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Structural analysis of an HCP-phase PdH nanoparticle using atomic electron tomography

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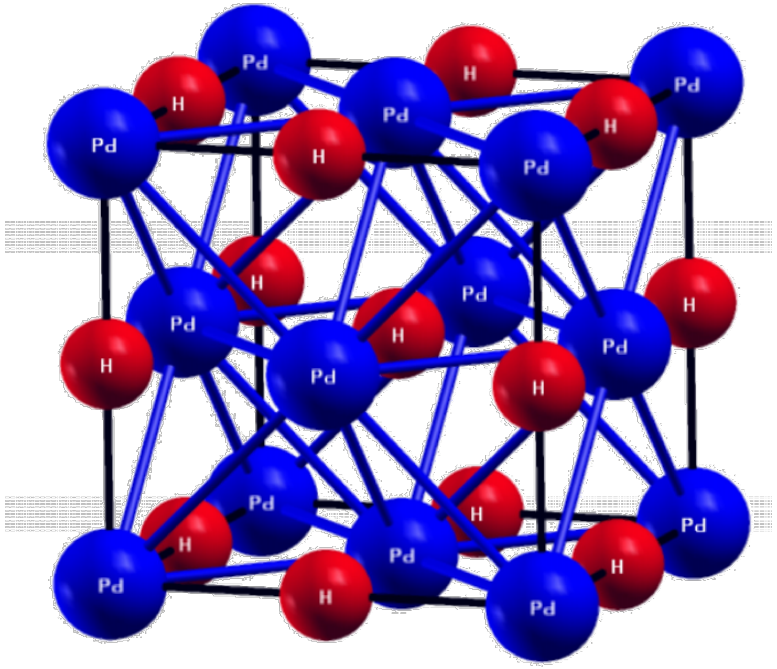
Multi-Dimensional Atomic Imaging Lab

Palladium(Pd) nanoparticle

Intro



Palladium Hydride (PdH)

- Lower activation energy of H_2 dissociation than other metals.
- Spotlighted as a hydrogen storage material and catalyst.
- PdH forms FCC structure (generally, H in octahedral site).
- Palladium absorbs no more than 1 H atom per Pd atom*

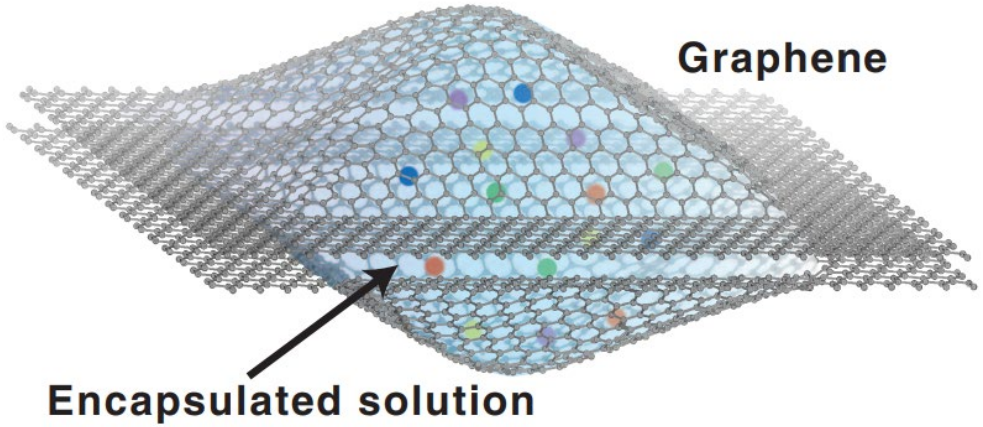
L. E. Isaeva et al. Journal of Hydrogen Energy 36, 1254–1258 (2011).

* Manchester, F., San-Martin, A., & Pitre, J.M. (1994). *Journal of Phase Equilibria, 15*, 62-83.

Unprecedented structure of Pd nanoparticle

Intro

- **New structural form of Pd nanoparticles can be synthesized** in H rich graphene liquid cell by controlling electron beam illumination.
- This is presumed to be an HCP structure, not a known FCC structure, indicating the discovery of an **unprecedented new structure**.
- The atomic structure is closely related to its storage capacity, catalytic function.

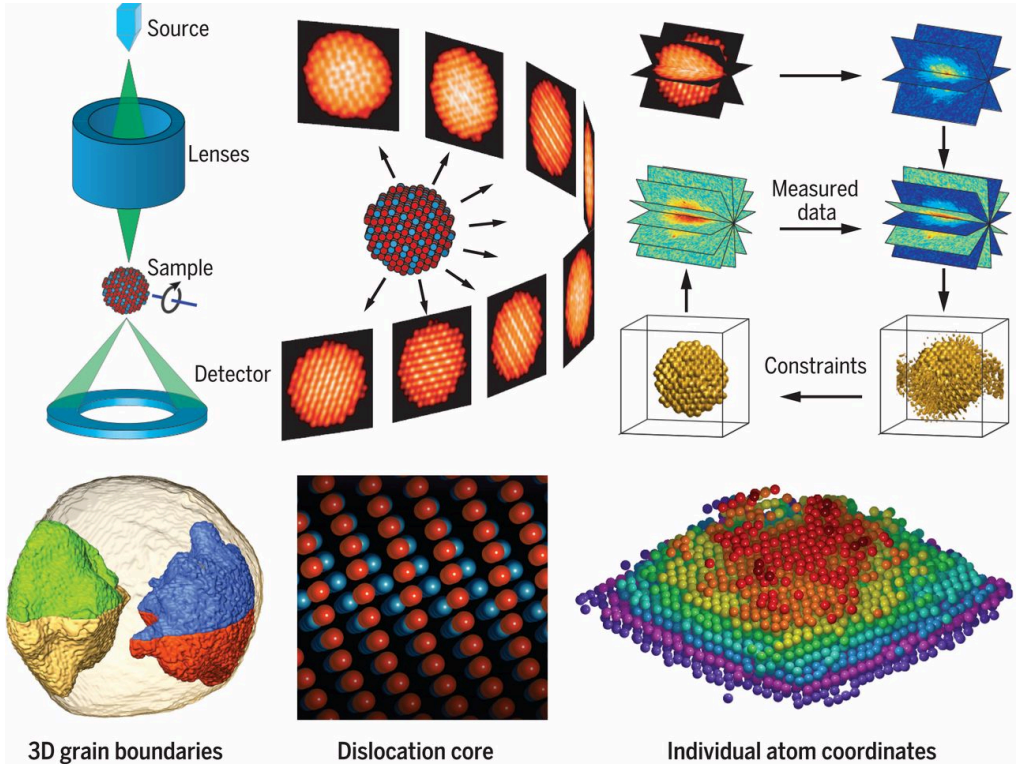


Graphene Liquid Cell

J. M. Yuk et al. Science 336 (2012), pp. 61–64.

Structure verifying & analysis through AET

Intro



Schematic layout and result of AET

- We don't know the exact structure information of this nanoparticles (such as internal structure, structural changes in synthesis process, and whether it is mainly single crystal)
- To understand the atomic arrangement, the most intuitive and easiest way is obtaining all 3D position of atoms in nanoparticles.
- **By using atomic electron tomography(AET), the structure can be accurately identified and quantitative properties can be obtained.**

1. **Determination of 3D position** PdH nanoparticle
2. **Find out what atomic structure** the PdH nanoparticles form.
3. **Obtain quantitative properties of** new structure PdH nanoparticles .

J. Miao, P. Ercius, and S. J. L. Billinge, Science **353**, (2016).

Description of data processing

1. Sample preparation

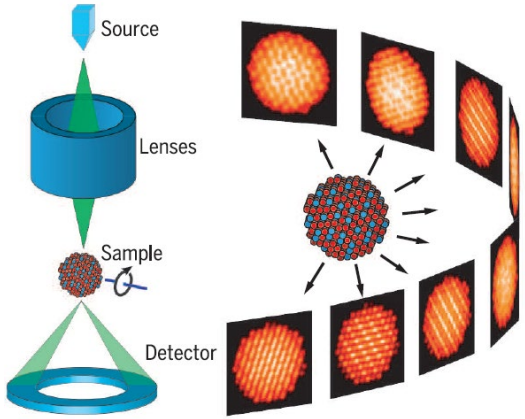
- Palladium hydride nanoparticles synthesized in GLC

2. Data acquisition through STEM(Scanning Transmission Electron Microscopy)

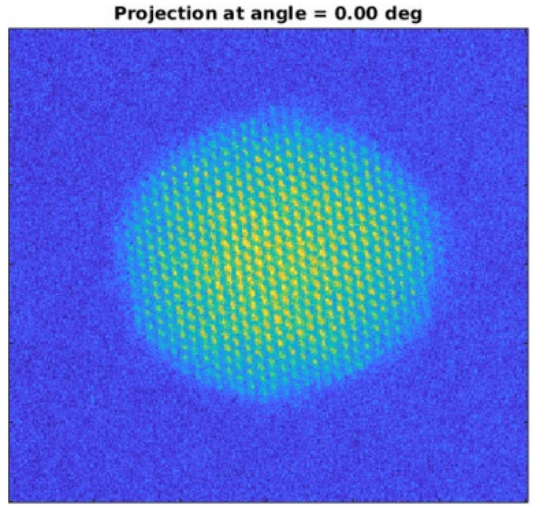
- Size of nanoparticle : about 8 nm diameter
- Accelerating voltage : 300 kV
- Detector : HAADF STEM mode
- # of projection : 33 projections (# of projection is determined by beam damage test)

  & 10 images per tilt angle (for drift correction)
- Angle range = [-70,70]
- Get projections and tilt angles.

Process of data acquisition



Experimental projections



J. Miao, P. Ercius, and S. J. L. Billinge, Science **353**, (2016).

Description of data processing

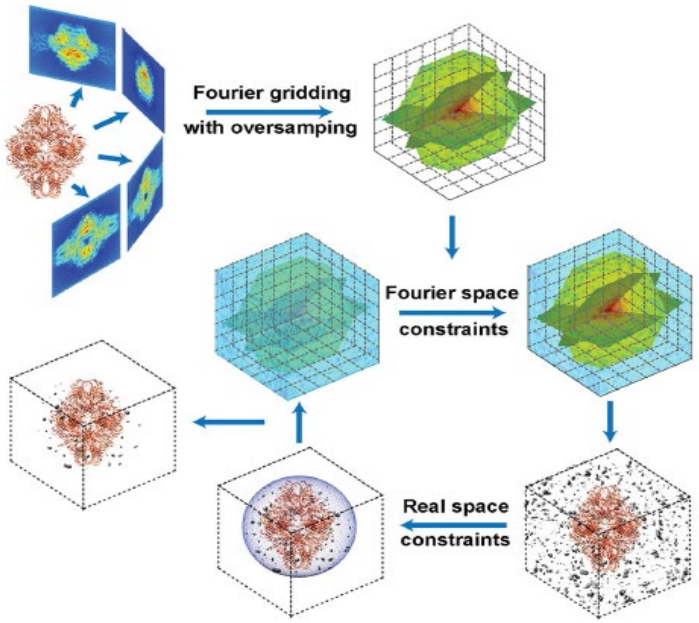
3. Post processing

- Drift correction, De-noising, Alignment

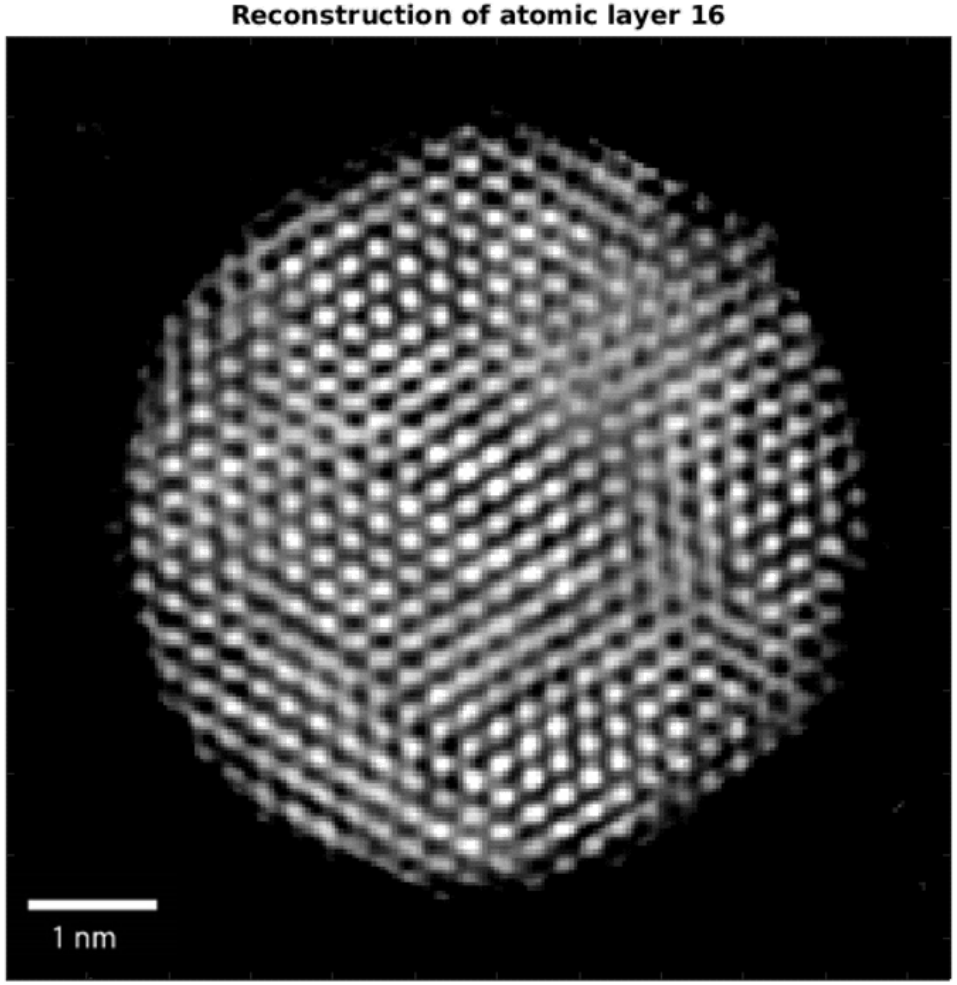
4. 3D reconstruction

- GENeralized Fourier Iterative Reconstruction

GENFIRE algorithm



Reconstruction layer by layer result

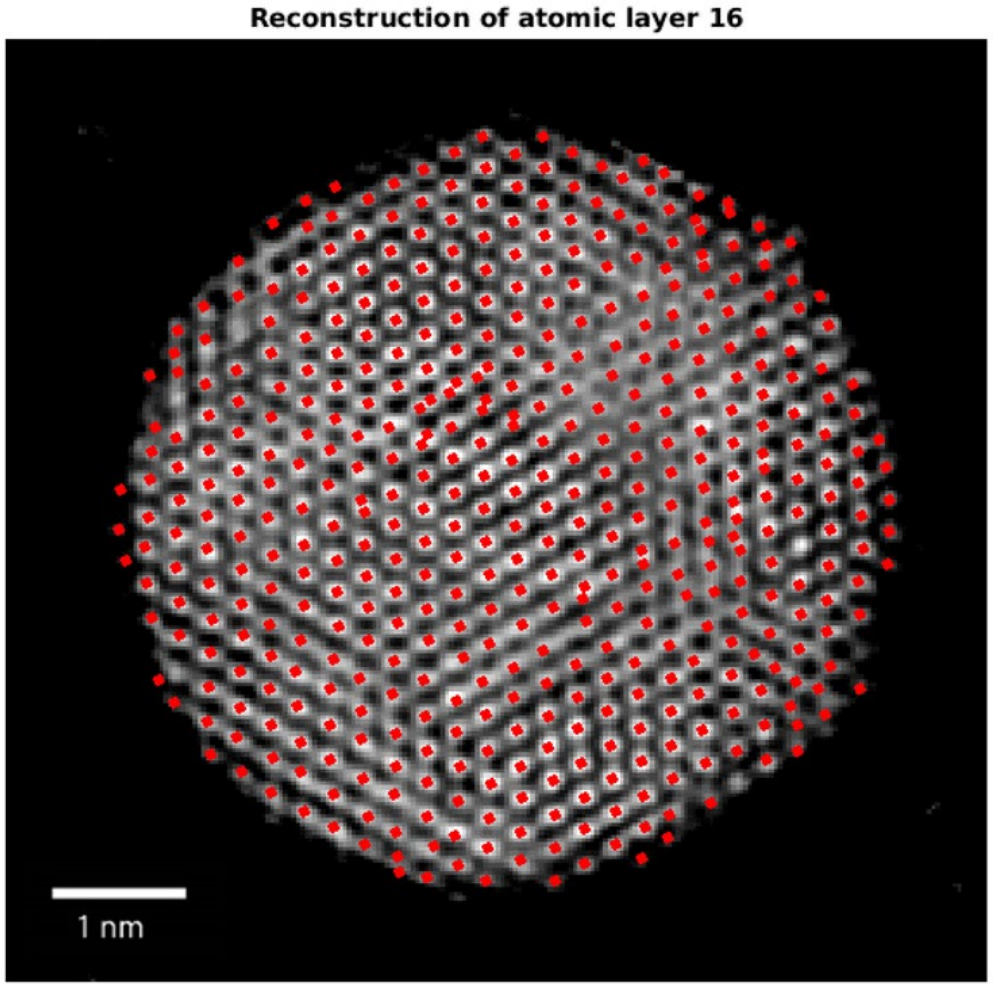


sliced along z axis (c axis of HCP structure)

A. Pryor, Y. Yang et al. Sci Rep **7**, 10409 (2017).

Description of data processing

5. Atom tracing

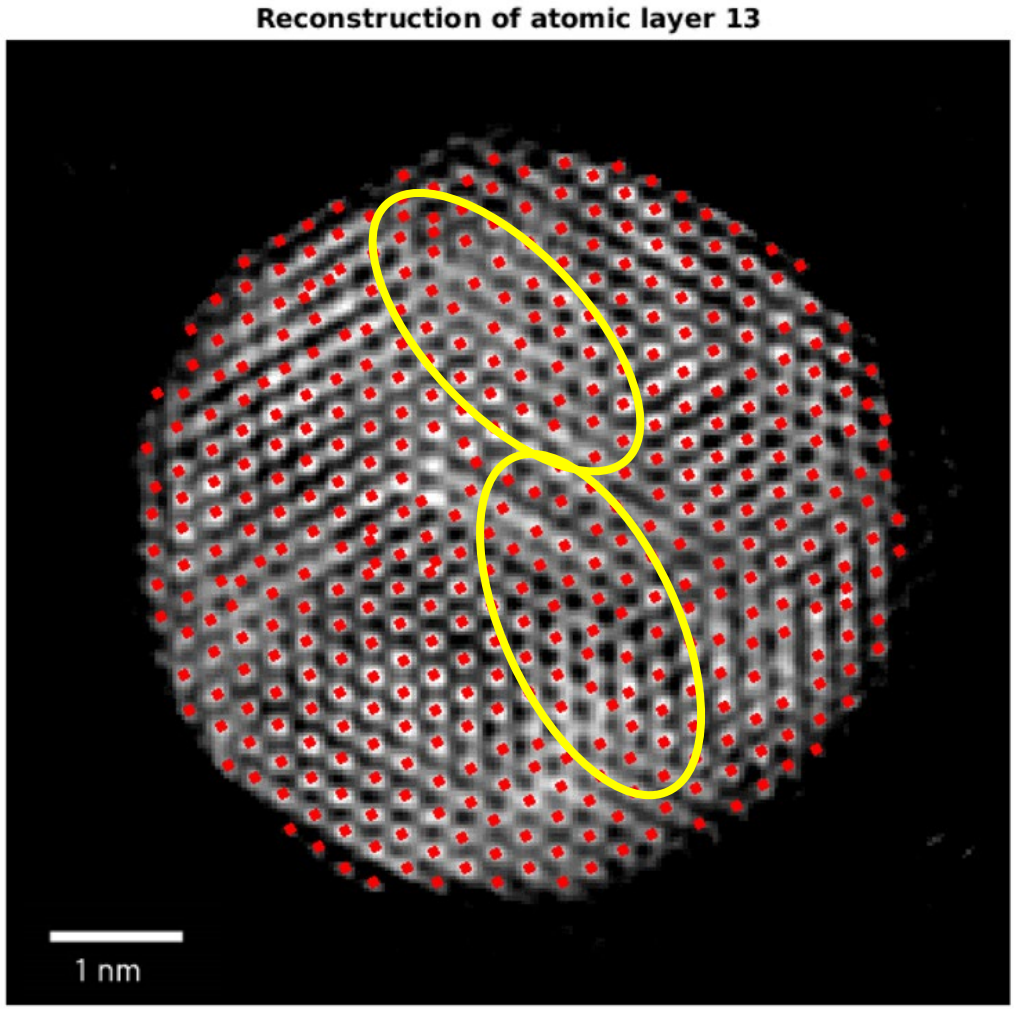


6. Fitting HCP structure

- Assume single crystal
- Fitting proper HCP lattice vector
- Assign atoms to the HCP structure created

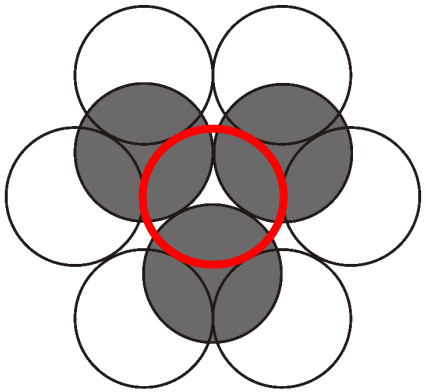
- Get lattice constant a & c
- 96 % assignment fraction

Grain structure of PdH nanoparticle

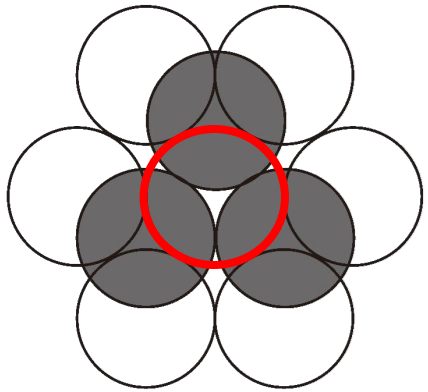


Problem of single crystal fitting

1. Lattice mismatch
2. Difference from lattice constant obtained by diffraction pattern
3. Low assignment fraction



ABAB stacking



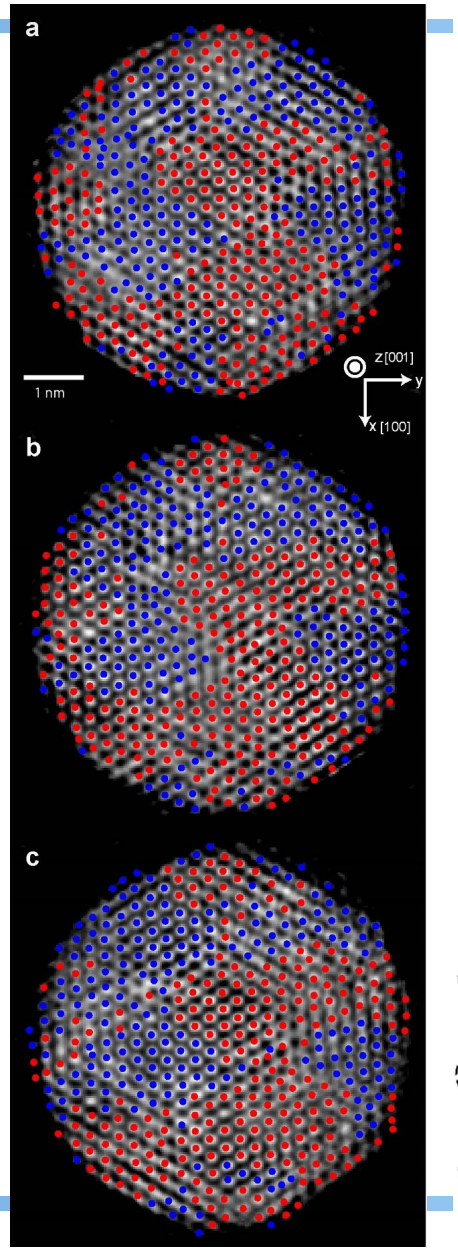
BABA stacking

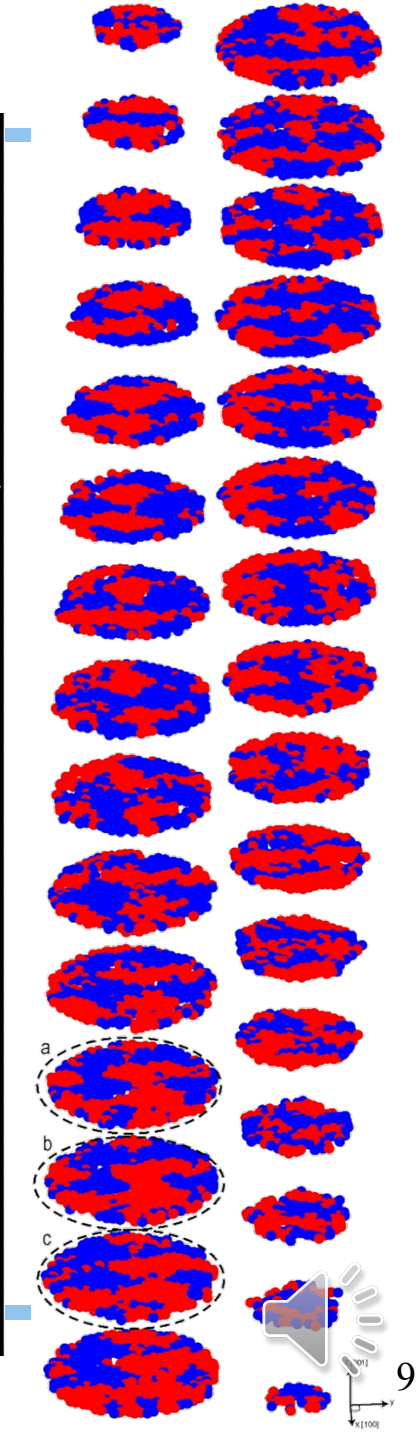
Grain structure of PdH nanoparticle

Assume non-single crystal

- Select a stacking type having a high fitting rate for each atom.
- Clear segregation and boundary are seen (multi-grain structure).
- HCP fitting is performed based on this grain structure.

Domain analysis is required based on how close it is to the locally ideal HCP structure





Domain analysis

- Higher assignment fraction

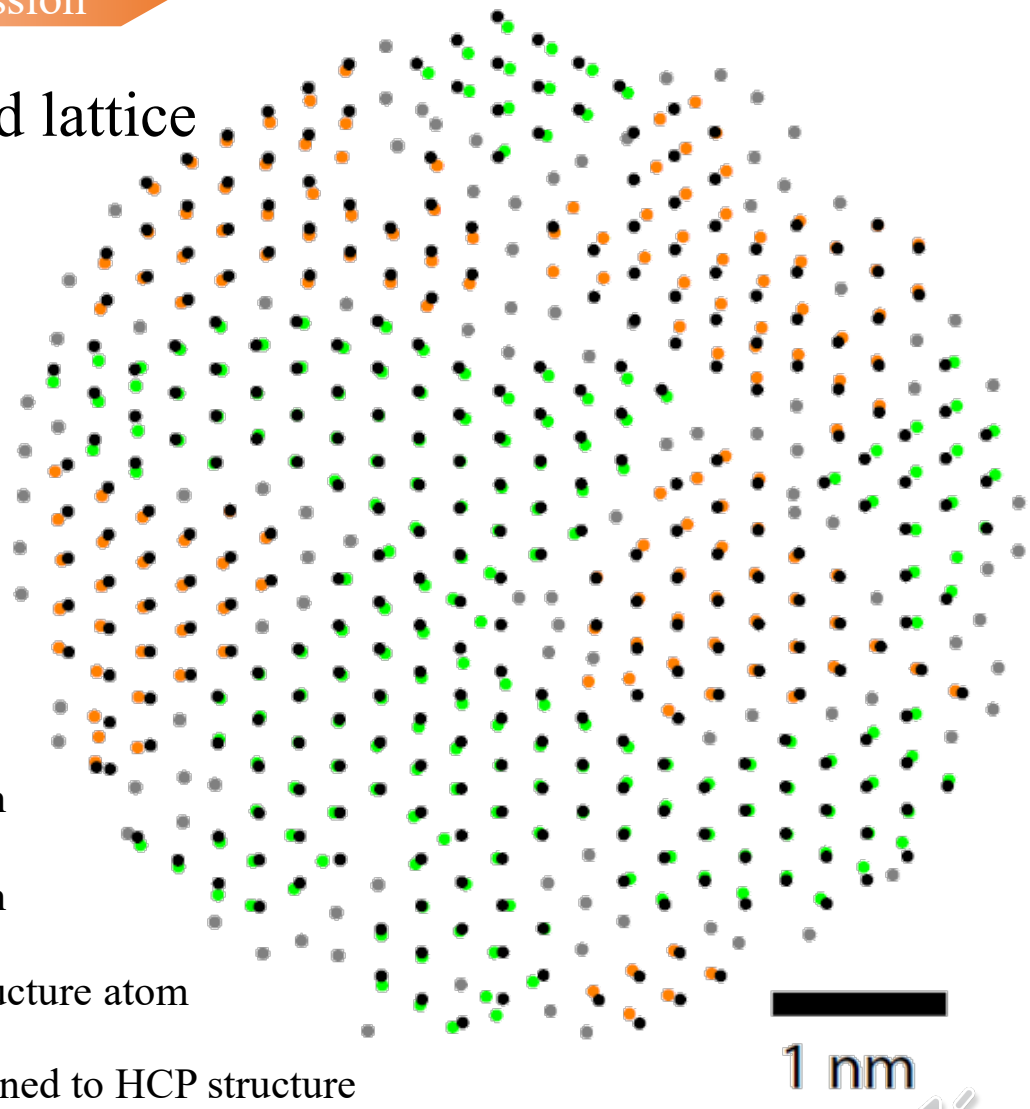
96 % → 98 %

- Lower lattice constant difference

a_{domain} = 295.30 pm
$a_{diffraction}$ = 290.36 pm → $\triangle a$ = 5.03 pm

c_{domain} = 466.92 pm
$c_{diffraction}$ = 466.18 pm → $\triangle c$ = 0.74 pm

- Well matched lattice



Local property analysis

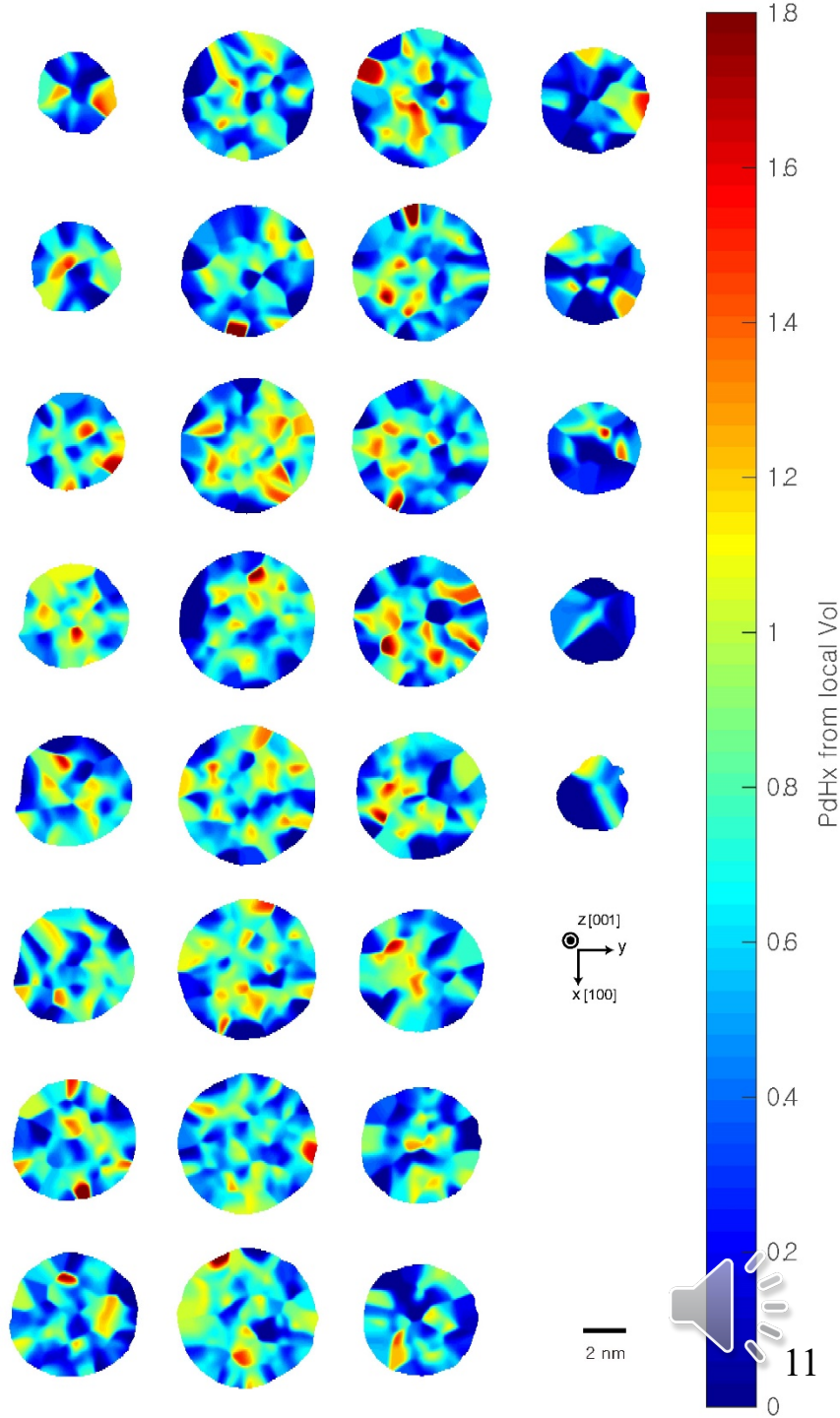
- Local property analysis is performed considering the region containing nearest neighbor of the ideal HCP structure.

- Calculate local cell volume and predict possible hydrogen storage capacity (H concentration) through density function theory.

- Spatial variation of hydrogen concentration in nanoparticles

Local volume per atom : $V_{FCC} = 14\ \text{Å}^3 < V_{HCP} = 18\ \text{Å}^3$

H concentration : $x_{FCC} < 1 < x_{HCP} = 1.3056$ (in PdH_x)



Summary

- Through AET, it is possible to **get precise 3D atomic position** of PdH nanoparticles.
- After confirming that it has a grain structure, **domain analysis** was performed.
- It was **confirmed that each domain has an HCP structure**, and its parameters are consistent with the results of the diffraction analysis.
- **Get local cell volume and local H concentration map.**
- Compared to the existing FCC palladium nanoparticles, it has a **larger local cell volume and more H concentration**.
- Through **local property analysis**, it is possible to quantitatively grasp the atomic scale mechanism and property of nanoparticle.