig. 1 a). This process of precursor aging was investigated with time-resolved UV-vis and small angle X-ray scattering (SAXS). Selected UV-vis spectra and scattering curves of the precursor solution within the first hour of aging are displayed in Fig 1 b and c. The UV-vis spectrum of a fresh K<sub>2</sub>PdCl<sub>4</sub> solution shows absorption maxima at 310 nm and

420 nm that are typical for ligand-to-metal charge transfer bands of [PdCl<sub>3</sub>H<sub>2</sub>O]<sup>-</sup> in water.<sup>32,35</sup> Within seconds, a broad background absorbance evolves with increasing intensities towards shorter wavelengths which most likely indicates the formation of PHC.<sup>32</sup> After several hours, the absorbance decreases caused by PHC precipitation (for details see S2 in SI).

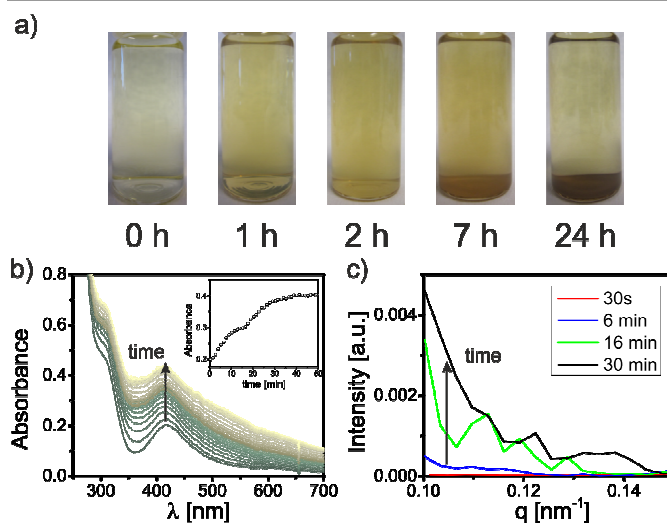


Figure 1: (a) Digital photographs of the aging process of an aqueous K<sub>2</sub>PdCl<sub>4</sub> solution (1 mM); (b) time-resolved UV-vis measurements of 1h aging of a 1 mM K<sub>2</sub>PdCl<sub>4</sub> solution (spectra were recorded in 1 min intervals); the inset shows the absorbance at 420 nm as a function of time (c) scattering curves of a 0.5 mM K<sub>2</sub>PdCl<sub>4</sub> solution in linear representation

The scattering curves of a K<sub>2</sub>PdCl<sub>4</sub> solution at different aging times are displayed in Fig. 1 c. Scattering of PHC is not observed for a fresh Pd precursor solution (aging time less than 30 s). At aging times larger than 2 min, the intensity increases at low q values, indicating the formation of larger colloidal PHC (for details see S2.4 in SI). The PHC size can be estimated to be larger than 20 nm in radius. Upon aging of the Pd solution, PHC grow further until precipitation. Scattering curves and UV-vis data for aging of Na<sub>2</sub>PdCl<sub>4</sub> and Pd(NO<sub>3</sub>)<sub>2</sub> solutions can be found in Fig. S3 - S6 of the SI. In general, they show the same characteristics.

The precipitation of PHC strongly depends on the presence of Cl<sup>-</sup> ions. In Pd solutions without Cl<sup>-</sup> (e.g. aqueous Pd(NO<sub>3</sub>)<sub>2</sub> solutions), the formed PHC do not precipitate within weeks. The addition of small amounts of Cl<sup>-</sup> to fresh Pd(NO<sub>3</sub>)<sub>2</sub> solution results in precipitation upon aging of few hours as known for the palladates.

The time-resolved UV-vis and SAXS measurements of the precursor aging show that Pd salts start to hydrolyze within seconds. This fast formation of PHC has to be considered for Pd-NP syntheses in aqueous solution. Thus, precursor solutions have to be used instantly after preparation (aging time < 10 s) for Pd-NP synthesis to avoid the formation of relevant amounts of PHC. At this extremely short aging time, formation of PHC is not observed by UV-vis and SAXS. Hence, in very fresh precursor solutions the formation of PHC can be neglected.

### Mechanistic studies

The synthesis of Pd-NPs is focus of many publications, yet the underlying mechanisms of particle formation are rarely investigated.<sup>36</sup> The investigation of the NP growth mechanism and parameters that determine the particle size are an essential step towards a directed nanoparticle design.<sup>37</sup>

Previously, we deduced growth mechanisms of gold and silver nanoparticle syntheses.<sup>37–40</sup> In a recent publication, we showed that reduction of gold and silver precursors by NaBH<sub>4</sub> is a very fast process which occurs within the mixing time of precursor and reducing agent solution. Thus, the reduction is much faster than the actual particle growth.<sup>38</sup> It was shown that the growth mechanism of gold NPs consists of one coalescent step whereby the corresponding silver NP synthesis comprises two well separated steps of coalescence.

For the synthesis of Pd-NPs a fresh 0.5 mM aqueous solution of K<sub>2</sub>PdCl<sub>4</sub> was mixed 1:1 with a 3 mM solution of NaBH<sub>4</sub> (for details see S1 in SI). Since NaBH<sub>4</sub> hydrolyzes in aqueous solution, it was prepared freshly and used within approx. 10 min.<sup>41</sup> Upon mixing of K<sub>2</sub>PdCl<sub>4</sub> and NaBH<sub>4</sub>, the solution turns immediately from yellow to light brown, indicating the formation of Pd-NPs. After approx. 10–20 min, a color change from brown to gray-black is observed.

The particle growth mechanism was investigated with time-resolved SAXS measurements. The first seconds of the particle growth were measured using a continuous flow setup (CFS). The further growth was monitored with a standard SAXS setup. The CFS was applied to overcome the limited time-resolution of lab scale SAXS setups. A detailed description of the CFS can be found in the SI (S6.1) and in a previous publication.<sup>38</sup> Briefly, a CFS transforms the time scale into a length scale. A syringe pump was used to mix the reactants via Teflon tubings and mixers. The adjustment of the tube length and flow rate enables a millisecond time resolution. The samples were measured using a standard SAXS flow through quartz capillary. The results of the CFS experiments are displayed in Fig. 2 a and b. Within the first seconds of the synthesis, Pd-NPs grow from 0.8 to 1.2 nm in radius (polydispersity of 20%). The volume fraction remains rather constant throughout the synthesis, while the relative number of particles decreases, indicating a growth by coalescence.<sup>38</sup>

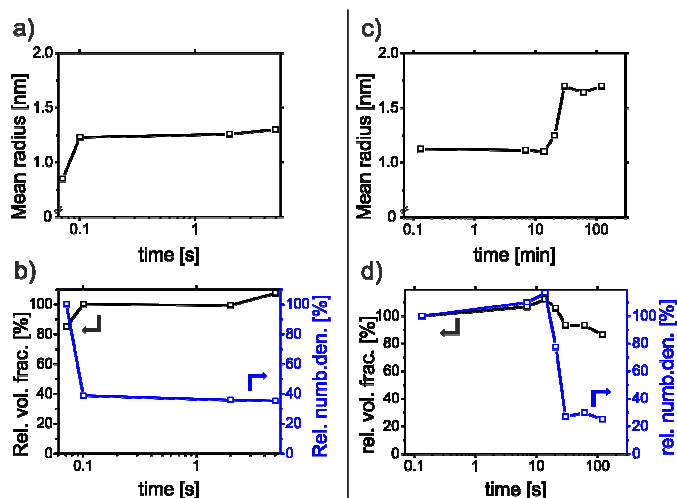


Figure 2: Results for time-resolved SAXS measurements for the investigation of the particle growth mechanism; a) mean particle radius (polydispersity 20%) and (b) relative volume fraction and relative number density for the first milliseconds of particle growth derived from the continuous flow setup (CFS) measurements; (c) and (d) results for the further particle growth within 2 h (polydispersity 25%).

The further particle growth was investigated by extracting samples from a stirred NP solution which were subsequently measured with a standard lab-scale SAXS setup (time-resolution in a range of about 1 min). A PVP solution was added to the samples to prevent NP aggregation during the measurement. Fig. 2 c and d show the SAXS results for reaction times up to 2 h. The first data point corresponds to a sample extracted at 8 s and reveals particles with a mean radius of approx. 1.1 nm. This is in accordance with the particles measured with the CFS at 5 s. After about 20 min, a further particle growth step is observed. At this point the color of the reaction solution changes from light brown to gray black. The final particles have a mean radius of approx. 1.8 nm (polydispersity 25%).

The growth is due to coalescence since the volume fraction remains rather constant throughout the synthesis. The results are similar to the corresponding Ag-NPs synthesized by the reduction of AgClO<sub>4</sub> with aqueous NaBH<sub>4</sub>.<sup>37,40</sup> As a result, particle growth and final size is only governed by colloidal stability.<sup>38,40</sup> The deduced growth mechanism is displayed schematically in Fig. 3. The particle growth consists of two distinct steps of coalescence separated by a metastable phase. The metastable particles are formed within seconds by the coalescence of Pd and clusters. After 10–20 min, the metastable particles grow in a second coalescent step to give the final particles.



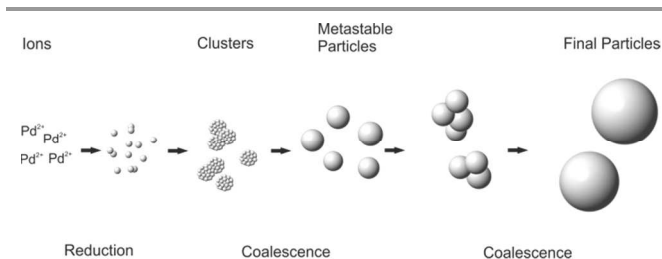


Figure 3: Schematic illustration of the deduced growth mechanism of Pd-NPs.

The second coalescence is a consequence of an abrupt decrease of colloidal stability. We assume that the decrease of colloidal stability coincides with the full consumption of  $\text{NaBH}_4$  as observed for Ag-NPs.<sup>37</sup> Pd-NPs were shown to form an oxide layer in aqueous solution<sup>42,43</sup> that can decrease the colloidal stability of the Pd-NPs. Excess  $\text{BH}_4^-$  in the reaction mixture could continuously reverse such a surface oxidation. With the full consumption of  $\text{BH}_4^-$ , an oxide layer would be formed on the surface, decreasing the colloidal stability. As a consequence, growth due to coalescence is induced.

The final Pd-NPs are not long time stable and precipitate within days. The particles should be used within 1-2 h after the synthesis or stabilized with a stabilizing agent to prevent aggregation. The stabilizing agent can be selected according to the required application.

#### Influence of precursor aging on NP growth

In a previous section it was shown that the formation of PHC is a fast process in aqueous Pd precursor solutions. To evaluate the influence of PHC on the NP formation, the Pd-NP synthesis was investigated using an aged precursor solution (6 min). SAXS measurements of final particles reveal a broad NP size distribution with mean radii between 2 nm and 20 nm.

An aged Pd precursor solution contains two Pd species in unknown concentrations: dissolved  $\text{Pd}^{2+}$ -ions and aggregated PHC. The growth mechanism for NP formed from the dissolved  $\text{Pd}^{2+}$  in an aged solution is most likely not influenced by the presence of PHC. Particles with radii of approx. 2 nm are also formed in the aged solutions. Furthermore, the characteristic color change from light brown to gray-black after approx. 20 min indicating the second growth step is still observed.

The large particles most likely result from the reduction of PHC since the PHC in aged precursor solution are in the same size range as the large Pd particles in the NP solution. Thus, the broad size distribution originates from the simultaneous reduction of dissolved  $\text{Pd}^{2+}$  and PHC leading to two different mechanisms of particle formation. The large particles originate from the reduction of PHC. In addition, the reduction of dissolved  $\text{Pd}^{2+}$  leads to small particles as described in the previous section and depicted in Fig. 4.

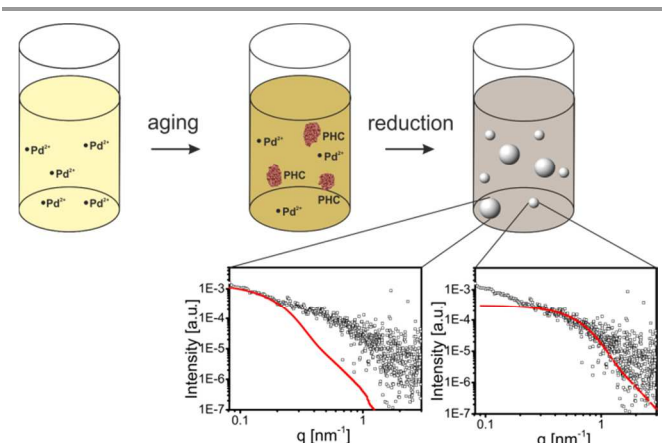


Figure 4: Schematic illustration of the Pd-NP synthesis with aged precursors; aged precursor solution contain  $\text{Pd}^{2+}$  and polynuclear hydroxo complexes (PHC). The chemical reduction of an aged Pd precursor solution leads to NPs with a broad size distribution; large particles originate from the reduction of PHC and cause scattering at low  $q$  values, while small particles derive from the reduction of dissolved  $\text{Pd}^{2+}$  and cause scattering at high  $q$  values.

#### Precursor stabilization and upscaling

It was shown that the hydrolysis of palladium salts and the formation of PHC is a crucial issue for the synthesis of monodisperse sub 10 nm Pd-NPs in aqueous solution. The formation of relevant amounts of PHC in precursor solutions can be avoided by using very fresh precursor solutions (aging time < 10 s). However, this is not practical and often not possible. Thus, hydrolysis of Pd complexes is a general issue for the synthesis of Pd-NPs that needs to be considered if precursor solution cannot be used within few seconds. This applies in particular to large-scale syntheses, seed-mediated growth procedures, synthetic procedures at elevated temperatures (which accelerate the hydrolysis<sup>43</sup>) and syntheses using mild reducing agents.

The stabilization of precursor solutions is necessary in order to overcome the issue of precursor instability. The formation of PHC can be delayed or inhibited at low pH values.<sup>34,45</sup> However, low pH values involve a high ionic strength which decreases the colloidal stability of NPs. As a result, NPs synthesized with strongly acidic precursor solutions ( $\text{pH} < 2$ ) precipitate immediately if no further stabilizing agents are used. Thus, very acidic precursor solutions are inappropriate for synthesis of sub 5 nm and in particular for “naked” Pd-NPs.

Consequently, for the synthesis of “naked” sub 5 nm Pd-NPs, a balance between precursor and colloidal stability is required. For the above described synthetic procedure such a balance is found at a pH value of 3.3 (pH value adjusted with  $\text{HClO}_4$ ). Formation of PHC at a pH value of 3.3 in the precursor solution is not observed for at least 30 min (scattering curves are displayed in Fig. 5 in the supporting information). From precursor solution with pH value of 3.3 stable particles with a mean radius of 2.3 nm (polydispersity 30%) are reproducibly formed without the addition of steric stabilizers as revealed from SAXS measurements. The particles formed from pH-stabilized precursors are only slightly larger than those synthesized with fresh and non-acidic Pd precursor solutions

(for details see S2 in SI). In accordance to the SAXS experiments, TEM images of the final particles show spherical NPs with a mean radius of 2.2 nm (see S4 in SI).

As shown, the pH-stabilization of precursor solutions is necessary for several synthetic procedures. The relevance of precursor stabilization is illustrated by upscaling the beforehand developed Pd-NP synthesis. This demonstrates a principal synthetic procedure for a large-scale synthesis.

The Pd-NP synthesis was upscaled to 500 ml by the reduction of 250 ml  $K_2PdCl_4$  (0.5 mM) with 250 ml  $NaBH_4$  (3 mM) using a peristaltic pump, a Teflon mixer and Teflon tubings (for details see S5 in SI). Note that the reactant volumes can easily be increased with appropriate pumping and mixing systems. The synthesis was conducted with and without pH-stabilized precursor solutions whereby the duration of mixing was varied to 1 and 10 min by adjusting the flow rates. The precursor solutions were always prepared freshly. Thus, for a mixing time of 1 and 10 min the precursor solution aged between 0-1 min and 0-10 min, respectively. At the relatively short mixing time of 1 min, SAXS measurements reveal final Pd-NPs with radii of 2.2 nm with broad size distribution (polydispersity  $\sim 50\%$ , see Fig. S10 in SI) if non-pH-stabilized precursor solution is used. Increasing the mixing time to 10 min results in NPs with a bimodal size distribution, typical for NPs synthesized with aged precursor solutions.

If a precursor solution with a pH value of 3.3 is used for the upscaled synthesis, the formation of PHC is inhibited and particle size and size distribution are not dependent on the mixing duration. Particles with a mean radius of 2.1 nm and a polydispersity of 25% are reproducibly formed for mixing durations of 1 and 10 min. As already stated, the addition of a stabilizing agent is necessary, approx. within 1-2 h after the synthesis, to assure long time stability of the as prepared particles.

The comparison of the final particle sizes from the lab-scale and the upscaled synthesis using pH-stabilized precursor reveals a dependency of the particle size distribution on the reactant mixing. It is found that uniform mixing (*i.e.* applying a pump and Teflon mixer) leads to slightly smaller NPs with a lower size distribution as for less uniform mixing (*i.e.* using simple Eppendorf pipettes). The influence of mixing conditions on the final particle size is described in the supporting information (see S7 in SI).

Hence, a precursor solution with a pH of 3.3 enables the reproducible large-scale synthesis of Pd-NPs with a mean radius of 2.1 nm.

## Conclusions

This contribution addresses major aspects that have to be considered for the synthesis of Pd-NPs in aqueous solution and investigates the growth mechanism of Pd-NPs. An approach for the synthesis of “naked” Pd-NPs is presented based on the reduction of aqueous  $K_2PdCl_4$  with  $NaBH_4$  which demands either fresh ( $< 10$  s) or pH-stabilized precursor solutions.

The hydrolysis of Pd complexes and the formation of PHC could be identified as crucial issues prohibiting a reproducible synthesis of Pd-NPs with low polydispersities in aqueous solutions. The formation of PHC in the precursor solution can easily be checked prior use with UV-vis spectroscopy by the increasing background absorbance.

To avoid the formation of PHC, precursor solutions have to be used immediately after preparation. If the immediate use is inappropriate, PHC formation can be delayed or inhibited by lowering the pH value of the precursor solution. This process is particularly important for all synthetic procedures applying slow reducing agents, elevated temperatures and for seeded-growth or large-scale syntheses.

Furthermore, it was shown that the growth of Pd-NPs in the investigated system is only due to coalescence in two separated steps similar to the corresponding Ag-NPs.

The mechanistic understanding and the use of mildly acidic precursor solutions enables the reliable synthesis of “naked” Pd-NPs (*i.e.* surfactant free Pd-NPs) in the sub 5 nm regime. The as prepared NPs are stable for 1-2 hours and could be used directly for catalytic applications applied on solid supports or functionalized with desired stabilizing agents.

## Acknowledgements

J.P. acknowledges generous funding by the Deutsche Forschungsgemeinschaft within Project PO 1744/1-1. F.K. acknowledges support by the IMPRS "Functional Interfaces in Physics and Chemistry". M.W. also acknowledges financial support by the Fonds der Chemischen Industrie. RK acknowledges generous BMBF funding (ELYKAT, FKZ 03EK3009).

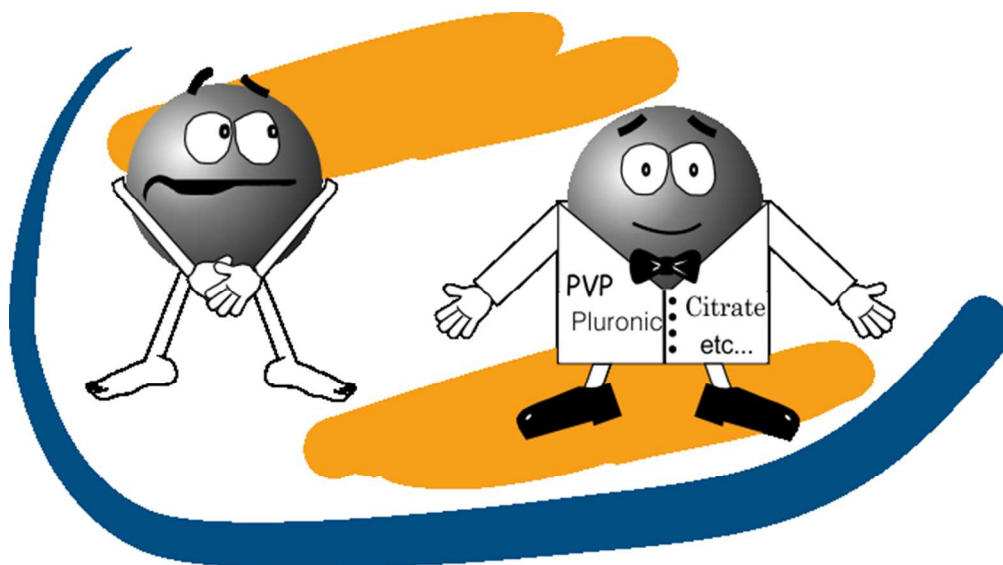
## Notes and references

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Supporting Information (SI) available: Additional text and experimental data, study on the precursor aging, including photographs time resolved UV-vis and SAXS experiments, XRD data; details on the synthesis of Pd nanoparticles; TEM images of Pd-NPs; experimental data of the large scale synthesis; a reproducibility study; experimental setups for the large scale synthesis and the CFS; study on the influence of mixing conditions; Evaluation of SAXS data.

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