Nanomaterials for energy applications: a single particle approach

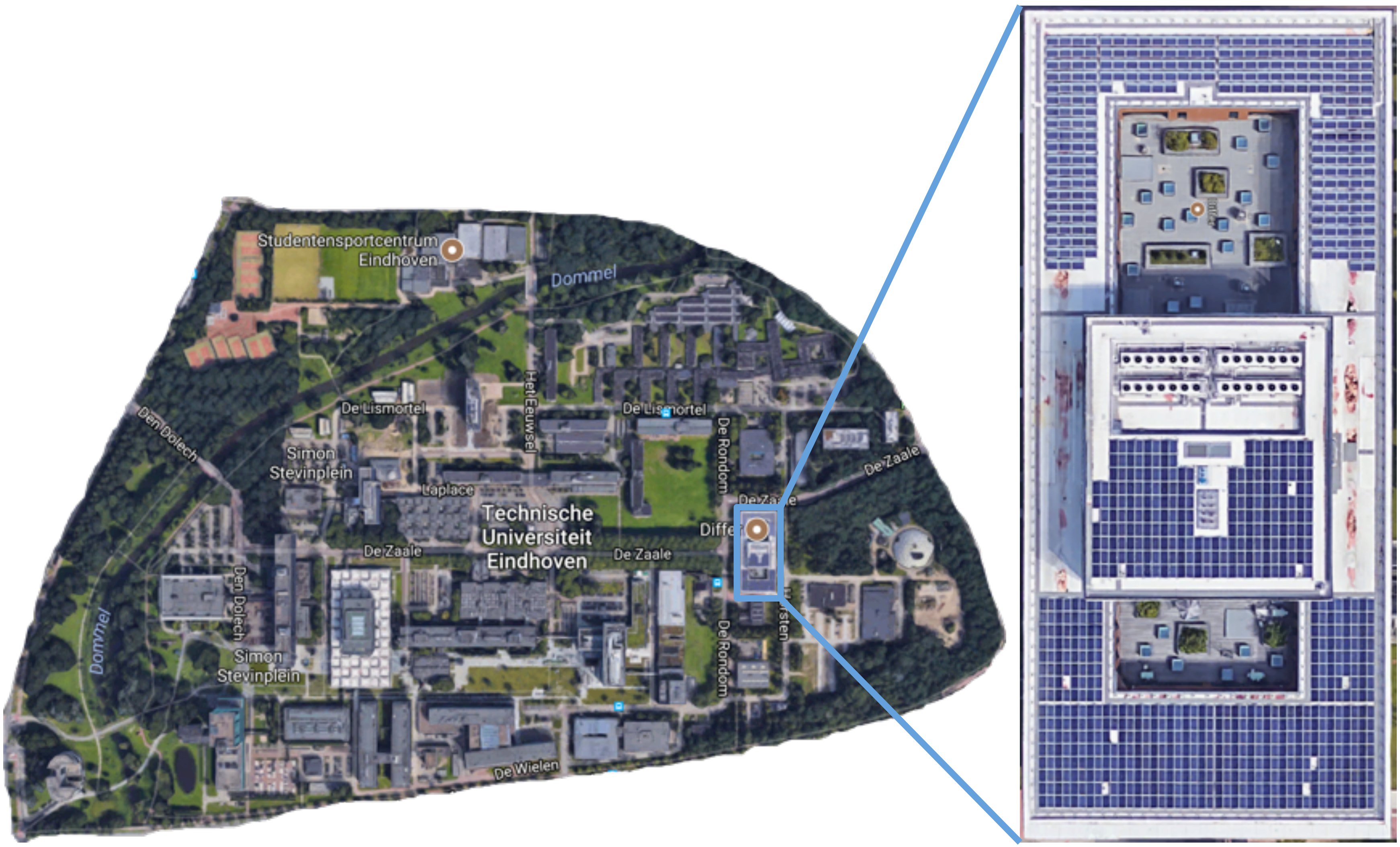
Andrea Baldi
DIFFER - Dutch Institute For Fundamental Energy Research

Tarun Narayan, Fariah Hayee, Ai Leen Koh, Bob Sinclair, Jen Dionne
Stanford University

October 13th, 2017

DIFFER: Dutch Institute For Fundamental Energy Research

Research Institute located inside the TU/e



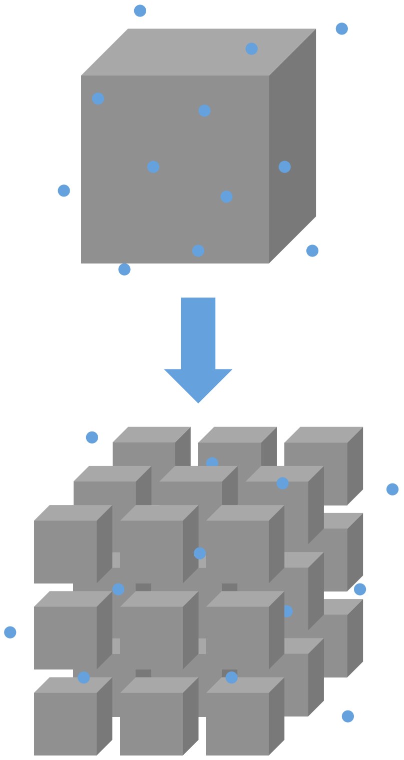
DIFFER: Dutch Institute For Fundamental Energy Research

Solar Fuels & Fusion Energy
~200 Employees

Nanomaterials for Energy Applications
Energy storage in nanomaterials
Plasmon-driven chemistry
Single-particle photo-catalysis

Energy storage in nanomaterials

Nanostructured materials for energy storage offer several advantages compared to bulk



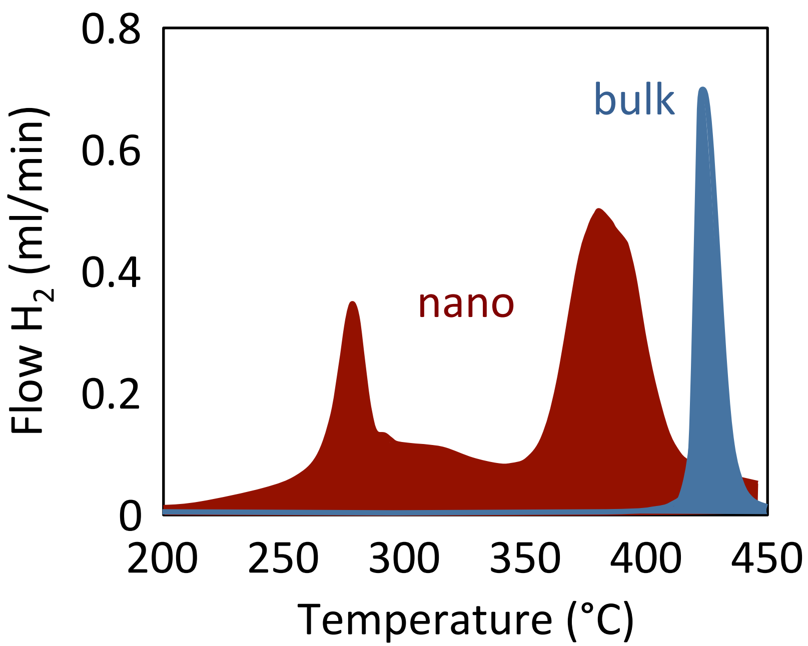
Faster kinetics
shorter diffusion lengths

Enhanced lifetime
reduced defects formation

Tunable thermodynamics
via surface, elastic or quantum effects

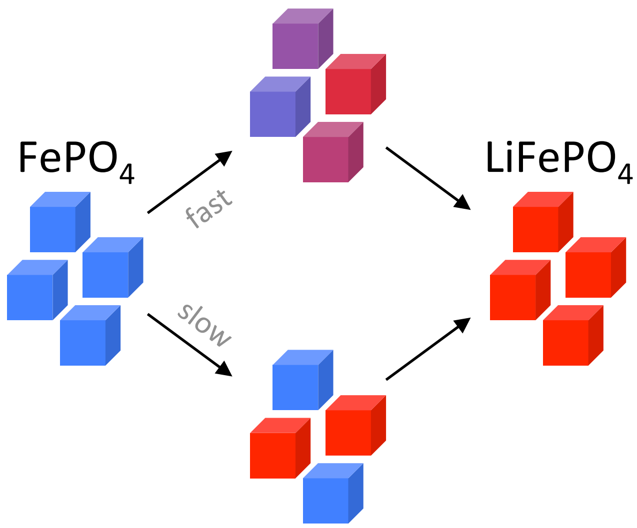
Nanostructured materials offer several advantages compared to their bulk counterpart

Hydrogen release from MgH_2



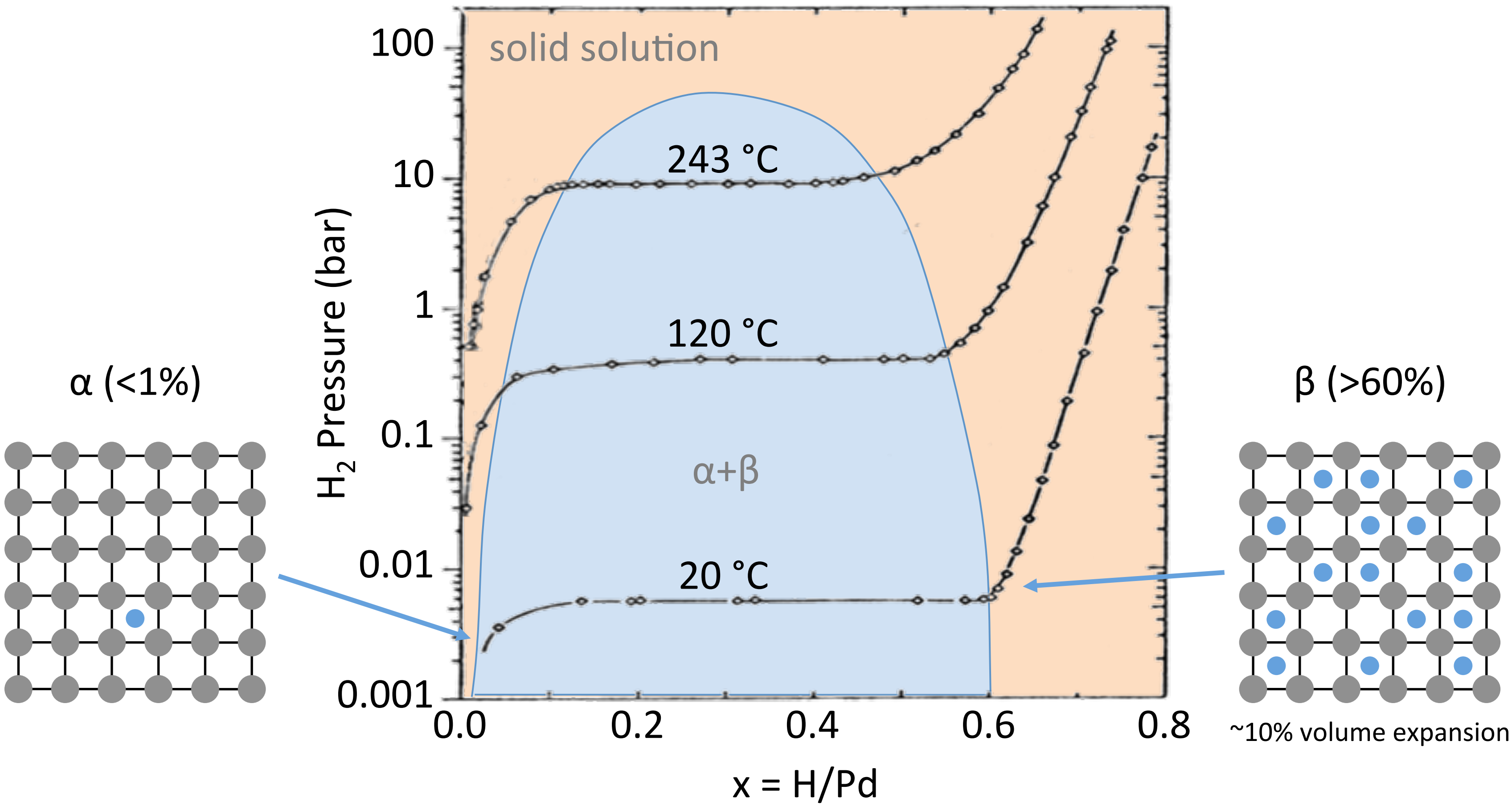
Au, Adv. Funct. Mater. (2014)

Lithiation of nanosized $FePO_4$

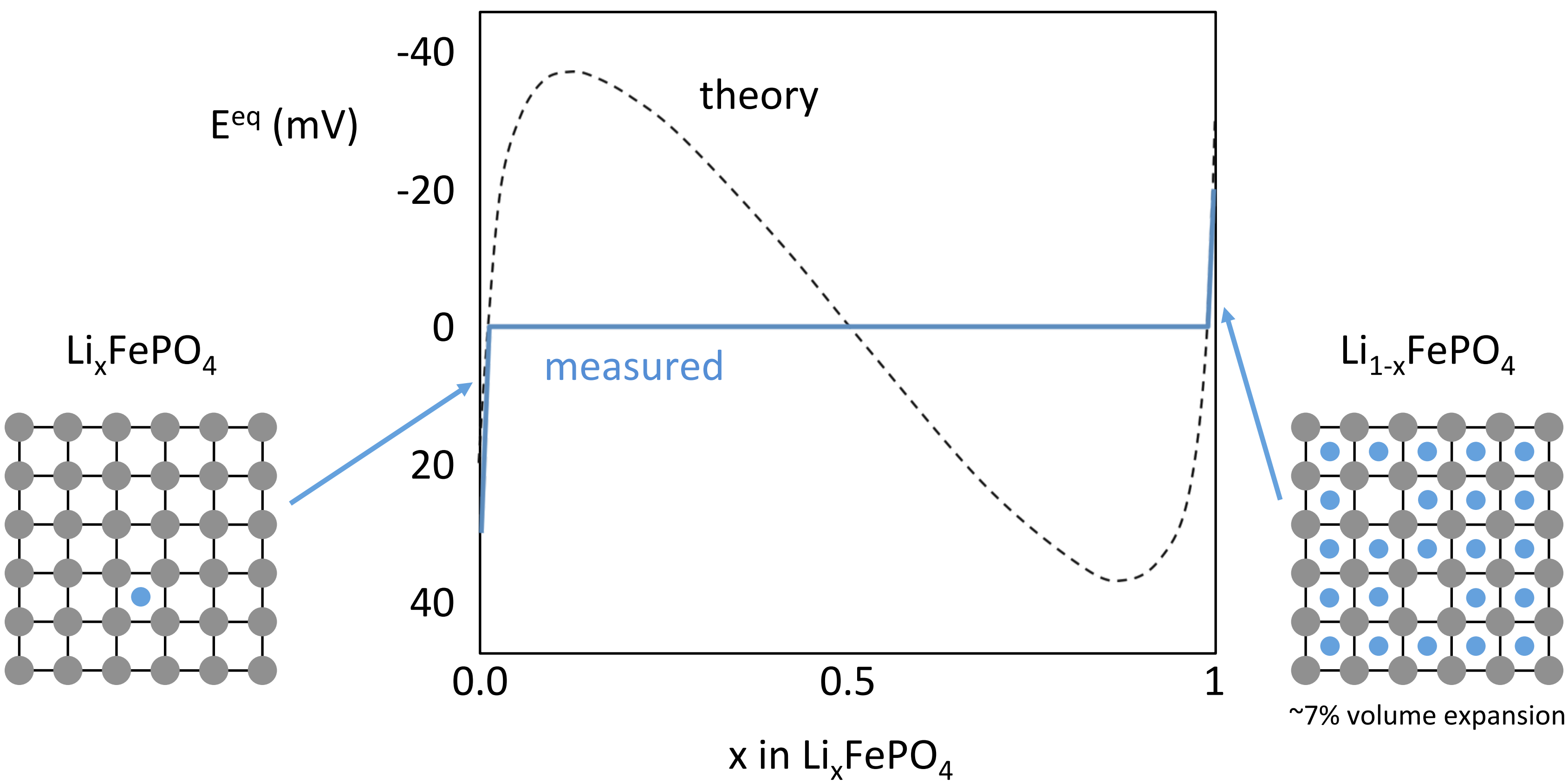


Delmas, Nature Mater. (2008); Liu, Science (2014)

Hydrogen is readily absorbed in palladium at standard temperatures and pressures

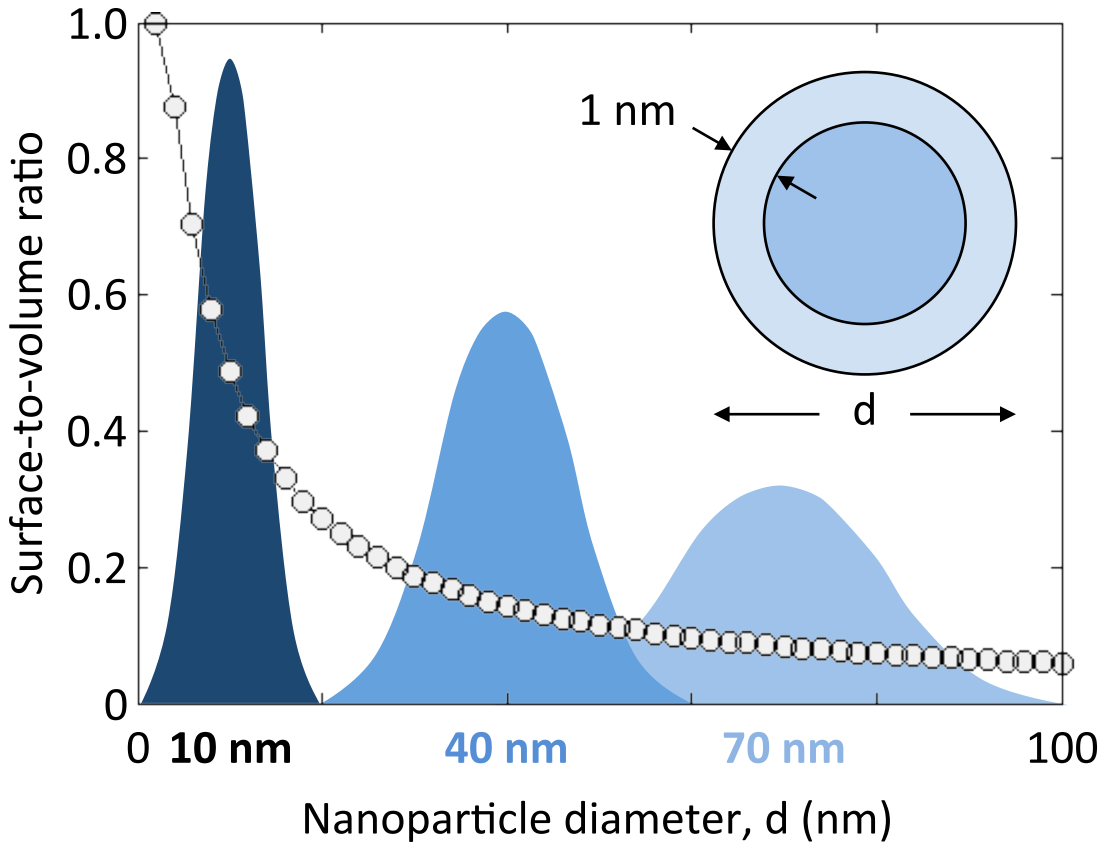


Electrode materials in Li-ion batteries undergo similar phase transitions upon lithium intercalation



Cogswell, Nano Letters (2013)

Ensemble measurements can be affected by sample dispersity particularly at very small scales



Prof. Zoric's question to God (2010):

"What is the mechanism of hydrogen absorption in a single metal nanoparticle?"

Liu, N., Tang, M., Hentschel, M., Giessen, H., & Alivisatos, A.
Nanoantenna-enhanced gas sensing in a single tailored nanofocus
Nature Materials 10, 631–636 (2011)

R. Bardhan, L. O. Hedges, C. L. Pint, A. Javey, S. Whitelam and J. J. Urban
Uncovering the intrinsic size dependence of hydriding phase transformations in nanocrystals
Nature Materials 12, 905–912 (2013)

G. Li, H. Kobayashi, J. M. Taylor, R. Ikeda, Y. Kubota, et al.
Hydrogen storage in Pd nanocrystals covered with a metal–organic framework
Nature Materials 13, 802–806 (2014)

A. Baldi, T. C. Narayan, A. L. Koh and J. A. Dionne
In situ detection of hydrogen-induced phase transitions in individual palladium nanocrystals
Nature Materials 13, 1143–1148 (2014)

S. Syrenova, C. Wadell, F. A. A. Nugroho, T. A. Gschneidtner, Y. A. Diaz Fernandez, et al.
Hydride formation thermodynamics and hysteresis in individual Pd nanocrystals with different size and shape
Nature Materials 14, 1236–1244 (2015)

A. Ulvestad, M. J. Welland, S. S. E. Collins, R. Harder, E. Maxey, et al.
Avalanching strain dynamics during the hydriding phase transformation in individual palladium nanoparticles
Nature Communications, 6, 10092 (2015)

R. Griessen, N. Strohfeldt and H. Giessen
Thermodynamics of the hybrid interaction of hydrogen with palladium nanoparticles
Nature Materials 15, 311–317 (2016)

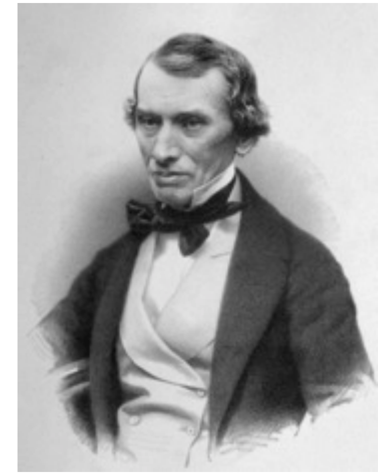
T. C. Narayan, A. Baldi, A. L. Koh, R. Sinclair and J. A. Dionne
Reconstructing solute-induced phase transformations within individual nanocrystals
Nature Materials 15, 768–774 (2016)

T. C. Narayan, F. Hayee, A. Baldi, A.-L. Koh, R. Sinclair, and J. A. Dionne
Direct visualization of hydrogen absorption dynamics in individual palladium nanoparticles
Nature Communications 8, 14020 (2017)

A. Ulvestad, M. J. Welland, W. Cha, Y. Liu, J. W. Kim, et al.
Three-dimensional imaging of dislocation dynamics during the hydriding phase transformation
Nature Materials 16, 565–571 (2017)

S. Alekseeva, A. Bastos da Silva Fanta, B. Iandolo, T. J. Antosiewicz, F. A. A. Nugroho, et al.
Grain-Boundary-Mediated Hydriding Phase Transformations in Individual Polycrystalline Metal Nanoparticles
Nature Communications (2017)

...



T. Graham (1866)

Liu, N., Tang, M., Hentschel, M., Giessen, H., & Alivisatos, A.
Nanoantenna-enhanced gas sensing in a single tailored nanofocus
Nature Materials 10, 631–636 (2011)

R. Bardhan, L. O. Hedges, C. L. Pint, A. Javey, S. Whitelam and J. J. Urban
Uncovering the intrinsic size dependence of hydriding phase transformations in nanocrystals
Nature Materials 12, 905–912 (2013)

G. Li, H. Kobayashi, J. M. Taylor, R. Ikeda, Y. Kubota, et al.
Hydrogen storage in Pd nanocrystals covered with a metal–organic framework
Nature Materials 13, 802–806 (2014)

A. Baldi, T. C. Narayan, A. L. Koh and J. A. Dionne
In situ detection of hydrogen-induced phase transitions in individual palladium nanocrystals
Nature Materials 13, 1143–1148 (2014)

S. Syrenova, C. Wadell, F. A. A. Nugroho, T. A. Gschneidtner, Y. A. Diaz Fernandez, et al.
Hydride formation thermodynamics and hysteresis in individual Pd nanocrystals with different size and shape
Nature Materials 14, 1236–1244 (2015)

A. Ulvestad, M. J. Welland, S. S. E. Collins, R. Harder, E. Maxey, et al.
Avalanching strain dynamics during the hydriding phase transformation in individual palladium nanoparticles
Nature Communications, 6, 10092 (2015)

R. Griessen, N. Strohfeldt and H. Giessen
Thermodynamics of the hybrid interaction of hydrogen with palladium nanoparticles
Nature Materials 15, 311–317 (2016)

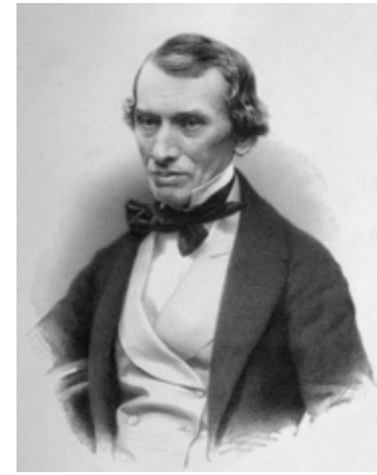
T. C. Narayan, A. Baldi, A. L. Koh, R. Sinclair and J. A. Dionne
Reconstructing solute-induced phase transformations within individual nanocrystals
Nature Materials 15, 768–774 (2016)

T. C. Narayan, F. Hayee, A. Baldi, A.-L. Koh, R. Sinclair, and J. A. Dionne
Direct visualization of hydrogen absorption dynamics in individual palladium nanoparticles
Nature Communications 8, 14020 (2017)

A. Ulvestad, M. J. Welland, W. Cha, Y. Liu, J. W. Kim, et al.
Three-dimensional imaging of dislocation dynamics during the hydriding phase transformation
Nature Materials 16, 565–571 (2017)

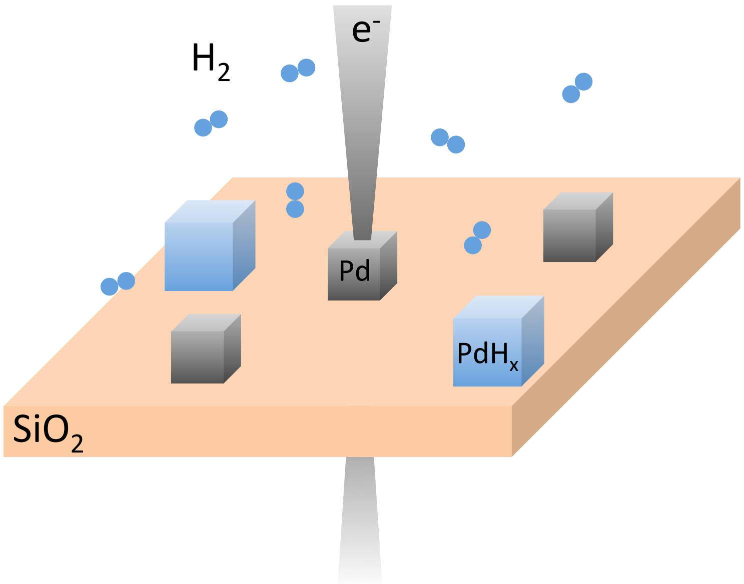
S. Alekseeva, A. Bastos da Silva Fanta, B. Iandolo, T. J. Antosiewicz, F. A. A. Nugroho, et al.
Grain-Boundary-Mediated Hydriding Phase Transformations in Individual Polycrystalline Metal Nanoparticles
Nature Communications (2017)

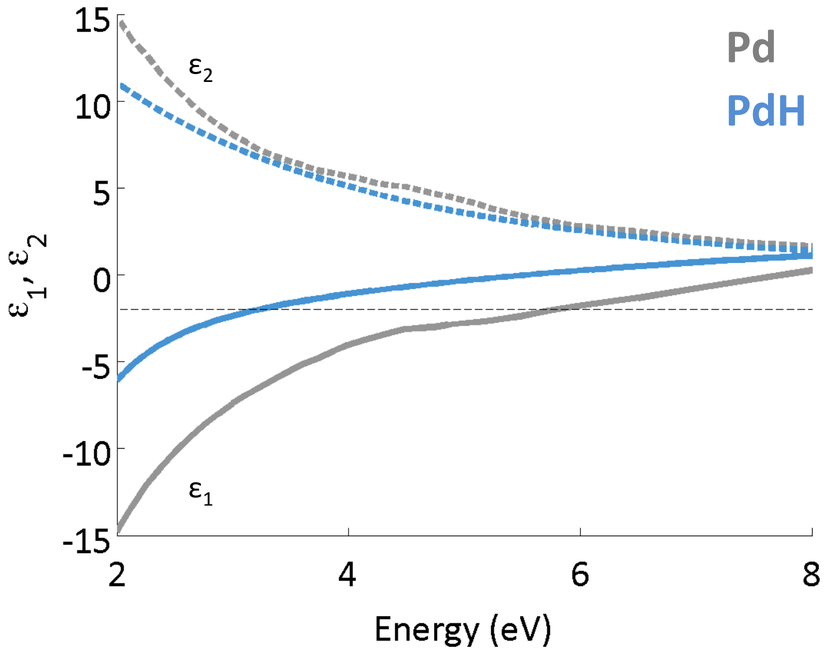
...



T. Graham (1866)

We study hydrogen absorption in single palladium nanocrystals using an environmental TEM

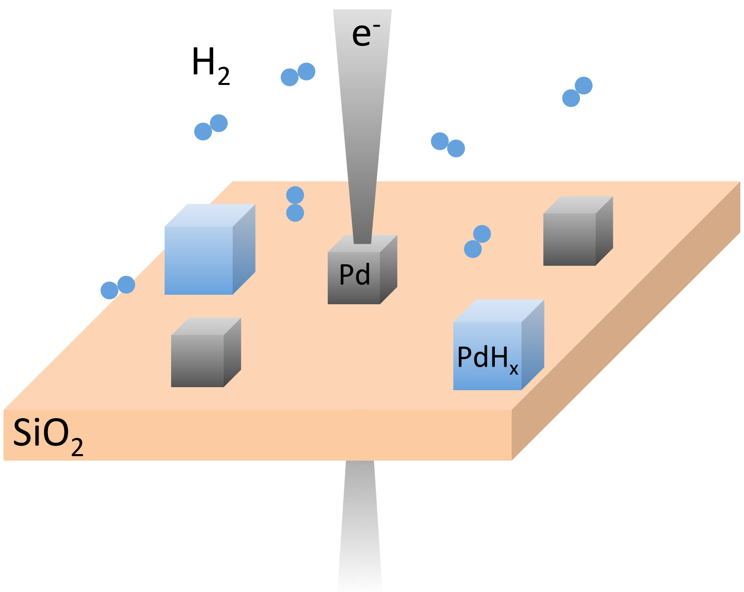


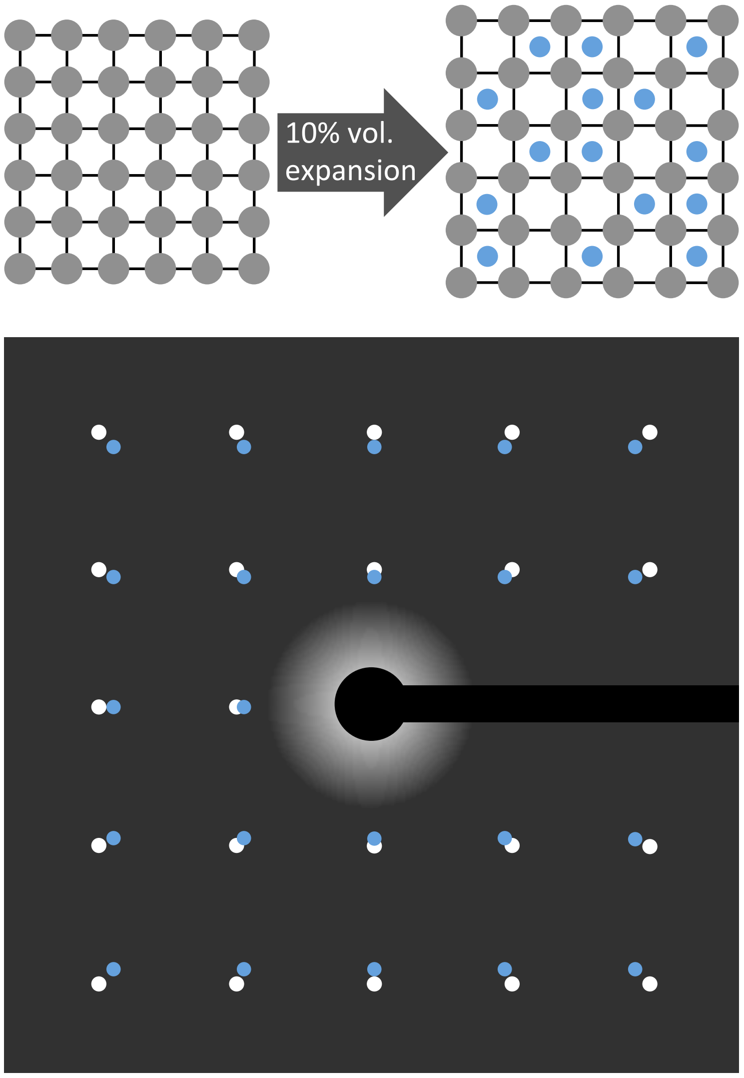


Electron Energy-Loss Spectroscopy (EELS) ⟷ dielectric function, ε

Garcia de Abajo, Rev. Mod. Phys. (2010)

We study hydrogen absorption in single palladium nanocrystals using an environmental TEM

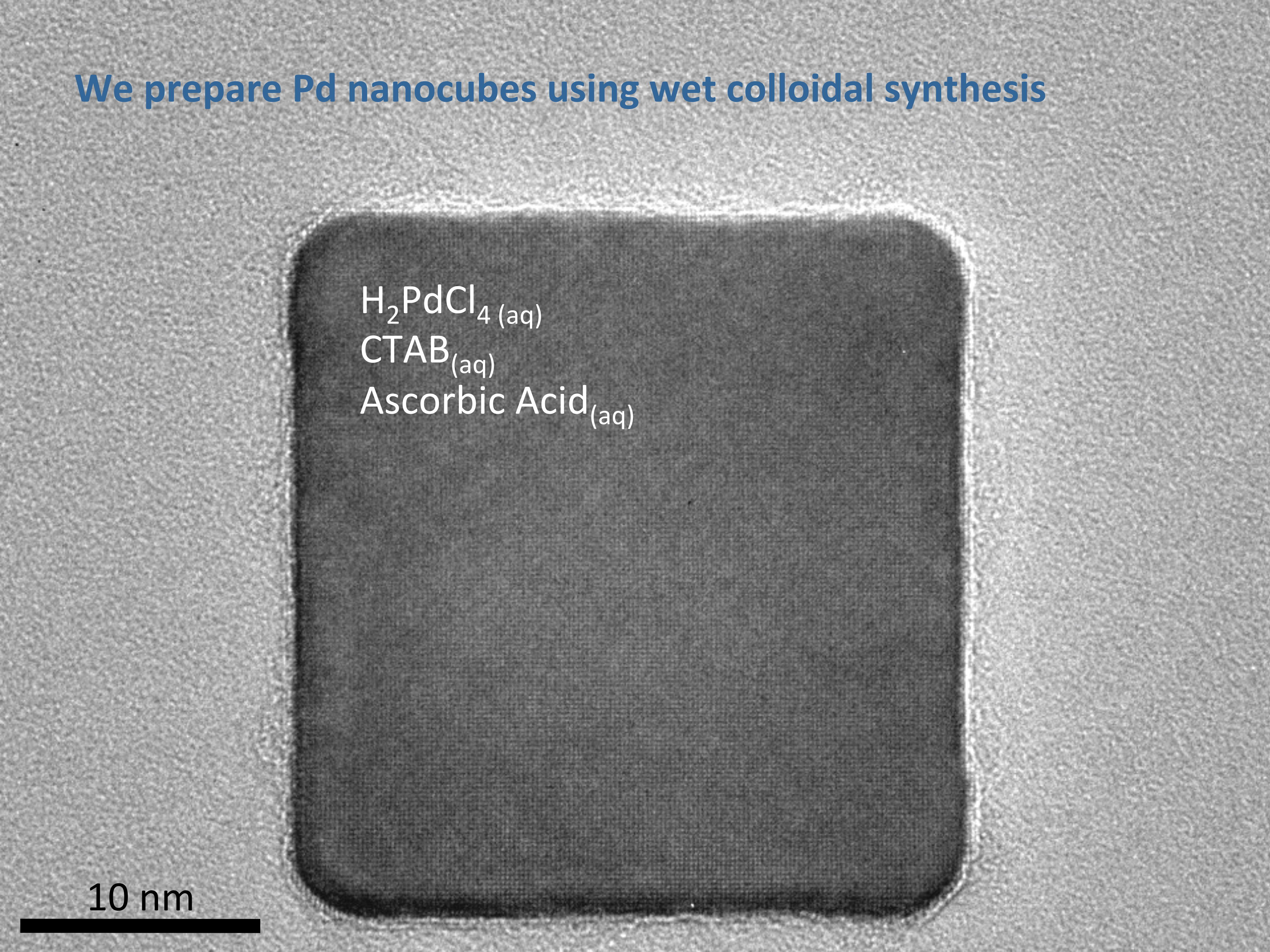




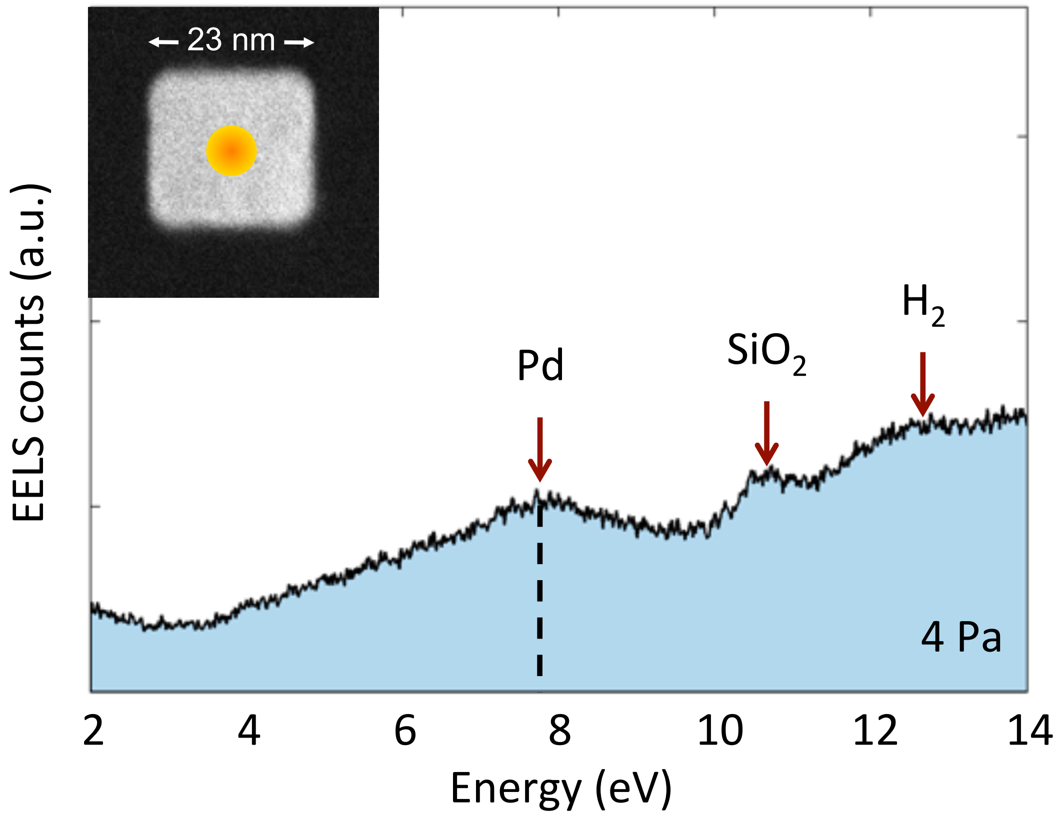
Electron Energy-Loss Spectroscopy (EELS)

Electron Diffraction (ED) ⟷ lattice expansion

We prepare Pd nanocubes using wet colloidal synthesis

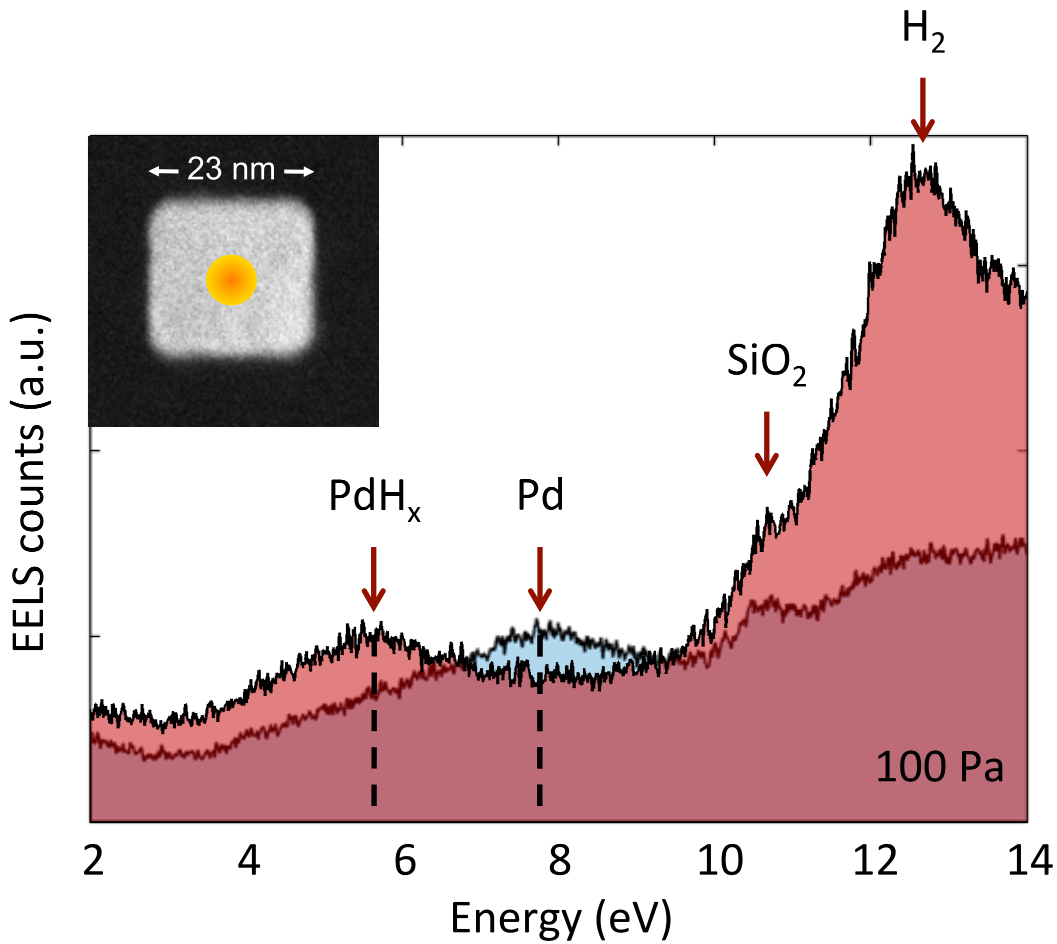


The bulk plasmon resonance of Pd red-shifts by 2 eV upon H absorption



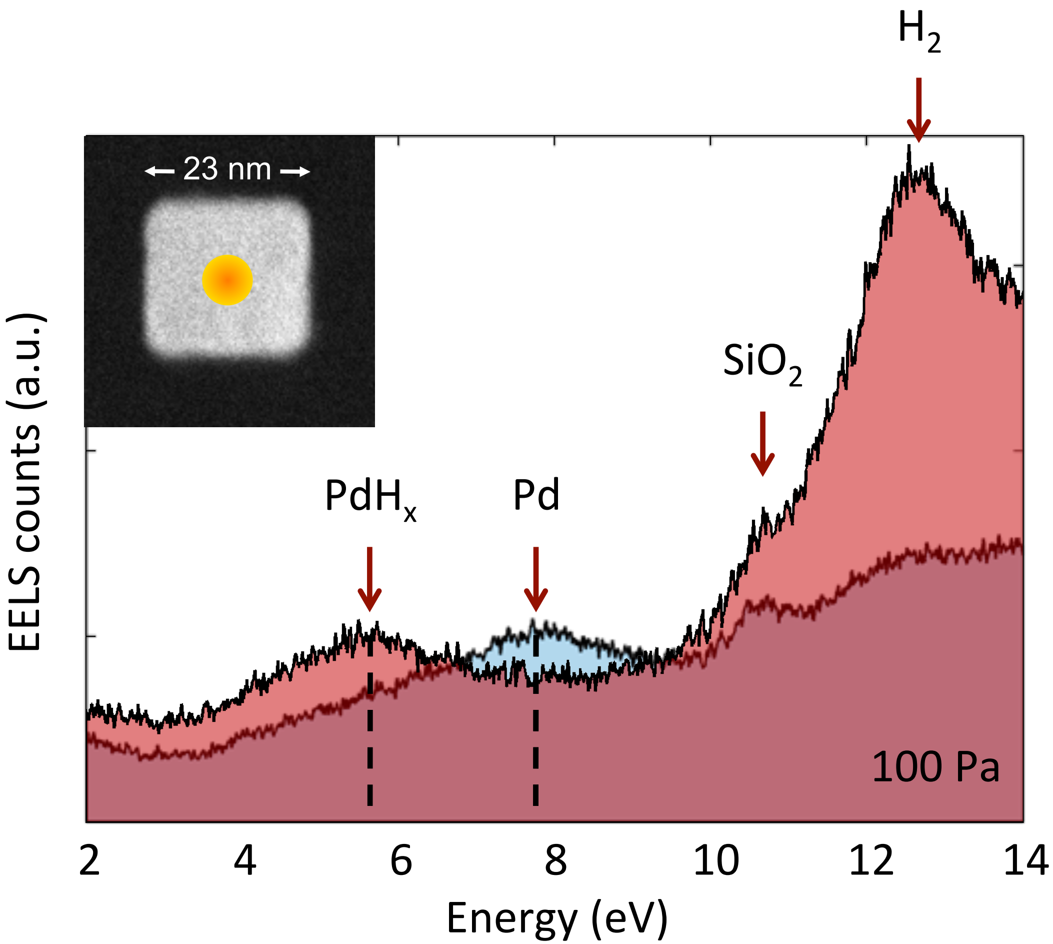
Baldi, Narayan, Koh and Dionne, Nature Materials (2014)

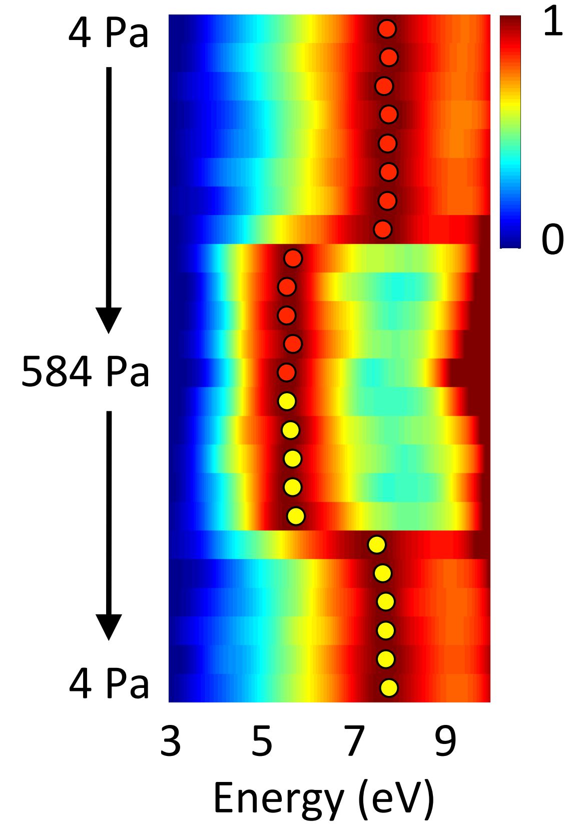
The bulk plasmon resonance of Pd red-shifts by 2 eV upon H absorption



Baldi, Narayan, Koh and Dionne, Nature Materials (2014)

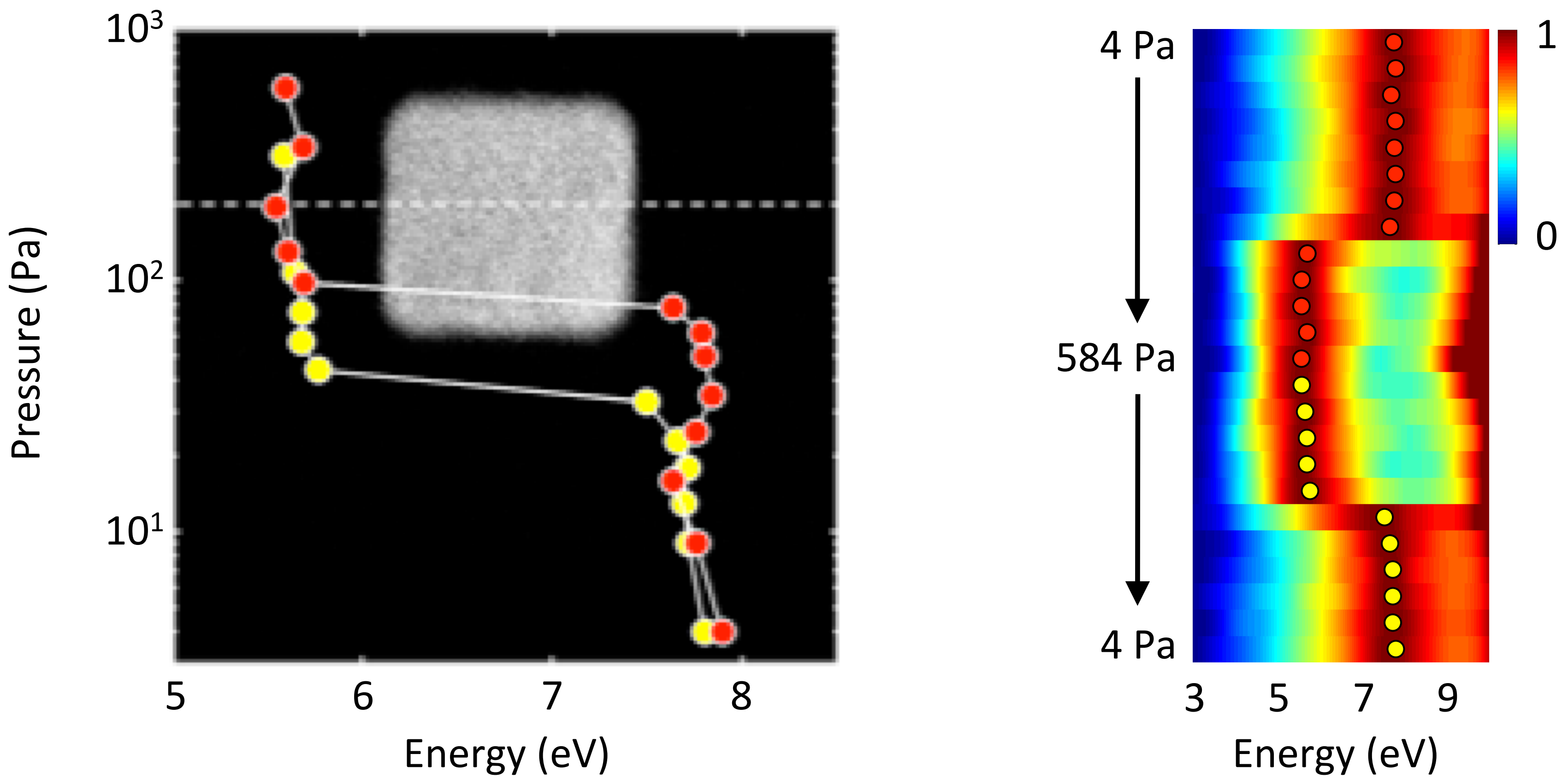
We construct single-crystal isotherms from the EELS peak energies at various H_2 pressures





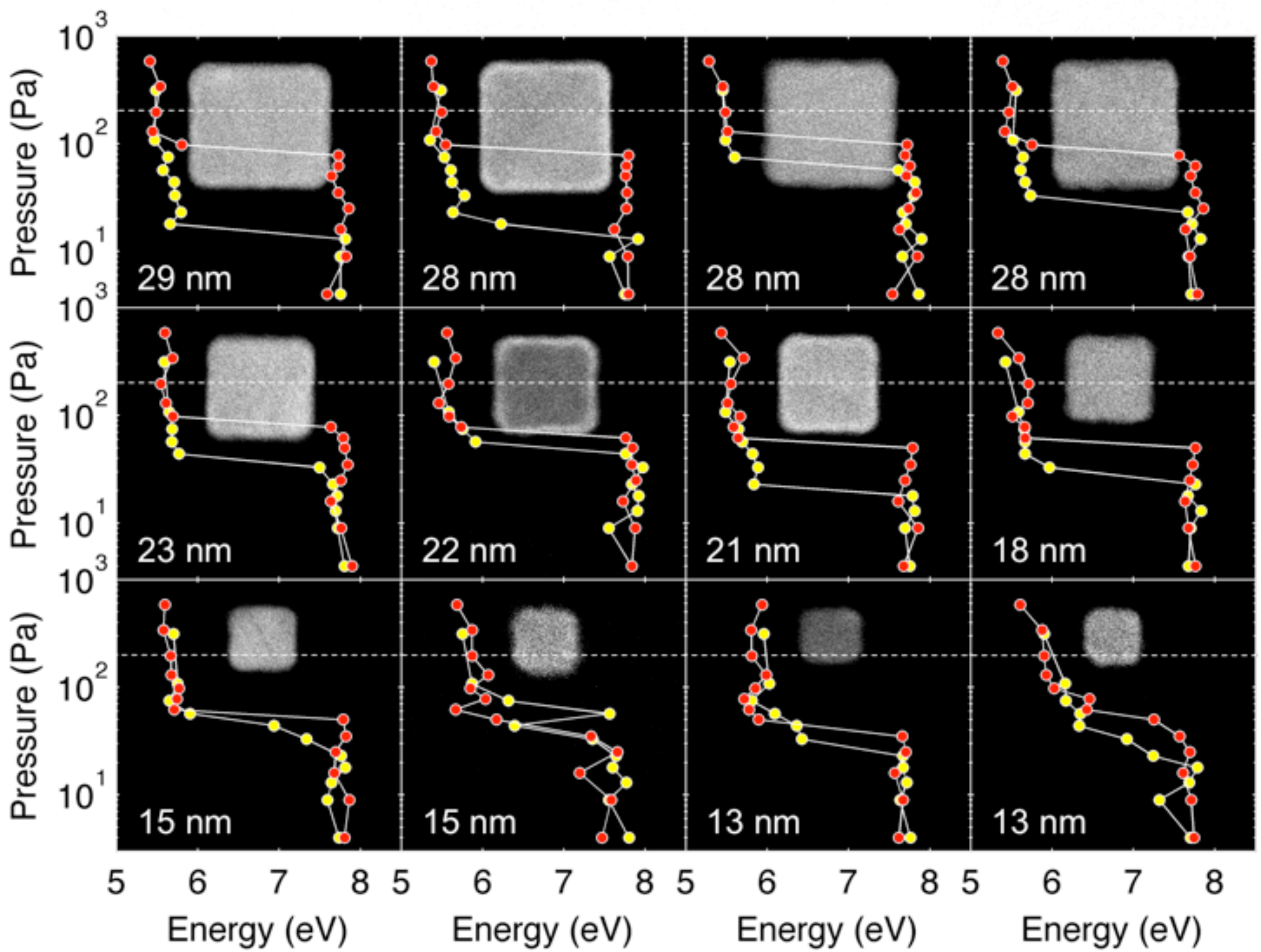
Baldi, Narayan, Koh and Dionne, Nature Materials (2014)

We construct single-crystal isotherms from the EELS peak energies at various H_2 pressures

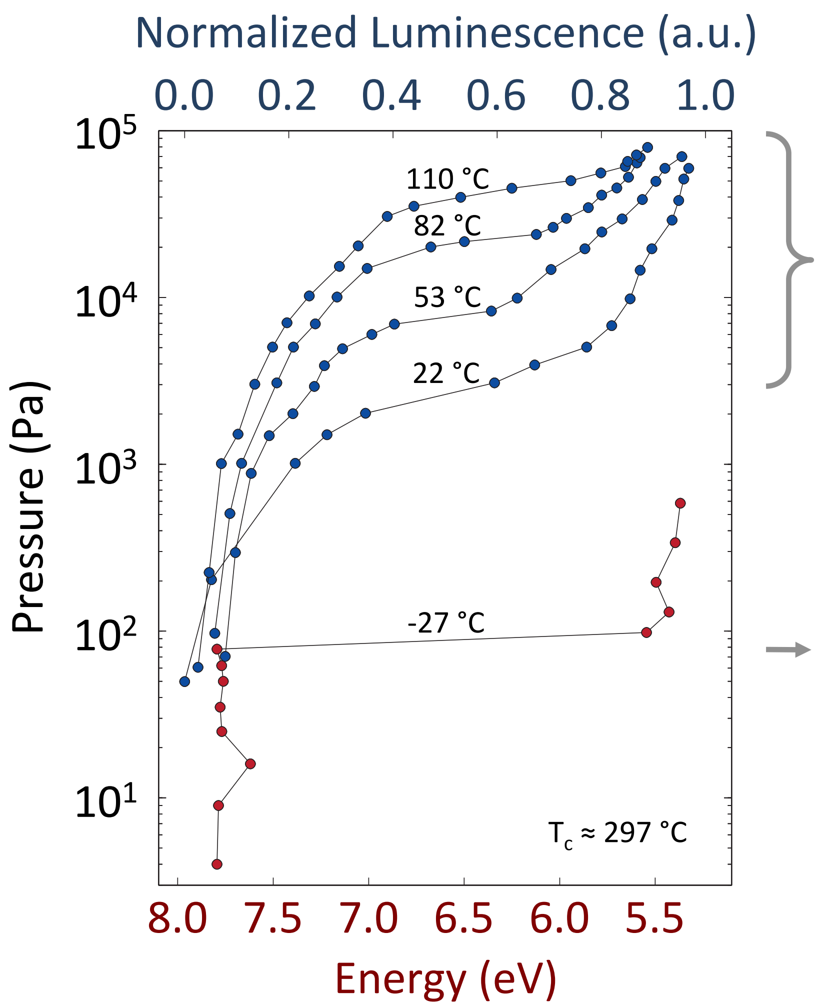


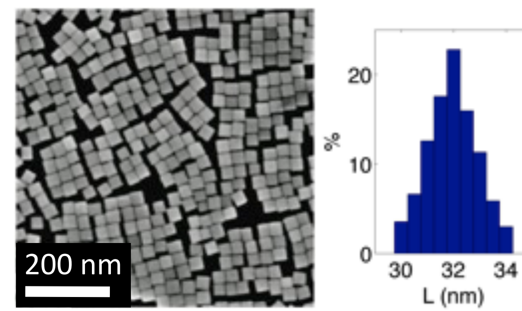
Baldi, Narayan, Koh and Dionne, Nature Materials (2014)

We construct single-crystal isotherms from the EELS peak energies at various H_2 pressures

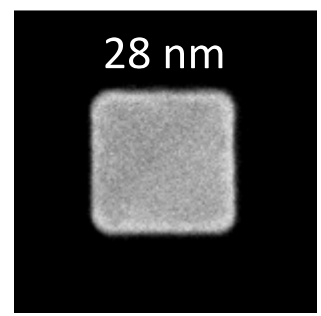


1st observation: isotherms of single-crystals are flat unlike suggested by ensemble measurements



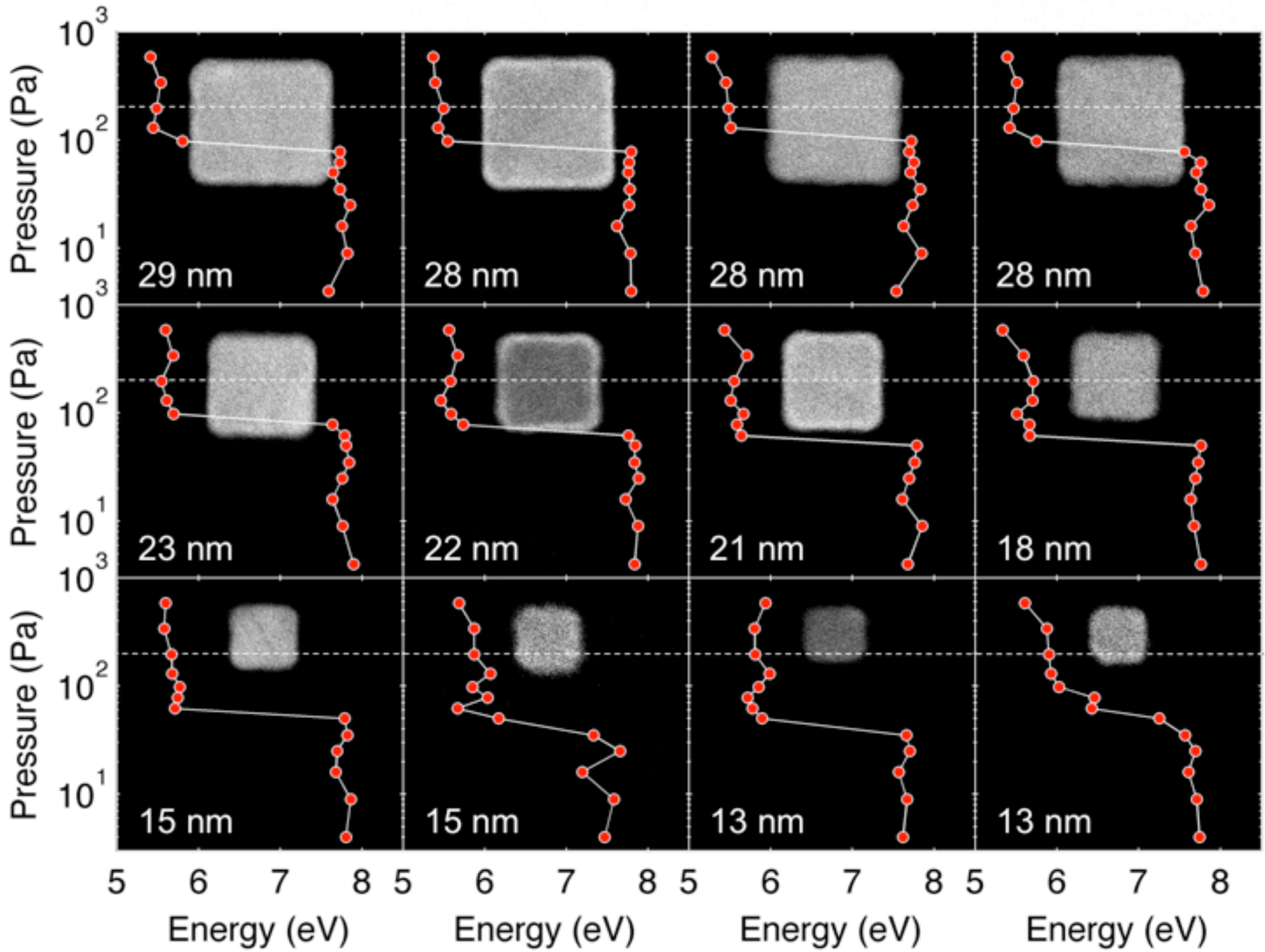


Bardhan et al., Nature Materials (2013)

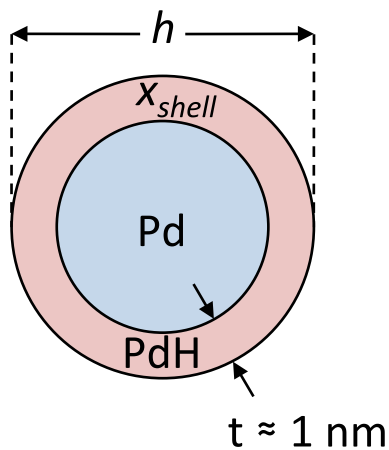


Baldi et al., Nature Materials (2014)

2^{nd} observation: smaller nanocubes absorb hydrogen at slightly lower H_2 pressures



2nd observation: smaller nanocubes absorb hydrogen at slightly lower H_2 pressures



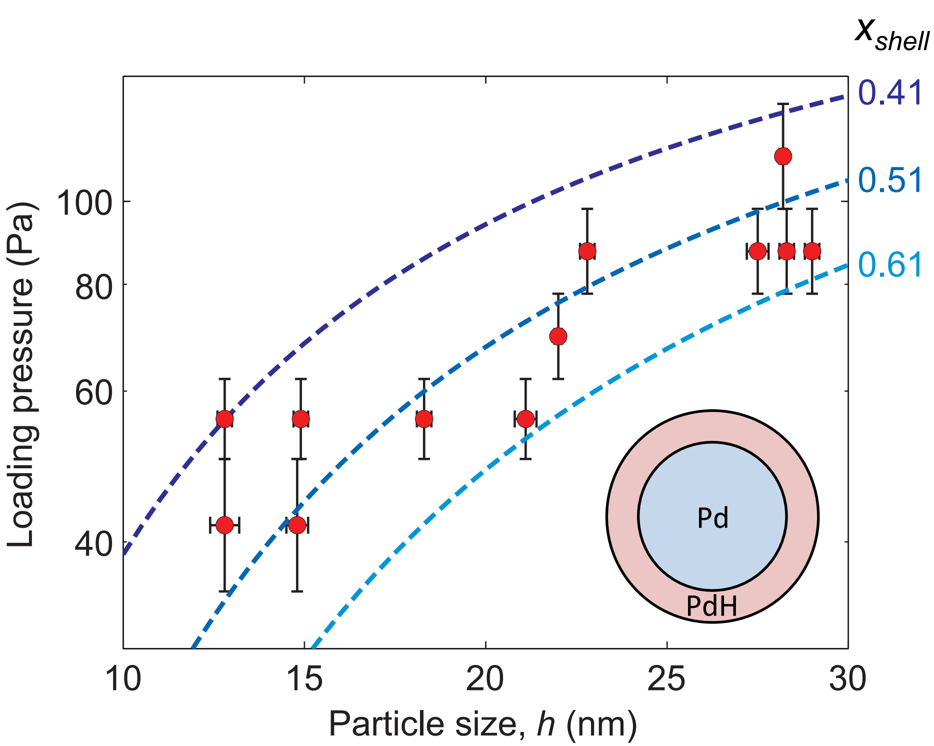
Surface stress induces a negative hydrostatic pressure on the core:

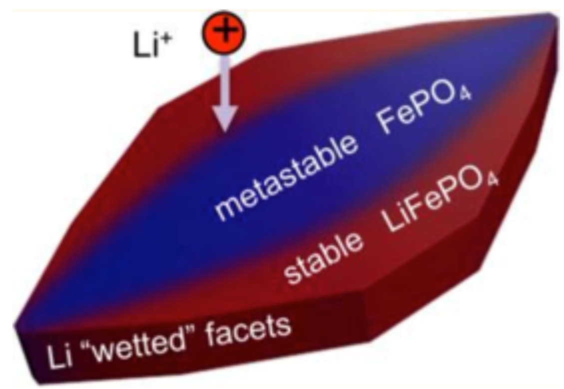
$$\mu_{H,elastic} \sim -3\varepsilon K \bar{V}_H$$

strain in the core — bulk modulus — partial molar volume of H

Mütschele, Scripta Metall. (1987); Weissmuller, PRL (1999); Sachs, PRB (2001)

2^{nd} observation: smaller nanocubes absorb hydrogen at slightly lower H_2 pressures



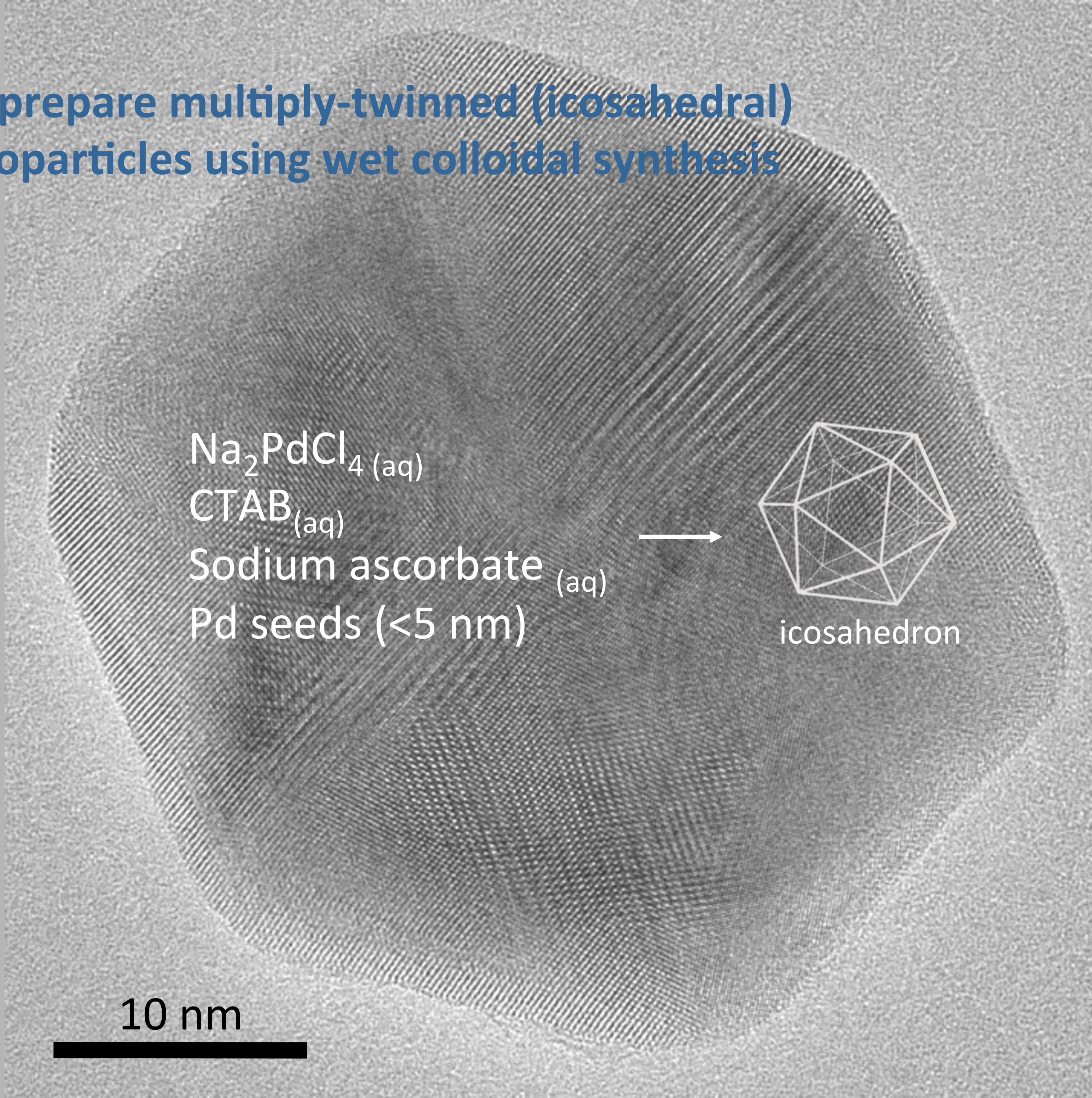


"nanoparticles tend to transform in order of increasing size."

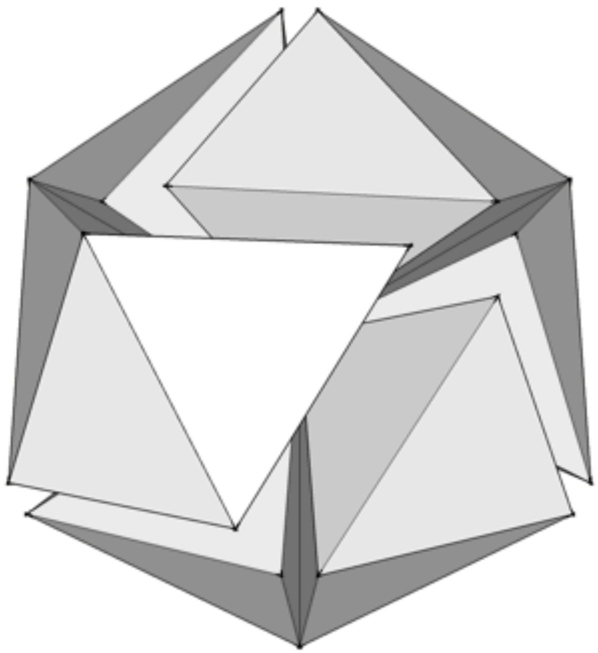
Baldi, Nature Materials (2014)

Cogswell, Nano Letters (2013)

We prepare multiply-twinned (icosahedral) nanoparticles using wet colloidal synthesis

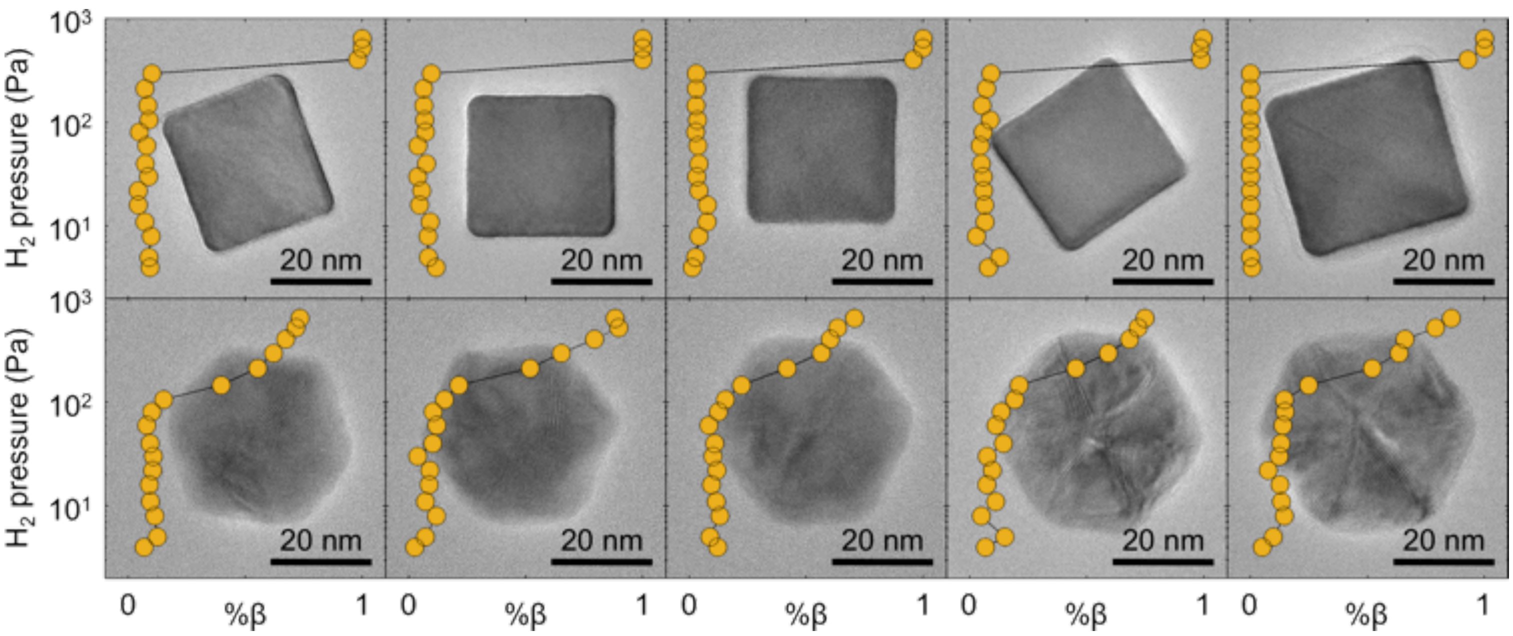


Icosahedral nanoparticles are made of 20 distorted tetrahedra



The misfit must be accommodated by strain and/or defects

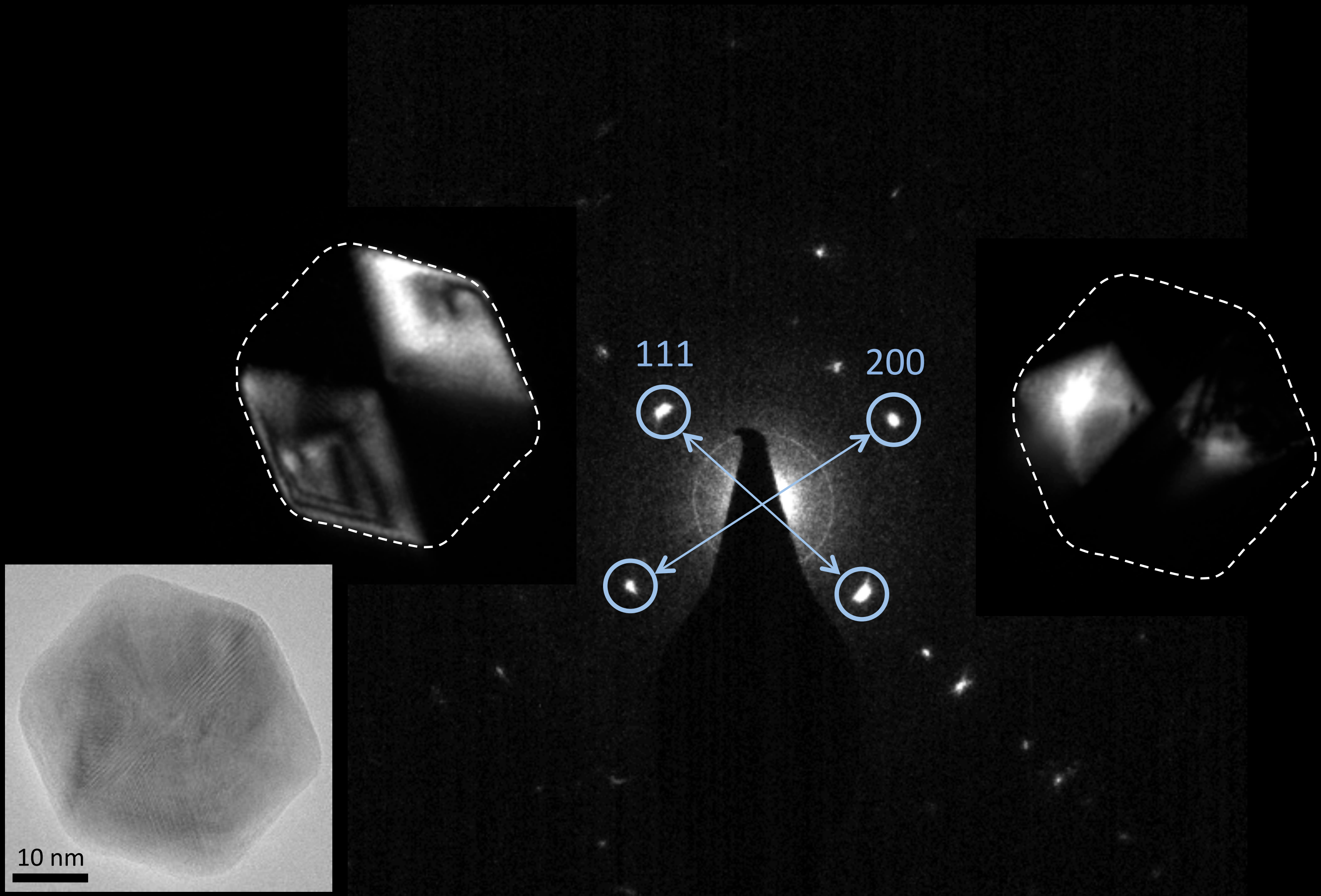
EELS loading isotherms of individual icosahedral nanoparticles show sloped isotherms



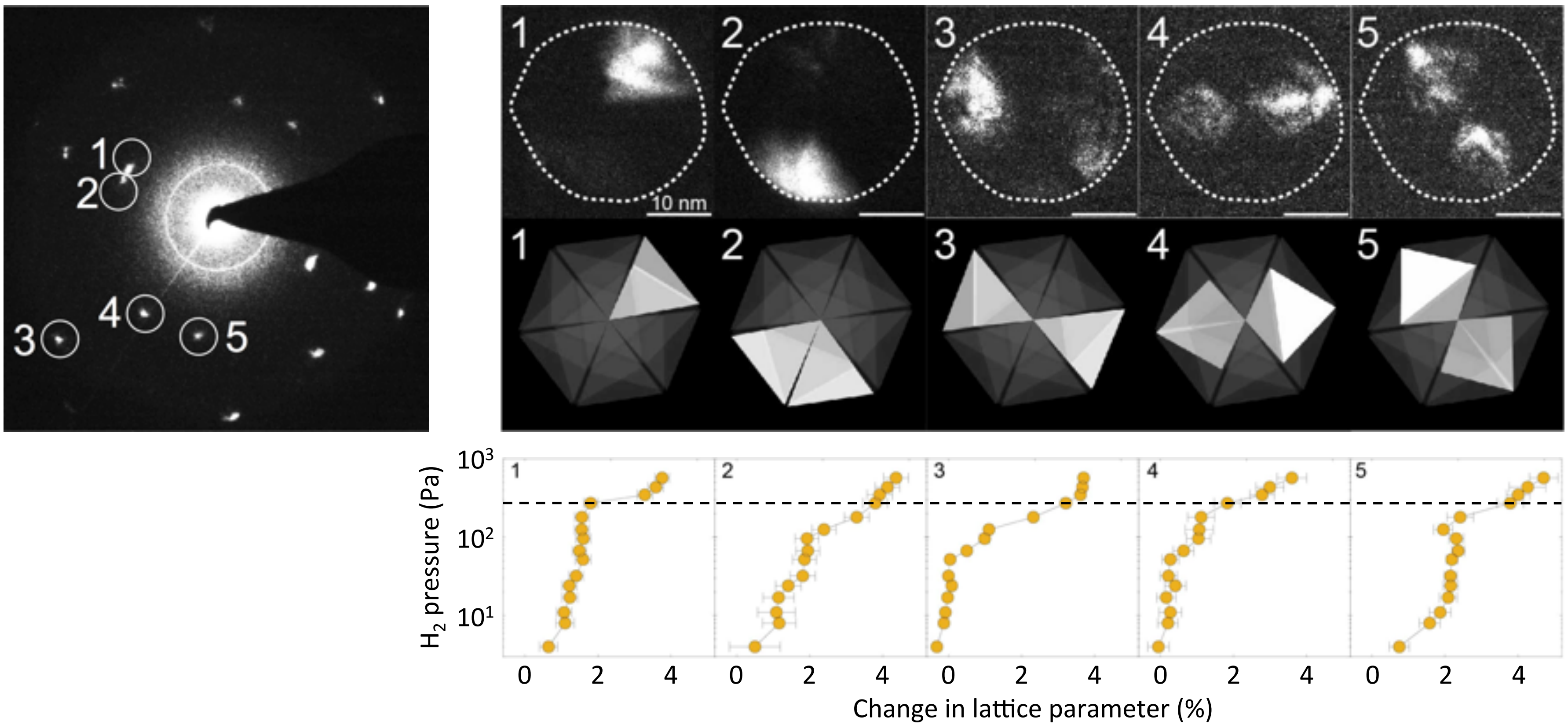
Why do they load gradually?

Narayan, Nature Materials (2016)

We can "look inside" a single nanoparticle by combining dark-field imaging + electron diffraction

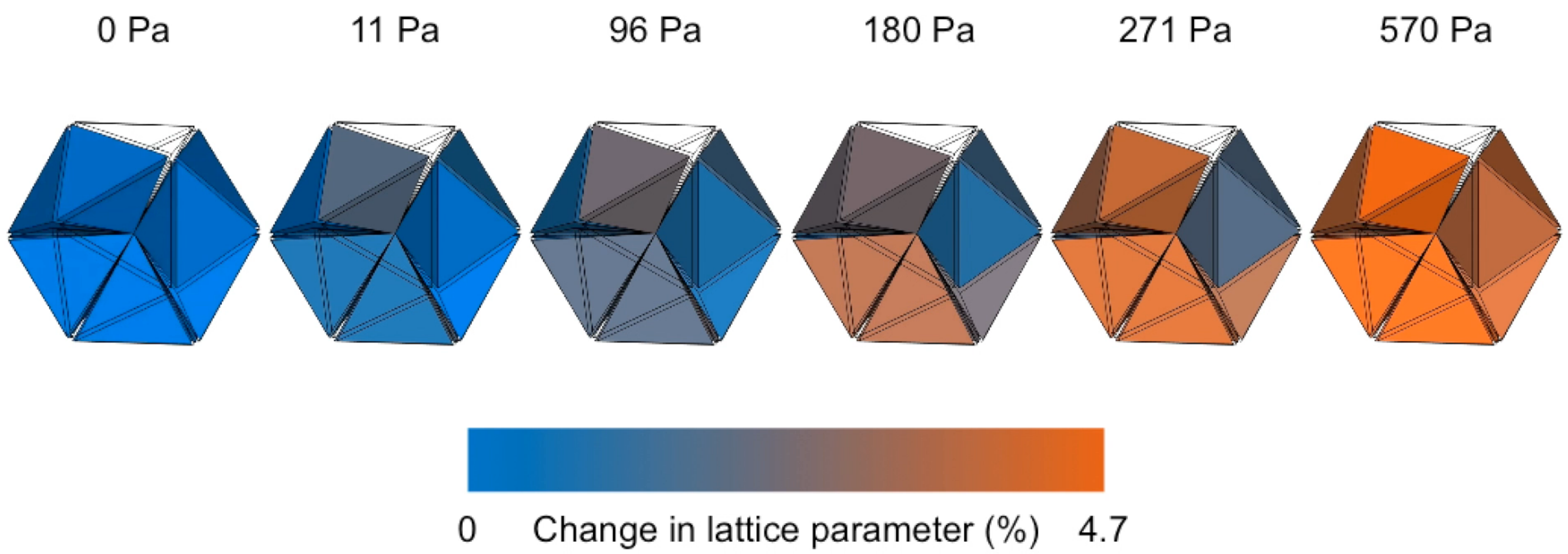


Using ED we can reconstruct the 3D hydrogen distribution *within* individual nanoparticles during hydrogen uptake



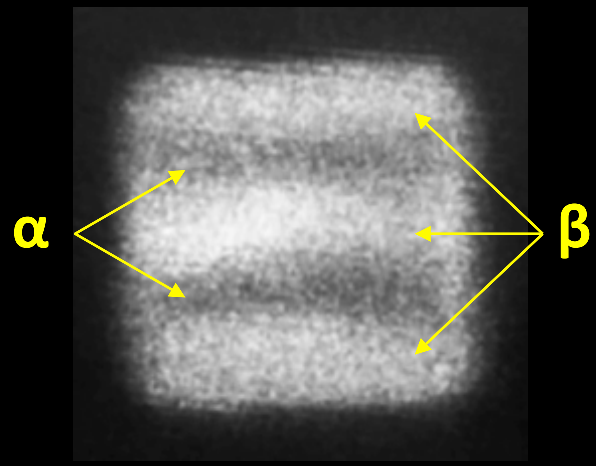
Narayan, Nature Materials (2016)

The sloped isotherms of icosahedral nanoparticles are due to the independent loading of the crystallites

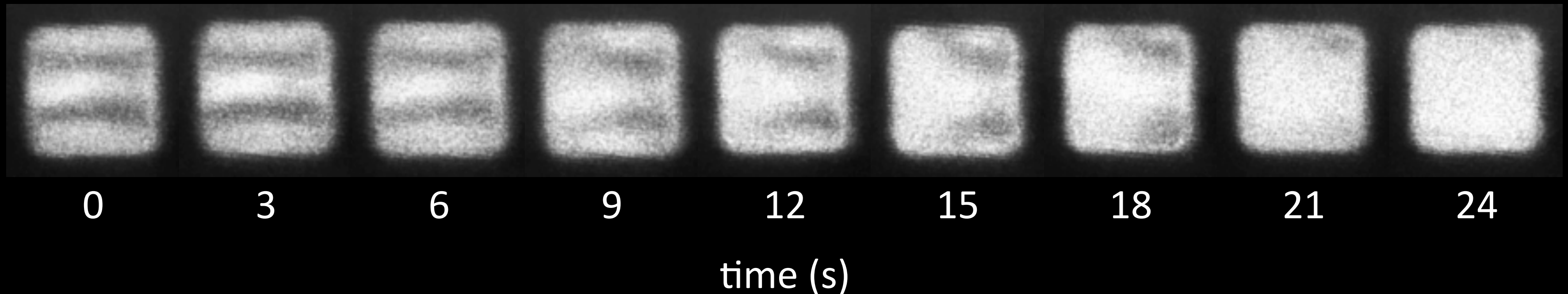


Narayan, Nature Materials (2016)

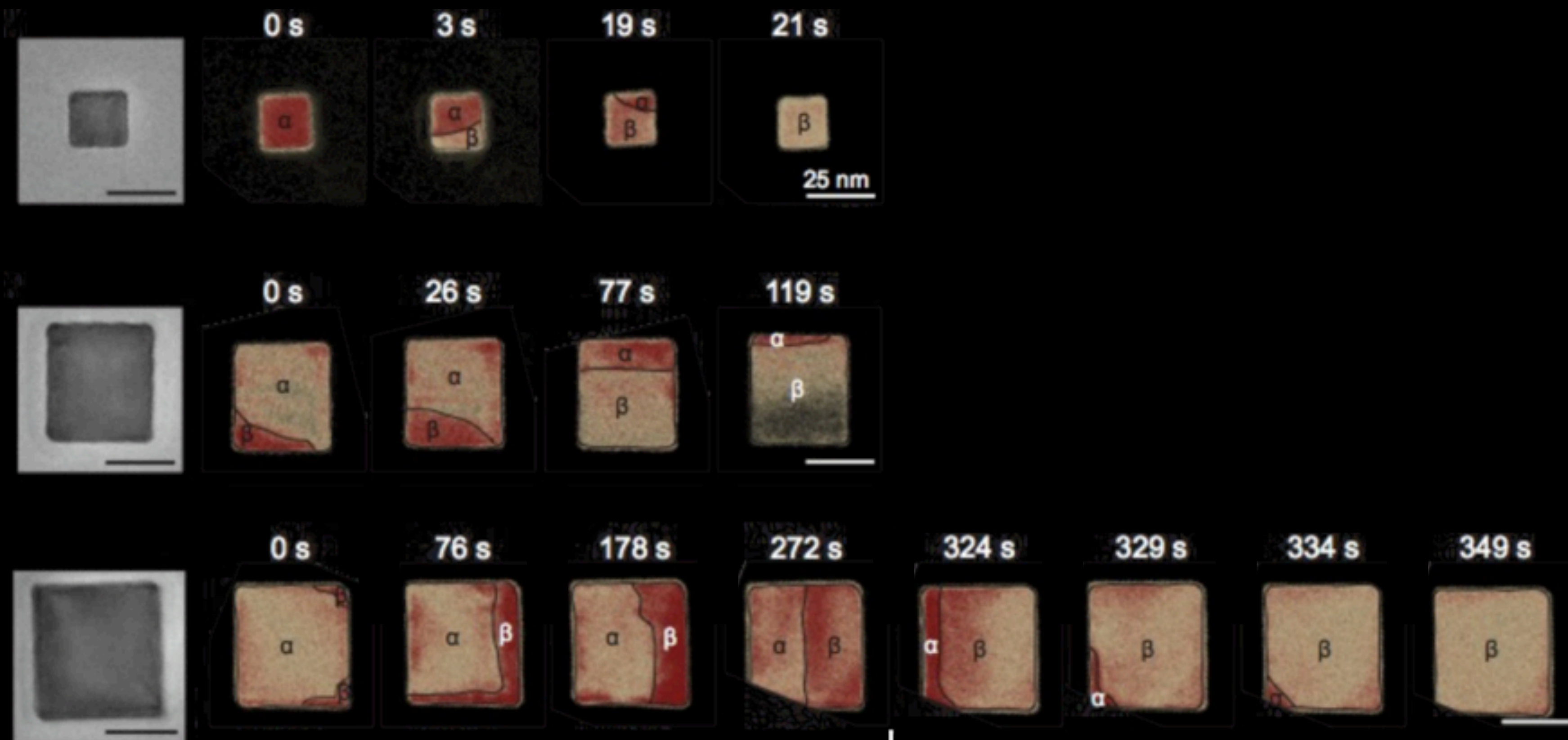
We can also monitor the dynamics of hydrogen absorption in real time with nm spatial resolution



STEM intensity contrast can be used to distinguish the α and β phases in real time with nm spatial resolution



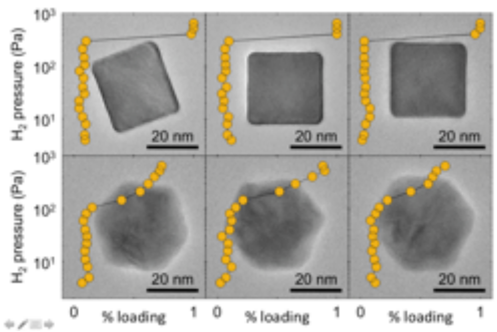
The hydrogenated phase nucleates at the cube corners and grows by minimizing elastic strain at the α/β interface



Narayan et al., Nature Communications (2017)

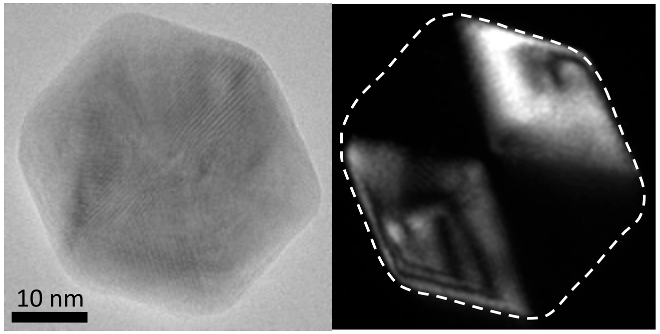
Summary

Single particle results differ from ensemble and highlight the role of surface stress



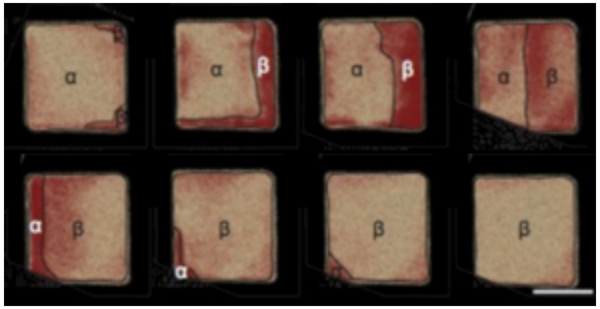
Baldi et al., Nature Materials (2014)

Elastic strain and defects dictate the phase distribution also within single nanocrystals



Narayan et al., Nature Materials (2016)

Nucleation and growth mechanism are influenced by the particle shape



Narayan et al., Nature Communications (2017)

Nanomaterials for energy applications: a single particle approach

Andrea Baldi
DIFFER - Dutch Institute For Fundamental Energy Research

Tarun Narayan, Fariah Hayee, Ai Leen Koh, Bob Sinclair, Jen Dionne
Stanford University

October 13th, 2017