

Noble Metal Nanoparticles

UV-Induced Synthesis and Stabilization of Surfactant-Free Colloidal Pt Nanoparticles with Controlled Particle Size in Ethylene Glycol

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Abstract: The conventional temperature-induced polyol synthesis of platinum nanoparticles is a powerful and well-established method for the preparation of stable, surfactant-free platinum nanoparticles (Pt NPs) with controlled shape, size and size distribution. Recently, we reported that exposure to daylight leads to the formation of Pt NPs from precursor solutions, suggesting that a parallel approach of UV-induced polyol synthesis could be a cheaper and more widely applicable alternative. Here we report a controlled size and size distribution for Pt NPs prepared using UV irradiation instead of thermal treatment. Results demonstrate that, depending on the concentration of NaOH in the reaction mixture, the size of produced nanoparticles can vary between 1 and 5.8 nm. We also show, for the first time, how NaOH affects the formation of organic side products, which alters Pt NPs stability, and demonstrate a method for the preparation of stable nanoparticle suspensions with an average particle size of 5.8 nm.

Due to their range of applications in catalysis, water remediation, and the health sector, various methods have been reported to produce metal nanoparticles (NPs): wet chemistry, im-

pregnation-reduction and colloidal methods, sputtering, ion/beam deposition and laser ablation.^[2] Because of its simplicity and easy control over the physical and electrochemical properties of NPs, the polyol method is one of the most popular routes to produce NPs for applications related to catalysis,^[3] such as oxygen reduction reaction^[4] or the electro-oxidation of methanol^[5] and ethanol.^[6] The synthesis of a broad variety of metal NPs was achieved using this method such as Pt, Ru, Rh, Co, and Os or bi-metallic particles like PtRu, PtFe, PtSn, and PtRh.^[4–7] In order to improve the desired properties of Pt NPs, various solvents have been investigated, but ethylene glycol (EG) was established as the best option.^[8] The narrow size distribution achieved by the polyol method has been attributed to the viscosity of the solvent, preventing fast growth of the NPs.^[9,10]

On the other hand, it has been shown that water can be a suitable solvent for the synthesis of metal NPs. However, capping agents are typically required,^[11] which need to be removed before applying the NPs in catalytic reactions. Similarly, the synthesis of Pt microstructures has been reported in mono-alcohols like ethanol^[12] or mono-alcohol mixtures like methanol and water,^[13] but in all cases a polymer/stabilizer is needed. Recently the synthesis of Pd particles was reported using only methanol as solvent and reducing agent in ambient conditions,^[14] but the obtained colloidal NP suspensions are typically not stable for more than a few hours.

Despite the success of the surfactant-free polyol method, the full control over the size of the NPs (typically 1–2 nm in diameter), their surface protection and stability is still only poorly understood. These properties, however, are decisive when implementing the metal NPs as catalysts.

Recently we reported that besides the conventional (thermal) treatment, light exposure can also be used for the surfactant-free polyol synthesis of Pt NPs in EG.^[1] Here we report a major step forward by achieving the size-controlled synthesis of Pt NPs via the polyol method using UV-irradiation. This relatively straightforward approach might reduce the price of equipment needed to prepare NP suspensions, decrease energy consumption for industrial applications, enable the localized formation of particles and provide a suitable alternative synthesis route in processes where higher temperatures are unfavorable.

Even though the conventional thermal polyol synthesis has been proven to be efficient, highly reproducible and scalable,

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relatively high temperatures (typically 160 °C) are necessary for the reaction to proceed. Most reports stress that the reaction occurs only in strictly alkaline solution, therefore an excess of NaOH is typically used for the syntheses.^[2,7,15] However, based on recent results we proposed that the use of no or low NaOH concentrations should allow for tuning the size of surfactant-free NPs.^[16] Here we demonstrate that this postulation was correct, but the use of UV light instead of thermal energy is needed as a driving force in order to kinetically inhibit sintering processes.

Figure 1 presents size distributions (obtained using both TEM and small angle X-ray scattering, SAXS) of Pt NPs synthesized under UV irradiation using different concentrations of NaOH in a controlled temperature environment of 18 °C.

It is found that introducing NaOH in increasing amounts leads to smaller particles and their size distribution narrows significantly; a behavior in agreement with results in previous reports for the corresponding thermal syntheses of ≈ 1–5 nm Pt NPs.^[16,17] The TEM histograms are based on a finite number of NPs (at least 50), while the SAXS analysis presents the bulk average of the colloidal suspension. The TEM and SAXS analysis are in a good agreement and the results show that depend-

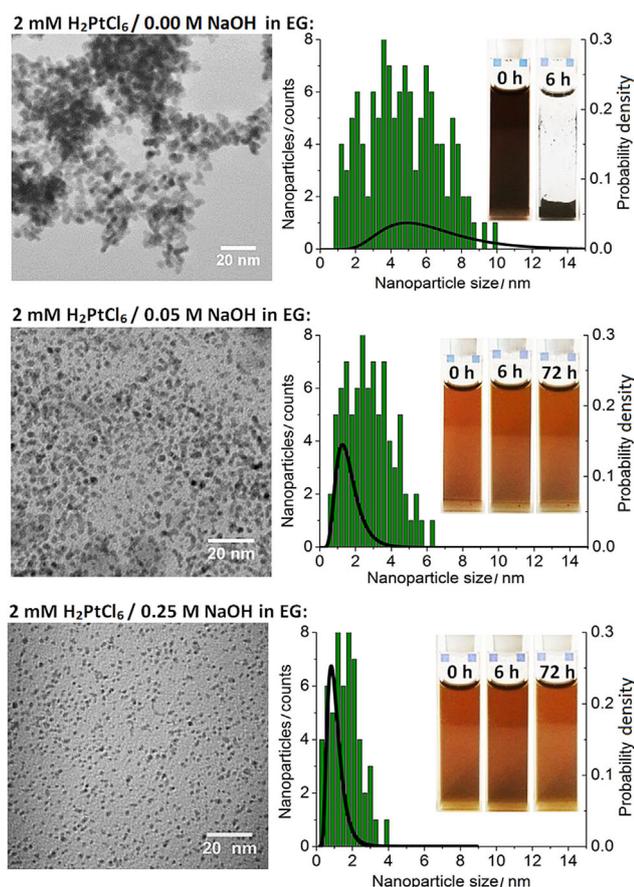


Figure 1. Comparison of sizes and size distributions of Pt NPs synthesized at constant temperature of 18 °C and using different amounts of NaOH (0 M, 0.05 M and 0.25 M). Histograms represent size distributions obtained from TEM graphs (left Y axis) as well as corresponding SAXS data (right Y axis) overlaid as black lines. Inserted photos of reaction mixtures show changes in NP stability in time after the UV-induced syntheses.

ing on the concentration of NaOH, the average size of Pt NPs synthesized using the UV-induced synthesis can be tuned in a range of ≈ 1 to ≈ 5.8 nm. Most importantly, it is found that using UV irradiation, Pt NPs can be obtained without any addition of NaOH. This observation is in clear contrast to the conventional thermal polyol synthesis where unstable suspensions are obtained if no NaOH is used. The size range between ≈ 1 and ≈ 6 nm is considered optimal for a number of applications.^[18] The fact that suspensions prepared without NaOH addition using conventional thermal polyol synthesis are highly unstable clearly inhibits the use of thus-prepared Pt NPs.

Even though it was shown that the particle size can be tuned significantly, the summary in Table 1 demonstrates that

Table 1. Sizes and size distributions (obtained using SAXS) of Pt NPs synthesized under UV-irradiation with varying concentrations of NaOH. The same concentrations of NaOH were used with two different synthesis temperatures (18 °C and ≈ 50 °C).

| T [°C] | NaOH concentration [M] | Mode [nm] | Mean diameter [nm] | Standard deviation [nm] | Relative deviation [%] |
|--------|------------------------|-----------|--------------------|-------------------------|------------------------|
| 18 | 0.00 | 5.0 | 5.8 | 0.08 | 1.4 |
| 18 | 0.05 | 1.2 | 1.5 | 0.08 | 5.5 |
| 18 | 0.25 | 0.7 | 0.9 | 0.09 | 10.0 |
| 18 | 0.50 | 0.8 | 0.9 | 0.09 | 9.8 |
| 18 | 0.75 | 0.8 | 0.9 | 0.08 | 8.3 |
| 50 | 0.00 | 2.8 | 3.3 | 0.08 | 2.5 |
| 50 | 0.05 | 1.2 | 1.5 | 0.10 | 6.5 |
| 50 | 0.25 | 0.7 | 0.9 | 0.10 | 10.5 |
| 50 | 0.50 | 0.7 | 1.0 | 0.15 | 14.4 |
| 50 | 0.75 | 0.6 | 1.0 | 0.15 | 14.4 |

the average size of Pt NPs does not decrease significantly anymore at concentrations > 0.25 M NaOH for the given concentration of H₂PtCl₆. However, NaOH is not the only parameter that alters the size of prepared Pt NPs. Comparison of the SAXS data in Figure S1 in the Supporting Information and Table 1 shows that smaller Pt NPs can be prepared under UV irradiation at higher temperature (≈ 50 °C), since these conditions lead to faster reduction and the formation of more seeds during nucleation. In agreement with the La Mer model,^[19] this results in higher amounts of smaller particles (in case of a constant initial concentration of the Pt salt). This means that the reduction of Pt salt in such reaction mixtures is very fast and the nucleation probably is the dominant step for the Pt NPs formation. Then just small/negligible amounts of “free” Pt is left in the reaction mixture for the growth step. Our results demonstrate that for the UV-induced synthesis, the reaction temperature, the NaOH concentration and their combination are suitable parameters to influence the reduction process, nucleation step and control the NP size as well as size distribution in the range of size 1–5.8 nm.

Inserted photos in Figure 1 also show that the attempt to prepare larger NPs without NaOH affects the colloidal stability: NPs suspensions made without base collapse within 6 hours while colloids with at least relatively small amounts of NaOH are stable for more than 72 hours. In other words, even

though the use of UV irradiation allows for obtaining Pt NPs without any addition of NaOH, the stability of these large NPs is significantly reduced compared to smaller Pt NPs (obtained with NaOH addition). For electrochemical applications additional post-synthesis steps like washing, re-dispersion and deposition on carbon are usually necessary, therefore long term stability of as-produced synthesis reaction mixture is not a prerequisite to prepare electrocatalysts from colloidal suspensions.^[20] Yet, controlling the stability of colloidal suspensions would not only help to limit agglomeration in such applications to a minimum. It is also a fundamental interest to control NP stabilization for long term storage and optimized processing. To investigate this effect and improve our understanding in NP stabilization, UV/Vis absorption of reaction mixtures containing 2 mM $\text{H}_2\text{PtCl}_6/0\text{ M NaOH}$ and 2 mM $\text{H}_2\text{PtCl}_6/0.25\text{ M NaOH}$ were measured as a function of time. Figure S2 in the Supporting Information reveals full Pt salt reduction to Pt^0 in both cases (with and without NaOH), followed by the formation of new absorption peaks discussed in Figure 2.

Figure 2A shows UV/Vis absorption and fluorescence spectra of synthesis reaction mixtures with different amounts of NaOH after 1 hour of UV irradiation. As can be seen, final absorption spectra of these mixtures change as the concentration of NaOH increases. Broad peaks around $\approx 280\text{ nm}$ and 360 nm in reaction mixtures with higher base concentrations were identified previously as fluorescent "carbon dots", formed when EG decomposes in the presence NaOH under thermal treatment.^[1,21] According to both absorption and emission spectra, it seems that similar fluorescent compounds are formed by UV-irradiation at 18°C in the nanoparticle synthesis mixtures. The absorption around 280 nm and 360 nm as well as the emission increase with higher base concentration, in line with an increased amount of reaction products formed. However, in case of little or no NaOH added, these absorption peaks are not pronounced and absorption around 248 nm becomes more dominant. At the same time fluorescence becomes negligible. Most likely this new arising absorption peak around 248 nm is related to organic decomposition products of EG, formed under UV-irradiation (see also Figure S3 in Supporting Information).

IR absorption spectra of platinum nanoparticle synthesis mixtures prepared using different NaOH concentrations in Figure 2B show concurrent results. Previous publications regarding experimental and theoretical calculations on IR absorption spectra of various platinum salts and its derivatives^[22] claim that almost all the absorption bands related to platinum atoms appear below 400 cm^{-1} and hence are not visible here in this range. However, organic compounds that play a role in the reaction mechanism and NP stabilization might be observable using IR. Consistent with previous results by Schrader et al.,^[16] the negative pointing absorption peaks around 2900 cm^{-1} can be attributed to ethylene glycol and the peak around 1650 cm^{-1} relates to water. In addition, the IR data shows a peak around 1600 cm^{-1} which could be due to C=C containing compounds that are produced as the reaction media becomes more alkaline and Pt NPs are present. Pt is known as an efficient catalyst and most likely helps to produce more fluorescent compounds than in the control reaction (orange spectrum in Figure 2B), in agreement with Gao et al.^[21] In cases of higher NaOH concentrations (0.25 M or 0.5 M), an additional small peak around 2015 cm^{-1} is observed in the IR spectra, which corresponds to CO adsorbed on the surface of Pt NPs.^[16] The same peak could not be observed in reaction mixtures without NaOH even when the initial concentration of Pt salt (and the expected amount of particles produced) was increased 30 times (data not shown). The lack of adsorbed CO signal might be simple a dilution effect (larger NPs have a considerable larger surface). It might also indicate that the reduced stability of the reaction mixtures prepared without NaOH is due to a lack of surface-bound CO on the Pt NPs. Since it was shown that Pt NPs can be synthesized under nitrogen atmosphere,^[23] it is very likely that the adsorbed CO originates from EG or its decomposition products in presence of a base.

In order to show the influence of these side products and NaOH concentration on the suspension stability, two types of Pt NPs (synthesized without NaOH and containing 0.25 M NaOH , respectively) are shown in Figure 3. As mentioned before, NPs initially synthesized without NaOH are not long-term stable and collapse after a few hours, while the NPs syn-

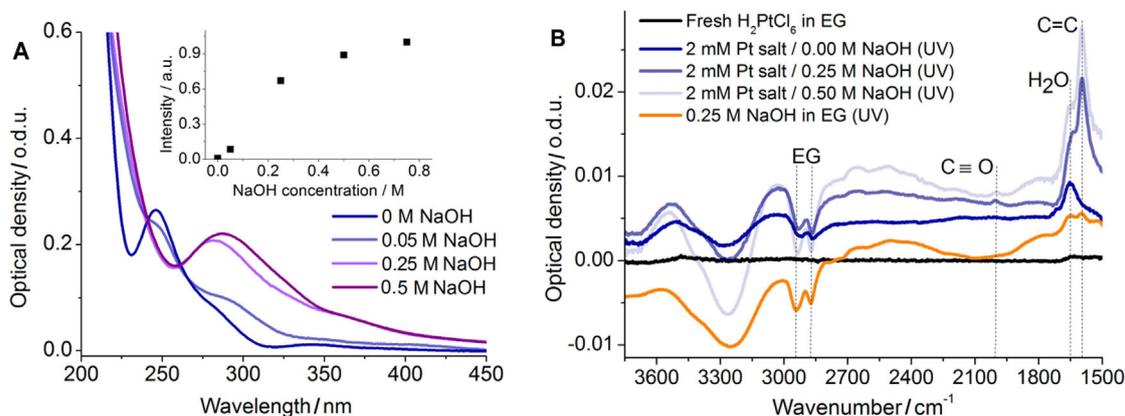


Figure 2. A) UV/Vis absorption and fluorescence (insert, ex.: 360 nm , em.: 450 nm) spectra of Pt NPs reaction mixtures, containing different concentrations of NaOH after 1 hour of UV-irradiation (18°C). B) IR absorption spectra of Pt NPs reaction mixtures, containing different concentrations of NaOH after 1 hour of UV-irradiation (18°C). Pure EG was subtracted as a reference from all the spectra.

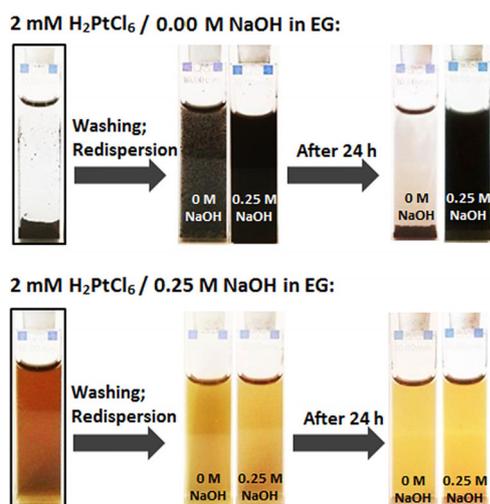


Figure 3. Photographs of NPs in two as-prepared synthesis reaction mixtures further redispersed in NaOH-free (0 M NaOH) as well as alkaline (0.25 M NaOH) EG solutions.

thesized in presence of NaOH remain stable over longer periods of time.

However, even though the as-prepared NPs synthesized without NaOH are not stable, their stability can be increased by washing and re-dispersion (see Experimental Section) in alkaline EG. This shows that precipitated Pt NPs are not fully sintered and can remain stable for at least 24 hours after re-dispersion. Hence, the here presented results allow for extending the available size range (from 1–2 nm up to ≈ 5.8 nm) of stable surfactant-free Pt NPs suspensions and potentially enable preparation of carbon supported electrocatalysts with larger Pt NPs, but narrow size distribution.^[20] By comparison, re-dispersion in pure EG does not lead to an increase in stability of the colloidal suspension. However, re-dispersed NPs made using 0.25 M NaOH remain stable over long periods of time independently on the base concentration in the re-dispersing solvent (EG), therefore could be used for wide range of applications where highly alkaline solutions are unfavorable. These results clearly indicate that even though NaOH is not necessary to produce Pt NPs under UV irradiation, it seems to be crucial for their stabilization over prolonged periods of time.

In conclusion, applying a UV-induced synthesis route we demonstrate the formation of Pt NPs with controlled size and size distribution. By changing the base concentration in the reaction mixture the average particle size can be tuned in a range from ≈ 1 nm to ≈ 5.8 nm.

Colloidal suspensions with large Pt NPs are obtained by avoiding the addition of base to the reaction mixture. Under such conditions, Pt NPs prepared by conventional thermal polyol synthesis are highly unstable. Also in the UV-induced synthesis, the lack of base leads to lower colloidal stability of a few hours. Although for the synthesis of supported catalysts, long-term stability of the colloid is not necessarily required, as it is only an “intermediate product”, for biological or nano-engineering related applications long term stability could be es-

sential. Pt NPs, which are produced without base, lack CO adsorbed on their surface. Stabilization, however, can be obtained by re-dispersion in alkaline EG, thus enabling the synthesis of stable colloidal suspensions of larger Pt NPs.

Experimental Section

Preparation of Pt NPs: Pt NPs were prepared using a modification of a previously described method.^[11] 4 mM (1.64 g L^{-1}) $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ (99.9%, Alfa Aesar) in EG (spectrophotometric grade, Alfa Aesar) and varying concentrations of NaOH (0 M, 0.1 M, 0.5 M and 1 M, 98%, Alfa Aesar) in EG were mixed together in equal volumes (in quartz cuvettes) to produce four different reaction mixtures all containing 2 mM H_2PtCl_6 and 0 M, 0.05 M, 0.25 M and 0.5 M of NaOH, respectively. These mixtures were placed in a home-built synthesis chamber equipped with temperature control (18°C , unless stated otherwise) and ten standard UV mercury lamps (PL-L-24 W/10/4P Hg, Philips) for 2 hours. For the syntheses of Pt NPs without temperature control, the temperature was not monitored during the reaction but reached $\approx 50^\circ\text{C}$ after 2 hours of UV-irradiation.

For stability investigations, Pt NPs were aged at room temperature conditions for 6 hours and then washed with 1 M aqueous solution of HCl in a volume ratio of around 1:3. The dark precipitate was centrifuged at 2400 relative centrifugal force (4000 rotations per minute, Sigma 2–5 laboratory centrifuge, Sigma) for 5 minutes. This washing step was repeated twice in order to remove any remaining EG or NaOH.

Characterization of Pt NPs: For UV/Vis absorption (Lambda UV/VIS/NIR absorption spectrometer, PerkinElmer), fluorescence (Cary Eclipse fluorescence spectrophotometer, Agilent Technologies) and FT-IR (Nicolet FT-IR spectrometer, Thermo Electron Corporation) measurements, pure EG was used as a baseline in all cases and samples were diluted up to 100 times for UV/Vis absorption and fluorescence measurements.

For TEM the Pt NPs were washed and redispersed in pure ethanol (99.9%, Kemetyl) and diluted 50 times. Small drops of colloids then were placed on carbon coated copper grids (300 mesh grids, Quantifoil) and dried in room conditions. TEM images were taken using a Philips CM20 microscope operated at 200 kV. Samples were characterized by taking images at different magnification in different areas of the TEM grids and the size analysis was performed by measuring the size of at least 50 NPs.

Small angle X-ray scattering measurements were performed with SAXSLab instrument (JJ-X-Ray) using Rigaku 100 XL+ micro focus sealed X-ray tube and a Dectris 2D 300 K Pilatus detector. For the measurement, small amounts of as-prepared particle suspensions were placed in capillary sample holders and data analysis was performed using a method described in [16].

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Keywords: nanoparticle stabilization · nanoparticle synthesis · platinum nanoparticles · UV-induced synthesis

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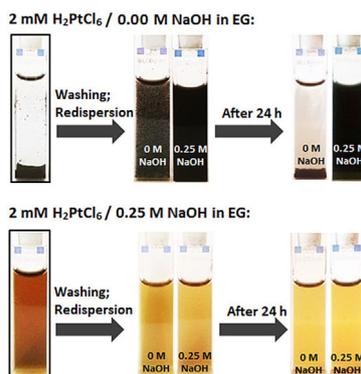
COMMUNICATION

Noble Metal Nanoparticles

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Matthias Arenz*



UV-Induced Synthesis and
Stabilization of Surfactant-Free
Colloidal Pt Nanoparticles with
Controlled Particle Size in Ethylene
Glycol



Surfactant-free Pt nanoparticles are prepared using UV irradiation instead of thermal energy. It is demonstrated that this synthesis route allows for the variation in particle size between 1 and ca. 6 nm, depending on NaOH concentration. An approach is shown how the large, relative instable nanoparticles can be stabilized after synthesis.