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Improved Scalability of Palladium Nanocrystal Synthesis

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Background:

Palladium nanoparticles aid the study of hydrogen interaction with solids. Hydrogen induces a phase transition to an expanded face-centered cubic lattice in Pd at specific temperatures and pressures, forming a near-stoichiometric hydride, $PdH_{0.6}$.

This phase transition displays hysteresis in macroscopic calorimetry experiments. Differential scanning calorimetry of 10.636 mg Pd at various H_2 pressures shows desorption-absorption hysteresis.

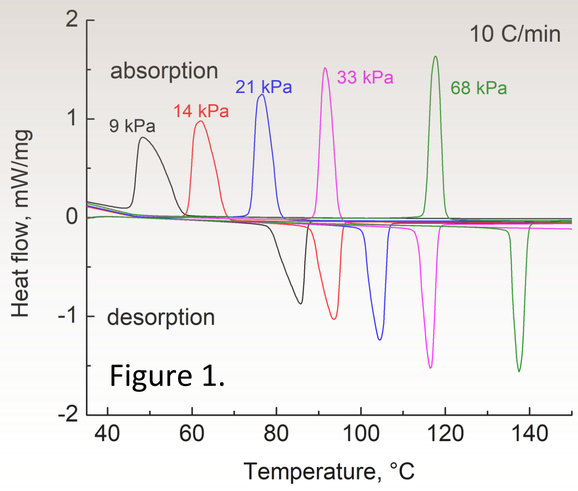
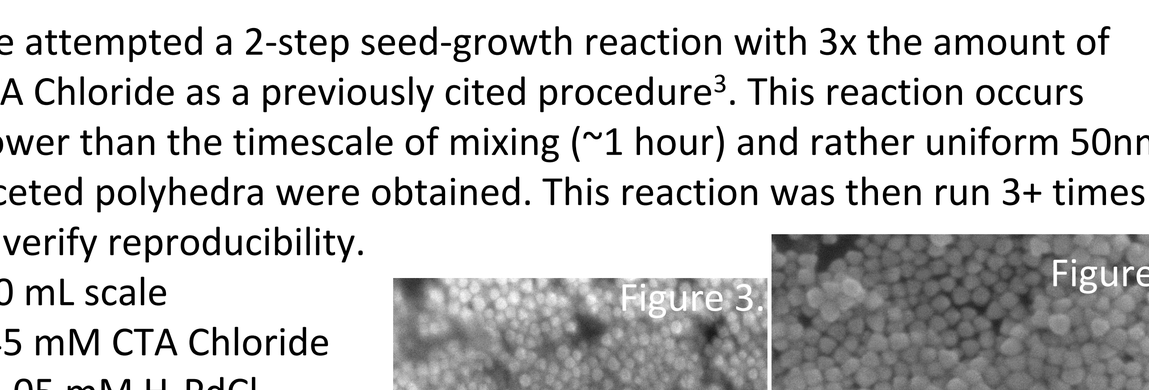


Figure 1.

To study the relationship between hysteresis and induced lattice defects,[5] large, single-crystal particles are preferred. This work is motivated by highly cited synthetic approaches that typically require 40L solution/g product[2] and aqueous suspensions that only require 1L/g product[1]. We aim to further decrease the required volume while uniformly increasing size to hundreds of nm.



Synthesis of Uniform, Single and Polycrystalline Nanoparticles:

Attempts to reproduce cited synthetic approaches[1,2] did not yield monodisperse seeds. We observed that the seed reaction occurred on the timescale of mixing. We think that this reaction is exceptionally sensitive to µM-level metal and halide impurities or other reaction conditions[4]. Experimental modifications were made to the procedures[1,2,3] in an attempt to slow down reaction time.

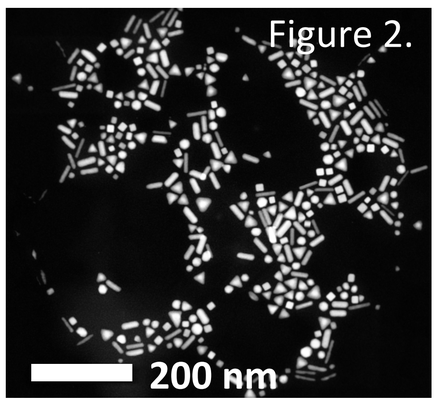


Figure 2.

We attempted a 2-step seed-growth reaction with 3x the amount of CTA Chloride as a previously cited procedure[3]. This reaction occurs slower than the timescale of mixing (~1 hour) and rather uniform 50nm faceted polyhedra were obtained. This reaction was then run 3+ times to verify reproducibility.

- 10 mL scale
- 45 mM CTA Chloride
- 1.05 mM H_2PdCl_4
- 0.75 µM KI
- 0.6 mM Ascorbic Acid (AA, less than 1 eq.)
- 45 °C 30 min
- Stir at 750 rpm

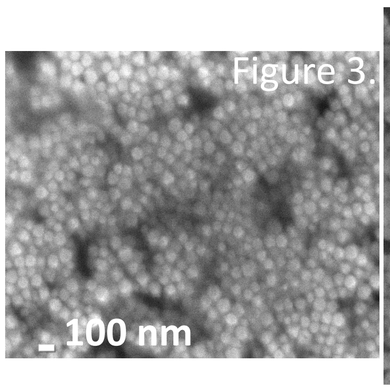


Figure 3.

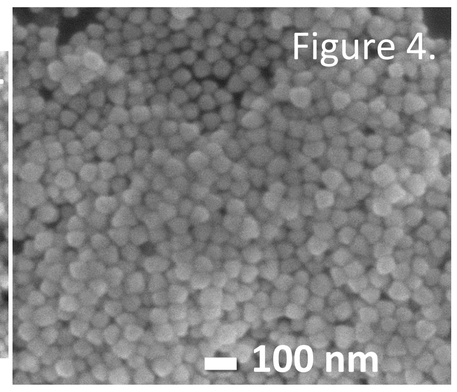
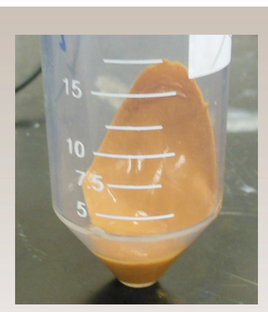


Figure 4.

Previous work[1,2] involves a 2-step process of synthesizing preliminary Pd seeds to grow the Pd nanocrystals from. Given that uniform seeds have been difficult to reproduce, we attempted a 1-step reaction to improve size and shape uniformity and improve yield/L of solvent used.

- Isolate CTA_2PdCl_4
- Suspend 1 eq. 1 M HCl, 15.6 eq. 1 M AA, 0.0007 eq. 1 mM KI
- Chill reagents to 13 °C to start reaction
- Stir at 22 °C for 4 hours



Isolated CTA_2PdCl_4

Performing subsequent trials reveals that the chilling step is not necessary.

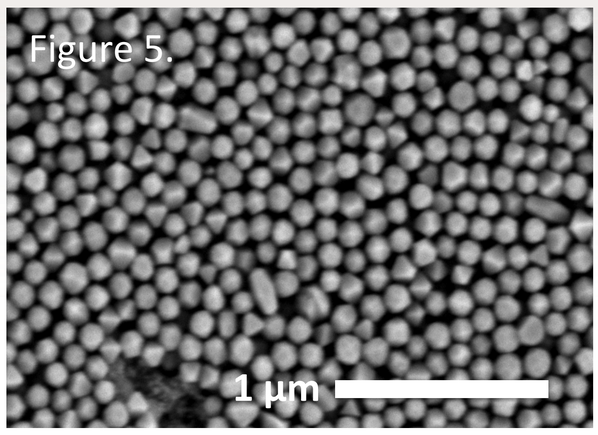


Figure 5.

This produces ~150nm faceted particles with visibly improved size and shape uniformity. Scalability is also increased; the concentration is 57 mmol Pd/L added liquid. This is 2x as concentrated as our previous 2-step reactions.

Scaling up to Larger Particles

However, we found that to create nanoparticles even larger than 150nm, seeds from the 2-step reaction procedure are useful. We used unpurified 50nm particle suspension for seeds (Fig. 3 and 4) and higher concentrations for all reagents. This produced ~200nm particles. Pd concentration is 24 mmol Pd/L added liquid, similar to previous work[1,2].

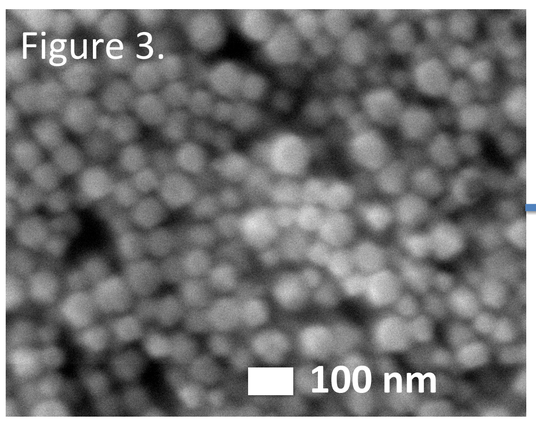


Figure 3.

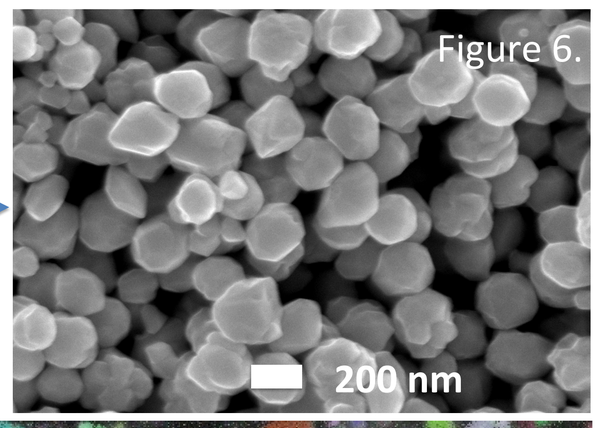


Figure 6.

- 461 mM CTA Chloride
- 0.32 mL 1 $(NH_4)_2PdCl_4$
- Stir at 22 °C
- 1.1 mL Pd seeds under stirring at 500 rpm
- 5 mL 1.0M AA
- Stirred at 45 for 4 hours

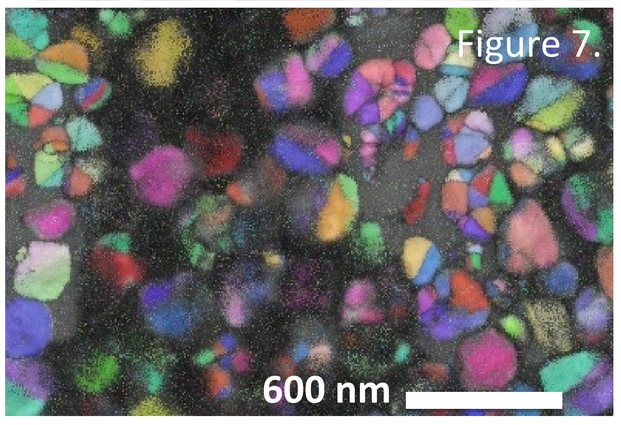


Figure 7.

Grain maps of these and similar samples obtained by transmission Kikuchi diffraction reveal that these nanoparticles consist of both single -crystal and polycrystalline particles.

Conclusion:

We have developed procedures to synthesize single and polycrystalline particles with narrow size distributions exceeding 100 nm. We have also demonstrated increased scalability by successfully decreasing reaction volume/g product to a few hundred mL/g. We expect these to be valuable in future studies of metal hydride formation and in expanding single-particle studies[5] to probe the behavior of bulk quantities in similar conditions.

References

[1] Klinkova, Anna et al. Large-Scale Synthesis of Metal Nanocrystals In Aqueous Suspensions. *Chem Mater* 2016, 28, 9, 3196-3202.
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[5] Ulvestad, A. et al. Three-dimensional imaging of dislocation dynamics during the hydriding phase transformation. *Nature Materials* 2017, 16, 565-571.

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