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In situ PDF study of the nucleation and growth of intermetallic PtPb nanocrystals

Dipankar Saha^[a], Espen D. Bøjesen^[a], Aref Hasen Mamakhel^[a], Martin Bremholm^[a], and Bo B. Iversen^{*[a]}

Dedication: This article is dedicated to Prof. T. N. Guru Row on the occasion of his 65th birthday.

Abstract: The mechanism of Pt and PtPb nanocrystal formation under supercritical ethanol conditions has been investigated by means of *in situ* X-ray total scattering and pair distribution function (PDF) analysis. The metal complex structures of two different platinum precursor solutions, chloroplatinic acid and Pt(acac)₂ (acac = acetylacetonate) provide atomic-scale detail about the nucleation mechanisms after initiation of the reaction with Pb(acac)₂ by heating. The stronger Pt-O chemical bonding in the Pt(acac)₂ precursor complex compared with the Pt-Cl bonding in the chloroplatinic acid precursor complex leads to a much slower reduction of the Pt center, and this allows more optimal co-reduction conditions providing a pathway for formation of phase-pure intermetallic PtPb product. The matching chemistry of the Pt(acac)₂ and Pb(acac)₂ precursors allow development of a facile continuous flow supercritical ethanol process for obtaining phase-pure hexagonal PtPb nanocrystals. The study thus highlights the importance of *in situ* studies in revealing atomic-scale information about nucleation mechanisms, which can be used in design of specific synthesis pathways, and the new continuous flow process to obtain PtPb nanocrystals holds potential for large scale production.

Introduction

There is a strong interest in developing new catalysts for electrocatalytic oxidation of small organic molecules (SOMs) such as formic acid or methanol in direct fuel cells.^[1] The development of efficient and durable catalysts for SOM oxidation is a key requirement for commercialization, and platinum and Pt-based alloys, especially Pt_{1-x}Ru_x, have been studied as promising candidates.^[2] However, in addition to the high cost of both Pt and Ru, these catalysts suffer from major drawbacks such as poisoning on the surface by CO and sulfur-containing compounds, and the instability of the Pt-Ru phase reduces the catalytic activity.^[2a] Current efforts include the search for alternative compounds with enhanced electrocatalytic activity and tolerance towards poisoning. PtPb has shown promising electrocatalytic activity compared with other Pt-based intermetallic compounds.^[3] Furthermore, PtPb nano-particles

show enhanced activity due to increased surface area.^[4] This makes a scalable and facile synthesis strategy for production of PtPb nanoparticles of substantial interest.

Several reports of PtPb nanoparticle synthesis exist. The main difficulty relating to the synthesis of pure-phase PtPb nanoparticles is the need for simultaneous co-reduction of Pt and Pb-based precursor salts.^[5] By rapid addition of a strongly reducing agent (NaBH₄ or sodium naphthalide) to metal-ion containing solutions, it has been demonstrated that co-reduction of Pt and Pb-salts is indeed possible in solution. A further development of this method was a water-in-oil microemulsion technique with NaBH₄ reduction.^[5e] Another method, termed “conversion chemistry”, relies on the synthesis of either supported or unsupported Pt-nanoparticles, which subsequently are mixed with a Pb-salt solution and heated in order to obtain the intermetallic PtPb phase.^[5f] Collectively these studies show that the synthesis of phase-pure PtPb requires very strongly reducing conditions, and all studies have involved multi-step synthesis procedures, which constitute a challenge to large scale production.

Large scale synthesis of nanoparticles requires facile synthetic routes as well as scalable procedures. Continuous flow supercritical synthesis poses an advantage over the previously discussed methods, because it is a one-step process without down time, and it is amenable for large scale implementation. Supercritical fluid methods utilize the unique properties of supercritical fluids, which allow tuning e.g. of solvent strength, viscosity, diffusivity, dielectric constant, ionic product and surface tension.^[6] In continuous flow reactors the supercritical fluid provides a very rapid heating at the mixing point with the precursor solution leading to high super-saturation conditions and thereby rapid nucleation of nanoparticles.^[7] The particle size, size distribution, crystallinity, and phase composition may be controlled through variation of reaction parameters such as temperature, pressure, precursor concentration, reactor residence time and choice of solvent.^[8] Reports of successful syntheses using this method are numerous, albeit most studies have concerned syntheses of metal-oxides.^[7a, 9] Reports on the successful formation of intermetallic compounds using continuous flow supercritical processes are scarce.^[10] Alcohols have been used efficiently in supercritical synthesis as it acts both as solvent and reducing agent in supercritical condition.^[11] Supercritical alcohols not only play the role of solvent but also acts as surface modification agents which in turn effects the size of nanocrystals.^[12] Here, we combine the two concepts of rapid nucleation and a reducing supercritical solvent to develop a new method for synthesizing intermetallic PtPb nanocrystals.

Alloys and intermetallic compounds are structurally very different. In an alloy the metal atoms are randomly placed in the crystal lattice, and only metals with similar crystal structures and

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similar chemical properties will form proper alloys. Intermetallics, on the other hand, are unique substances with specific structural arrangement of metal atoms and therefore highly specific properties. In energy terms alloys have high entropy whereas intermetallics have low entropy. It is therefore often possible by heating to convert an intermetallic to an alloy, whereas the opposite is very rare. In formation of an intermetallic nanoparticle the placement of the metal atoms and their individual chemical state during the reaction needs to be much more delicately tuned than for formation of alloys. The criterium of metal co-reduction is therefore more severe for intermetallic systems than for alloys. Indeed it was indirectly found through *in situ* powder X-ray diffraction (PXRD) analysis of unit cell evolutions that the formation of PtRu alloy nanoparticles does not take place through co-reduction, but through a complex multi-step mechanism.^[13] It was suggested that Pt nanoparticles are first deposited and then serve as secondary nucleation sites for Ru. A subsequent diffusion process then leads to alloy formation. In contrast, an *in situ* PDF study of the formation of Pt₃Gd nanoparticles reveal no peculiarities in the unit cell evolution and thus appears to support a co-reduction mechanism.^[14] The present study attempts to add further experimental evidence to the general understanding of formation of alloys and intermetallic compounds.

Total scattering (TS) and subsequent PDF analysis is gaining momentum because of its versatile applicability towards structural problems where conventional crystallographic methods have limitations. In PDF analysis Bragg diffraction and diffuse scattering are treated on equivalent terms, and this allows extraction of structural information on both crystalline and amorphous materials.^[15] With the better availability of high energy X-ray sources and strong development of analytical software for treating the TS data, PDF analysis is being applied to diverse fields of science.^[16] In this respect *in situ* PDF studies of nanoparticle formation under solvothermal conditions have severely challenged both classical and non-classical nucleation theories. It has been suggested that a paradigm shift is needed towards focus on the atomic scale chemistry of nucleation.^[17] In the conventional nucleation approach, one global model is assumed to fit all nucleation phenomena, but the *in situ* PDF analysis has revealed that in reality a diverse array of nucleation mechanism take place depending on the chemical system.^[14, 18] Another recent example of the strength of the PDF technique is the experimental verification of the restructuring of solvent molecules on nanoparticle surfaces in solution.^[19] Moreover PDF analysis has been applied to determine both intra- and intermolecular correlations of organic molecules with various solvents,^[20] and also amorphous pharmaceuticals have been characterized by PDF analysis.^[21] In this study we use *in situ* PDF analysis to understand the formation of intermetallic PtPb nanoparticles under different experimental conditions. By exploring different starting materials and reaction conditions we obtain information that is subsequently used to design an efficient and scalable continuous flow supercritical process to synthesize phase-pure hexagonal PtPb nanocrystals.

Results and Discussion

In situ synthesis

Table 1 summarizes the *in situ* PDF experiments for synthesis of PtPb and Pt. In the *in situ* experiments Pt(acac)₂ and Pb(acac)₂ precursors were used but in order to obtain a sufficient signal to noise ratio in the TS data, higher metal ion concentrations were necessary. Whenever H₂PtCl₆·6H₂O was used in the *in situ* reaction impurities (Table 1) were observed (supporting Information Figure S2). Previous reports emphasize that simultaneous co-reduction of the platinum and the lead source is crucial if phase-pure PtPb is to be obtained.^[5e] Consequently, it is essential to compare the rate of the metal reduction for different precursor sources in ethanolic solutions. Previously we have shown that the formation of Pt nanoparticles under solvothermal condition (ethanol solvent) from H₂PtCl₆·6H₂O occurs via a two-step reaction mechanism. The octahedral PtCl₆²⁻ complex (Pt is tetravalent) exists in the precursor solution and upon heating it first reduces to a square planar PtCl₄²⁻ (Pt is divalent) before further reduction allows formation of metallic nanoparticles.^[14, 22] The second reduction step occurs only after the first reduction from Pt⁴⁺ to Pt²⁺ is completed.

Table 1. Details of different *in situ* total scattering experiments carried out at various temperatures. The molar ratio of Pt:Pb was always kept at 1:1 and absolute ethanol was used as solvent. In all syntheses P = 250 bar.

Temp. (°C)	Precursor materials	Identified product phases
300	H ₂ PtCl ₆ ·6H ₂ O + Pb(acac) ₂	Pt + PtPb + PbPt _x
250	Pt(acac) ₂ + Pb(acac) ₂	PtPb + PtPb ₄
300	Pt(acac) ₂ + Pb(acac) ₂	PtPb + Pt ₃ Pb
350	Pt(acac) ₂ + Pb(acac) ₂	Pure PtPb
250	Pt(acac) ₂	Pure Pt

Here the formation of Pt nanoparticles was observed after 10 s of reaction in the case of H₂PtCl₆·6H₂O at a temperature of 250 °C.^[14] For comparison we first investigated the formation of pure Pt nanoparticles from Pt(acac)₂ under the same conditions. Before heating the precursor, Bragg peaks were observed on the detector due to the not fully dissolved Pt(acac)₂ crystalline phase. However, after initiation of heating all the Bragg peaks disappeared. PDF analysis of the signal obtained from the heated solution reveals that a square planar molecular Pt(C₅H₇O₂)₂ complex exists in the solution (Figure 1(a)). Pt is four-fold coordinated to two bidentate acetylacetonate ligands. The first peak at 1.98 Å can be attributed to the Pt-O bond and other main Pt-O/C bond distances are marked in Figure 1a. With time the area under the Pt-O peak decreases and the area under the Pt-Pt peak at 2.77 Å (Figure 1(c)) increases signaling the formation of the Pt nanoparticles.

Figure 1. Synthesis of Pt nanoparticles using $\text{Pt}(\text{acac})_3$ as precursor. (a) Fitted PDF for square planar $\text{Pt}(\text{acac})_3$ complex (20 min after heating). First coordination Pt- O/C bond distances are marked in the figure (b) PDF refinement confirming the formation of pure Pt synthesized from $\text{Pt}(\text{acac})_3$ at 250 °C after a reaction time of 20 min ($R_w=0.17$). Inset shows time resolved PDF of Pt synthesis. (c) Normalized peak area for the Pt-Pt bond fitted with a modified AE model (Open circle). The peak area of the Pt-O peak is shown with open squares.

The area under these two “fingerprint” peaks were normalized and plotted with respect to time in order to understand the growth mechanism. After 20 min of reaction the PDF could be fitted with the crystalline Pt structure (Figure 1b). Although the reaction conditions were exactly the same as in case of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, the first signal from metallic Pt nanoparticles is not observed until after 25 sec of reaction (Figure 1(c)), which is slower than the 10 s observed in the synthesis based on

chloroplatinic acid precursor. Following the initial nucleation the Pt-Pt signal keeps increasing, while the Pt-O peak area is simultaneously decreasing. The Pt-Pt peak area can increase either due to smaller nanoparticles being formed or due to growth of the existing particles. No matter what the origin, a simple Avrami-Erofe'ev (AE) model,^[23] can be fitted to the Pt-Pt curve yielding $k = 0.264 \text{ min}^{-1}$, $n = 1.55(1)$ (Figure 1(c)). No indication of Ostwald ripening was observed during the 20 min of the reaction as there was no rising slope of the curve of the normalized area, contrasting the synthesis based on $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$. A similar fit to the Pt-Pt peak area in the case of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ gave $k = 2.43 \times 10^{-2} \text{ s}^{-1}$, $n = 4.3$, $k_{\text{OR}} = 5.4 \times 10^{-3} \text{ s}^{-1}$ and $t_{\text{OR}} = 40 \text{ s}$ where Ostwald ripening occurs.^[14] In fact in this case all initial precursor is used up after only ~ 90 sec, whereas it takes ~5 minutes in the case of $\text{Pt}(\text{acac})_3$. The differences in the increase of the Pt-Pt peak area indicates that the reduction of Pt^{2+} to Pt is much slower for $\text{Pt}(\text{acac})_3$ than in the case of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$. It should be noted that the reduction potential (0.743 V) of $[\text{PtCl}_6]^{2-}$ to $\text{Pt}(\text{s})$ is much higher than reduction potential (-1.7 V) of $\text{Pt}(\text{acac})_3$ to $\text{Pt}(\text{s})$.^[24] Therefore, it may be argued that reducing chloroplatinic acid should be much easier than $\text{Pt}(\text{acac})_3$. This indicates that the formation of Pt impurities during PtPb synthesis with chloroplatinic acid may be attributed to a too fast reduction of octahedral $[\text{PtCl}_6]^{2-}$. In combination this suggests that the initial period of the reaction is crucial for the product formation as the reduction process occurs during this period and the rate of the reduction process controls the final product composition. Since the rate of the reduction process depends on the nature of the precursor complex different Pt sources were investigated.

Peak area analysis of the peaks corresponding to Pt-O (1.98 Å) and Pb-O (2.37 Å) shows a comparable reduction rate of $\text{Pt}(\text{acac})_3$ and $\text{Pb}(\text{acac})_3$ within 20 s of the reaction (Figure 2(b)). This suggests that the reduction rates for both the starting materials are comparable. After 20 sec. of reaction new peaks appear in the PDF due to the formation of PtPb nanoparticles which grow with increasing reaction time (Figure 2(a)). The size of the PtPb nanoparticles were found to be ~7 nm after PDF refinement, which is in agreement with the PXRD Rietveld refinement. Fitting of PDF peaks in order to find growth kinetics of PtPb was unsuccessful since the peaks of PtPb were overlapped with many peaks, corresponding to precursor. Therefore, the growth curve for PtPb nanoparticles was fitted with a kinetic model by analyzing the particle size obtained after PDF refinement.

A modified AE equation was introduced to fit the data since a simple AE model was unable to fit the rising slope at the later time of the reaction. ^[23, 25] Figure 3 shows that modified AE model provides an excellent fit to normalized data giving the parameters $k = 0.49 \text{ min}^{-1}$, $n = 0.44$, $k_{\text{OR}} = 1.32 \times 10^{-3} \text{ s}^{-1}$ and $t_{\text{OR}} = 11.3 \text{ min}$. In the case of bulk nucleation mechanisms for solid-state reactions the n parameter is normally larger than 1, whereas it approaches 1 for surface nucleation mechanisms. Solvothermal formation conditions are not the same as a solid-state transformations, but even so the AE equation is often used to analyze the kinetics of such processes.

Figure 2. (a) Time resolved PDF of the reaction using Pt(acac)₂ and Pb(acac)₂ precursors at 350 °C. (b) Normalized peak area for the Pt-O and Pb-O bonds. Only the first 60 sec of the reaction are shown (Initiation of heating was set to zero for plotting). (c) Real space PDF refinement of data obtained after a reaction time of 25 min confirming the formation of pure hexagonal (P6₃/mmc). The inset shows the low r -range ($R_w=0.08$).

The value of $k = 0.264 \text{ min}^{-1}$ and $n = 1.55$ for Pt(acac)₂ were obtained after fitting the Avrami-Erofe'ev (AE) model, whereas the values of k and n were 0.49 min^{-1} and 0.44 for PtPb. Thus, it is clear from the rate constant that the rate is faster in case of PtPb. As seen above the growth of Pt nanoparticles have $n > 1$ ($n = 4.3$ for platinumic acid and $n = 1.55$ for Pt(acac)₂) indicating inhomogeneous distribution of nuclei^[26] and showing that in this case the supercritical ethanol solvent has limited impeding effects. It is, however, conspicuous that n is much smaller than unity in the case of PtPb nanocrystal growth ($n = 0.44$). Thus, PtPb formation is far from a bulk solid state reaction and presumable considerable structural rearrangements are necessary with significant influences from the surrounding solvent system.

Since the standard reduction potentials of pure Pb and Pt are -0.13 V and $+1.3 \text{ V}$, respectively,^[27] Pt is more easily and rapidly reduced than Pb. Therefore, instead of the ordered intermetallic compound PtPb, only Pt or Pb nanoparticles would be formed by selective reduction of the metals as confirmed by *in situ* measurements. If a two step reduction takes place then Pt is first reduced and then secondly Pb producing a multiphase mixture of nanoparticles, or perhaps core-shell morphologies. Another possibility is the alloy formation which is observed in case of PtRu nanoparticles where initially formed Pt cluster nanocrystals act as a nucleation point for Ru, and the alloy forms by diffusion of Ru in Pt matrix.^[13] Co-reduction of the metals is crucial for formation of ordered PtPb intermetallics, and here it was achieved by selecting the correct precursor materials unlike previous syntheses where co-reduction of the metals was achieved by addition of a very strong reducing agent.^[5]

Figure 3. Rate curve for PtPb growth. The first term in the equation corresponds to the nucleation and aggregative particle growth, while the second term accounts for Ostwald ripening. At a given time t , k is the rate parameter for the nucleation, n is dimensionality of the reaction. t_{OR} and k_{OR} are the time of the onset of Ostwald ripening and a rate parameter. The start of the heating was set to zero seconds for the fitting of the data.

Figure 4. (a) Rietveld refinement of PXRD data of PtPb synthesized in the flow reactor at 300 °C. (b-d) TEM micrographs and STEM-EDX analysis showing faceted PtPb nanoparticles with homogeneously distributed Pt and Pb and (e) HRTEM micrograph of PtPb nanoparticle.

Flow synthesis of phase pure PtPb

The *in situ* PDF data discussed above suggest a possible route to synthesize phase pure PtPb using $\text{Pt}(\text{acac})_2$ and $\text{Pb}(\text{acac})_2$ with a 1:1 molar ratio as starting materials. Indeed, phase-pure hexagonal PtPb nanoparticles can be obtained at temperatures of 250 °C and 300 °C in the continuous flow reactor. Figure 4 shows a Rietveld refinement of the diffraction pattern collected for PtPb synthesized at 300 °C (details are given in the supplementary information). The average PtPb crystallite size was found to be 45(1) nm for a synthesis temperature of 300 °C, whereas an average particles size of 34(1) nm was obtained at

250 °C. Figure 4 also shows TEM images recorded on the PtPb nanoparticles synthesized at 300 °C as well as an overlay of the elemental distribution maps obtained from STEM-EDS on a selection of particles. It is clearly seen that the PtPb nanoparticles are well crystallized, and many particles are partially faceted with no particular defect features visible in the HR-TEM images. Furthermore, both Pt and Pb are distributed evenly throughout the particles. The particle sizes observed by TEM are in good agreement with the crystallite sizes obtained from Rietveld refinement. The present synthesis route opens up the possibility of synthesizing pure PtPb hexagonal phase in large quantities, which is essential for industrial application of nanoparticles.

Conclusions

Synthesis of phase pure intermetallic nanoparticles requires strong control of the reaction conditions in order to obtain simultaneous co-reduction of the metals and avoid impurity formation. Total scattering analysis reveals that for a $\text{Pt}(\text{acac})_2$ precursor Pt exists as square planar complex in solution, coordinated by two acetylacetonate ligand. PDF analysis was also used to estimate the reduction rates of different Pt precursors, and suitable co-reduction conditions were found to be achievable only for $\text{Pt}(\text{acac})_2$ and $\text{Pb}(\text{acac})_2$ precursors in supercritical ethanol. Modelling of the crystal growth kinetics using an AE model shows that formation of pure Pt nanoparticles with different precursor solutions have $n > 1$, which is similar to bulk solid state reactions. In contrast the formation of PtPb has $n \sim 0.4$ suggesting that substantial structural rearrangement is taking place leading to impeding effects of the surrounding solvent. The *in situ* reaction conditions were subsequently transferred to synthesis in a continuous flow supercritical reactor, and phase pure PtPb nanocrystals with a size of 34 nm ($T = 250$ °C) and 45 nm ($T = 300$ °C) were obtained. The highly efficient process uses supercritical ethanol both as solvent and metal reductant, and it holds promise for large scale production of nanoscale catalysts e.g. for electrocatalytic oxidation of small organic molecules in fuel cells.

Experimental Section

Chemicals

The following reagents were used as purchased: $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (Strem Chemicals, 78-0200), $\text{Pt}(\text{C}_5\text{H}_7\text{O}_2)_2$ (Sigma Aldrich, 4136189), and $\text{Pb}(\text{C}_5\text{H}_7\text{O}_2)_2$ (Sigma Aldrich, 401684), Absolute ethanol (Sigma Aldrich, 02865).

Supercritical flow synthesis

The continuous flow synthesis was carried out using a modular supercritical flow reactor developed at Aarhus University.^[8c] The details of the reactor and synthesis condition are included in the supporting information.

Total scattering experiment

In situ total X-ray scattering experiments were carried out at beam line P02.01 at PETRA III, DESY, Germany, using a wavelength of 0.207 Å (59.9 keV).^[28] For the synthesis of intermetallic PtPb, two different types of Pt precursors, H₂PtCl₆·6H₂O and Pt(C₅H₇O₂)₂ were used. The concentration of the solution was kept at 0.5 M. The molar ratio was 1:1 for all the intermetallic synthesis. For Pt synthesis only Pt(C₅H₇O₂)₂ was dissolved in ethanol (0.5 M). Clear precursor solutions were used for the *in situ* experiments in a custom-made capillary reactor.^[29] The syntheses were performed by loading the precursor into a 0.6/0.7 (inner/outer) mm diameter fused silica capillary. The capillary was pressurized to 250 bar by a LabAlliance HPLC pump using water (99%) as the pressurizing medium. Afterwards, the capillary was heated to set temperatures by a hot air jet with temperature measured by a K-type thermocouple. Due to the small volume of the capillary and the efficiency of the heater, 90% of the set-temperature was reached within the first 10 seconds of heating. Concurrent with initiation of the heating, scattering from a monochromatic X-ray beam ($\lambda = 0.207$ Å) was recorded by a fast area detector, Perkin Elmer XRD1621. The sample-to-detector distance was 194 mm. Detector frames were read out continuously, giving an effective time resolution of 1 second. The center heating of the capillary creates a density plug of heavy solvent in the ends, which keeps the growing particles in the X-ray beam under well defined thermodynamic conditions. During the experiment it has been found that the actual temperatures are 10 % lower than the set temperatures.^[30] The FIT2D software^[31] was used to integrate the 2D data sets. Prior to integration, the X-ray wavelength was calibrated. The detector geometry, such as distance from the sample and obliquity, was then determined using a LaB₆ (NIST) sample. The integrated total scattering data were analyzed with the PDFgetX3 program.^[32] Prior to the Fourier transformation, the data were corrected for background scattering using measurements of ethanol in the same capillary at appropriate temperatures. Structure functions were used up to a $Q_{\max}$ of 17.5 Å⁻¹, where the Q-range was limited from the theoretical maximum in this case by signal to noise issues after subtracting the background. The resulting PDFs were refined using PDFgui.^[33] Rietveld refinements were carried out using the FullProf suite.^[34]

Characterization

The flow synthesis products were collected as black suspensions which were allowed to dry in air and characterized with PXRD. The PXRD data were measured on a Rigaku Smart Lab powder diffractometer with Bragg-Brentano geometry. A Ge(111) single crystal monochromator was used to produce Cu K α_1 radiation. HR-TEM, STEM and STEM-EDS data were obtained on a TALOS F200A with a TWIN lens system, X-FEG electron source, Ceta 16M Camera and a Super-X EDS Detector. Spatially resolved elemental analysis, was obtained using the same TALOS microscope in STEM mode. Exposure times of 8 minutes were used to create elemental distribution maps with satisfactory counting statistics, while minimizing potential problems such as beam damage and specimen drift. STEM pictures were obtained using a High Angle Annular Dark Field detector (HAADF). A drop of a sonicated ethanolic nanoparticle suspension was deposited on a holey carbon film on copper grid and allowed to dry at ambient conditions.

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Keywords: Pair Distribution Function • nanoparticle • intermetallic, continuous flow synthesis, supercritical ethanol

- [1] aC. Lamy, A. Lima, V. LeRhun, F. Delime, C. Coutanceau, J.-M. Léger, *J. Power Sources* **2002**, 105, 283-296; bB. D. McNicol, D. A. J. Rand, K. R. Williams, *J. Power Sources* **2001**, 100, 47-59; cC. Rice, S. Ha, R. I. Masel, P. Waszczuk, A. Wieckowski, T. Barnard, *J. Power Sources* **2002**, 111, 83-89.
- [2] aJ.-M. Léger, *J. Appl. Electrochem.* **2001**, 31, 767-771; bM. Watanabe, M. Uchida, S. Motoo, *J. Electroanal. Chem. Interfacial Electrochem.* **1987**, 229, 395-406; cJ. W. Long, R. M. Stroud, K. E. Swider-Lyons, D. R. Rolison, *J. Phys. Chem. B* **2000**, 104, 9772-9776; dX. Ren, P. Zelenay, S. Thomas, J. Davey, S. Gottesfeld, *J. Power Sources* **2000**, 86, 111-116.
- [3] E. Casado-Rivera, D. J. Volpe, L. Alden, C. Lind, C. Downie, T. Vázquez-Alvarez, A. C. D. Angelo, F. J. DiSalvo, H. D. Abruña, *J. Am. Chem. Soc.* **2004**, 126, 4043-4049.
- [4] C. Roychowdhury, F. Matsumoto, V. B. Zeldovich, S. C. Warren, P. F. Mutolo, M. Ballesteros, U. Wiesner, H. D. Abruña, F. J. DiSalvo, *Chem. Mater.* **2006**, 18, 3365-3372.
- [5] aL. R. Alden, C. Roychowdhury, F. Matsumoto, D. K. Han, V. B. Zeldovich, H. D. Abruña, F. J. DiSalvo, *Langmuir* **2006**, 22, 10465-10471; bL. R. Alden, D. K. Han, F. Matsumoto, H. D. Abruña, F. J. DiSalvo, *Chem. Mater.* **2006**, 18, 5591-5596; cC. Roychowdhury, F. Matsumoto, P. F. Mutolo, H. D. Abruña, F. J. DiSalvo, *Chem. Mater.* **2005**, 17, 5871-5876; dT. Ghosh, F. Matsumoto, J. McInnis, M. Weiss, H. D. Abruña, F. J. DiSalvo, *J. Nanopart. Res.* **2009**, 11, 965-980; eL. M. Magno, W. Sigle, P. A. van Aken, D. G. Angelescu, C. Stubenrauch, *Chem. Mater.* **2010**, 22, 6263-6271; fJ. C. Bauer, X. Chen, Q. Liu, T.-H. Phan, R. E. Schaak, *J. Mater. Chem.* **2008**, 18, 275-282; gR. E. Cable, R. E. Schaak, *Chem. Mater.* **2005**, 17, 6835-6841.
- [6] aE. Reverchon, R. Adami, *J. Supercrit. Fluids* **2006**, 37, 1-22; bT. Adschiri, K. Kanazawa, K. Arai, *J. Am. Ceram. Soc.* **1992**, 75, 1019-1022.
- [7] aC. Aymonier, A. Loppinet-Serani, H. Reverón, Y. Garrabos, F. Cansell, *J. Supercrit. Fluids* **2006**, 38, 242-251; bE. Lester, P. Blood, J. Denyer, D. Giddings, B. Azzopardi, M. Poliakoff, *J. Supercrit. Fluids* **2006**, 37, 209-214; cT. Adschiri, Y. Hakuta, K. Sue, K. Arai, *J. Nanopart. Res.* **2001**, 3, 227-235.
- [8] aP. Hald, J. Becker, M. Bremholm, J. S. Pedersen, J. Chevallier, S. B. Iversen, B. B. Iversen, *J. Solid State Chem.* **2006**, 179, 2674-2680; bL. L. Toft, D. F. Aarup, M. Bremholm, P. Hald, B. B. Iversen, *J. Solid State Chem.* **2009**, 182, 491-495; cJ. Becker, P. Hald, M. Bremholm, J. S. Pedersen, J. Chevallier, S. B. Iversen, B. B. Iversen, *ACS Nano* **2008**, 2, 1058-1068.
- [9] aK. Sue, M. Suzuki, K. Arai, T. Ohashi, H. Ura, K. Matsui, Y. Hakuta, H. Hayashi, M. Watanabe, T. Hiaki, *Green Chem.* **2006**, 8, 634-638; bH. Reverón, C. Elissalde, C. Aymonier, O. Bidault, M. Maglione, F. Cansell, *J. Nanosci. Nanotechnol.* **2005**, 5, 1741-1744; cW. E. Stallings, H. H. Lamb, *Langmuir* **2003**, 19, 2989-2994; dA. Cabanas, M. Poliakoff, *J. Mater. Chem.* **2001**, 11, 1408-1416; eG. Philippot, K. M. Ø. Jensen, M. Christensen, C. Elissalde, M. Maglione, B. B. Iversen, C. Aymonier, *J. Supercrit. Fluids* **2014**, 87, 111-117; fF. Cansell, C. Aymonier, *J. Supercrit. Fluids* **2009**, 47, 508-516.
- [10] aJ.-L. Mi, M. Christensen, C. Tyrsted, K. M. Ø. Jensen, J. Becker, P. Hald, B. B. Iversen, *J. Phys. Chem. C* **2010**, 114, 12133-12138; bJ.-L. Mi, T. N. Jensen, P. Hald, J. Overgaard, M. Christensen, B. B. Iversen, *J. Supercrit. Fluids* **2012**, 67, 84-88.
- [11] aJ. Kim, D. Kim, B. Veriansyah, J. Won Kang, J.-D. Kim, *Mater. Lett.* **2009**, 63, 1880-1882; bC. Morin, A. Loppinet-Serani, F. Cansell, C. Aymonier, *J. Supercrit. Fluids* **2012**, 66, 232-240; cC. Słostowski, S. Marre, O. Babot, T. Toupance, C. Aymonier, *Langmuir* **2014**, 30, 5965-5972.
- [12] C. Słostowski, S. Marre, O. Babot, T. Toupance, C. Aymonier, *Langmuir* **2012**, 28, 16656-16663.
- [13] J.-L. Mi, P. Norby, M. Bremholm, J. Becker, B. B. Iversen, *Nanoscale* **2015**, 7, 16170-16174.
- [14] D. Saha, E. D. Bøjesen, K. M. Ø. Jensen, A.-C. Dippel, B. B. Iversen, *J. Phys. Chem. C* **2015**, 119, 13357-13362.
- [15] aT. Egami, S. J. Billinge, *Underneath the Bragg Peaks: Structural Analysis of Complex Materials*, Vol. 16, Pergamon, **2012**; bS. J. L. Billinge, M. G. Kanatzidis, *Chem. Commun. (Cambridge, U. K.)* **2004**, 749-760.
- [16] C. A. Young, A. L. Goodwin, *J. Mater. Chem.* **2011**, 21, 6464-6476.
- [17] E. D. Bøjesen, K. M. Ø. Jensen, C. Tyrsted, A. Mamakhel, H. L. Andersen, H. Reardon, J. Chevalier, A.-C. Dippel, B. B. Iversen, *Chemical Science* **2016**.
- [18] aK. M. Ø. Jensen, M. Christensen, P. Juhas, C. Tyrsted, E. D. Bøjesen, N. Lock, S. J. L. Billinge, B. B. Iversen, *J. Am. Chem. Soc.* **2012**, 134, 6785-6792; bC. Tyrsted, K. M. Ø. Jensen, E. D. Bøjesen, N. Lock, M. Christensen, S. J. L. Billinge, B. B. Iversen, *Angew. Chem., Int. Ed.* **2012**, 51, 9030-9033; cD. Saha, K. M. Ø. Jensen, C. Tyrsted, E. D. Bøjesen, A. H. Mamakhel, A.-C. Dippel, M. Christensen, B. B. Iversen, *Angew. Chem., Int. Ed.* **2014**, 53, 3667-3670; dC. Tyrsted, N. Lock, K. M. Ø. Jensen, M. Christensen, E. D. Bøjesen, H. Emerich, G. Vaughan, S. J. L. Billinge, B. B. Iversen, *IUCrJ* **2014**, 1, 165-171; eK. M. Ø. Jensen, H. L. Andersen, C. Tyrsted, E. D. Bøjesen, A.-C. Dippel, N. Lock, S. J. L. Billinge, B. B. Iversen, M. Christensen, *ACS Nano*

- 2014, 8, 10704-10714; fJ.-L. Mi, K. M. O. Jensen, C. Tyrsted, M. Bremholm, B. B. Iversen, *CrystEngComm* **2015**, 17, 6868-6877.
- [19] M. Zobel, R. B. Neder, S. A. J. Kimber, *Science* **2015**, 347, 292-294.
- [20] D. Prill, P. Juhás, M. U. Schmidt, S. J. L. Billinge, *J. Appl. Crystallogr.* **2015**, 48, 171-178.
- [21] aS. J. L. Billinge, T. Dykhne, P. Juhas, E. Bozin, R. Taylor, A. J. Florence, K. Shankland, *CrystEngComm* **2010**, 12, 1366-1368; bT. Dykhne, R. Taylor, A. Florence, S. L. Billinge, *Pharm. Res.* **2011**, 28, 1041-1048.
- [22] A.-C. Dippel, N. Bindzus, D. Saha, J. T. Delitz, H.-P. Liermann, N. Wahlberg, J. Becker, E. D. Bøjesen, B. Brummerstedt Iversen, *Z. Anorg. Allg. Chem.* **2014**, 640, 3094-3099.
- [23] M. Avrami, *J. Chem. Phys.* **1939**, 7, 1103-1112.
- [24] aY. Li, Y. Jiang, M. Chen, H. Liao, R. Huang, Z. Zhou, N. Tian, S. Chen, S. Sun, *Chem. Commun. (Cambridge, U. K.)* **2012**, 48, 9531-9533; bS. Sultana, N. Tachikawa, K. Yoshii, L. Magagnin, K. Toshima, Y. Katayama, *J. Electrochem. Soc.* **2016**, 163, D401-D406.
- [25] aM. Avrami, *J. Chem. Phys.* **1940**, 8, 212-224; bM. Avrami, *J. Chem. Phys.* **1941**, 9, 177-184; cS. P. Shields, V. N. Richards, W. E. Buhro, *Chem. Mater.* **2010**, 22, 3212-3225; dV. N. Richards, N. P. Rath, W. E. Buhro, *Chem. Mater.* **2010**, 22, 3556-3567; eV. N. Richards, S. P. Shields, W. E. Buhro, *Chem. Mater.* **2011**, 23, 137-144.
- [26] N. Sun, X. Liu, K. Lu, *Scr. Mater.* **1996**, 34, 1201-1207.
- [27] R. C. Weast, D. Lide, M. Astle, W. Beyer, *Handbook of Chemistry and Physics. -1989-1990*, Boca Raton: CRC Press, **1989**.
- [28] A.-C. Dippel, H.-P. Liermann, J. T. Delitz, P. Walter, H. Schulte-Schrepping, O. H. Seeck, H. Franz, *J. Synchrotron Rad.* **2015**, 22, 675-687.
- [29] J. Becker, M. Bremholm, C. Tyrsted, B. Pauw, K. M. O. Jensen, J. Eltzholt, M. Christensen, B. B. Iversen, *J. Appl. Crystallogr.* **2010**, 43, 729-736.
- [30] P. J. Chupas, K. W. Chapman, C. Kurtz, J. C. Hanson, P. L. Lee, C. P. Grey, *J. Appl. Crystallogr.* **2008**, 41, 822-824.
- [31] A. Hammersley, S. Svensson, M. Hanfland, A. Fitch, D. Hausermann, *Int. J. High Pressure Res.* **1996**, 14, 235-248.
- [32] P. Juhas, T. Davis, C. L. Farrow, S. J. L. Billinge, *J. Appl. Crystallogr.* **2013**, 46, 560-566.
- [33] C. L. Farrow, P. Juhas, J. W. Liu, D. Bryndin, E. S. Božin, J. Bloch, T. Proffen, S. J. L. Billinge, *J. Phys.: Condens. Matter* **2007**, 19, 335219-335226.
- [34] J. Rodríguez-Carvajal, *Physica B* **1993**, 192, 55-69.

FULL PAPER

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**In situ PDF study of the nucleation
and growth of intermetallic PtPb
nanocrystals**

In situ total scattering studies provide a deeper understanding of the nucleation mechanism kinetics of Pt nanoparticle formation, and allow structural modelling of the precursor structure. The similar reaction kinetics of $\text{Pt}(\text{acac})_2$ and $\text{Pb}(\text{acac})_2$ precursors lead to development of a facile continuous flow supercritical ethanol process for obtaining phase pure hexagonal PtPb nanocrystals.