Journal Club

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Single-nanoparticle phase transitions visualized by four-dimensional electron microscopy

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1. TEM observation

1.1. Fast imaging of a single particle

• Why fast imaging? (Figure 1)

–> Single/ multimolecular events take place within ms-order.

• Why single particle?

–> Bulk property (ensemble of ensemble) is not the same as single particle properties.

◊ Fast microscopic observation is required for analysis of single particle.

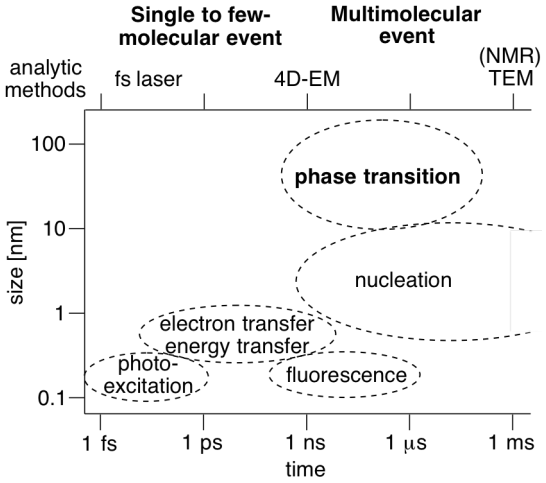

Figure 1. Size and timescale of chemical events.

1.2. Four-dimensional electron microscopy (4D-EM, Figure 2)[1]

• Transmission electron microscopy (TEM): Similar setup with optical microscopy using electron & magnetic lens instead of light & glass lens, respectively.

• Problems in TEM:

1) Slow shutter speed (~ 30 ms)

–> Low time resolution

2) Continuous irradiation of convergent e^- beam to single particle

–> Severe sample damage

◊ Avoiding these problems by 4D-EM (3D TEM + time)

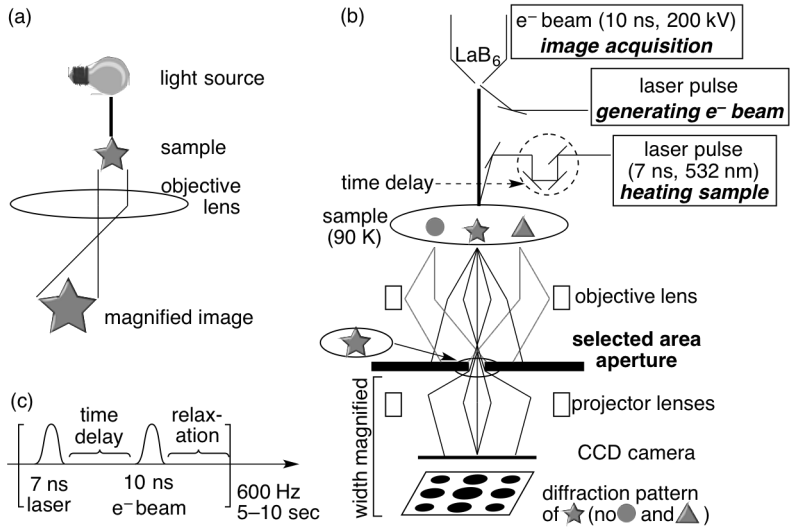

Figure 2. 4D-EM setup. (a) Setup of an optical microscopy, for comparison. (b) A schematic image of 4D-EM image acquisition of diffraction pattern. Real image can be acquired by changing the focal length of the projector lens. (c) Pulse sequence of electron beam and laser.

• Observation of chemical dynamics induced by laser irradiation
• Time resolution by changing the time delay between e^- beam & laser pulse (Figure 2c)

◊ Merits in 4D-EM

1) Fine-tunable time delay
   –> High time resolution (~ 1 ps) against heat-induced phenomena
2) Pulsed e^- beam irradiation to wide area
   –> Reducing sample damage

◊ Analyte: Fe(pyrazine)Pt(CN)$_4$ (Figure 3)

• Tetragonal spin-crossover (SC) complex with plate-like morphology (600 x 600 x 30 nm^3)[2]

–> (001) plane is parallel to the substrate.

• Heat-induced SC with size expansion

–> Visualization of phase transition (PT) by TEM image and diffraction pattern.

2. Phase transition of Fe(pyrazine)Pt(CN)$_4$

2.1. Single particle vs. bulk in equilibrium state (Figure 4)

• Single particle:

Reflection of the [001] crystal zone axis (planes perpendicular to (001) plane) –> single crystal

• Particle ensemble (crystal aggregate: bulk):

Spherical diffraction image –> polycrystal

• PT analysis by position of (110) diffraction (Figure 4c)

–> Shallow curve & small hysteresis in single particle

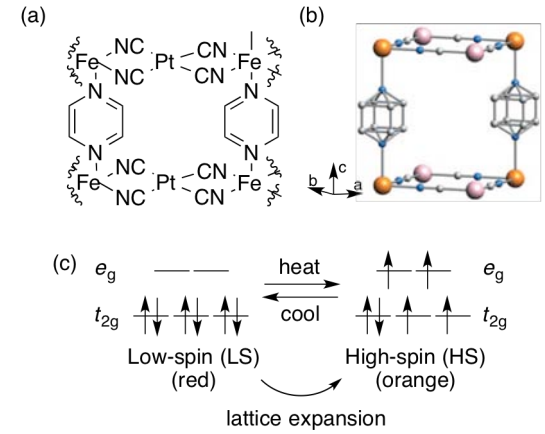

Figure 3. Structure of analyte, Fe(pyrazine)Pt(CN)$_4$. (a) Chemical structure. (b) Crystal structure. Pyrazine group is disordered. (c) Heat-induced spin-crossover.

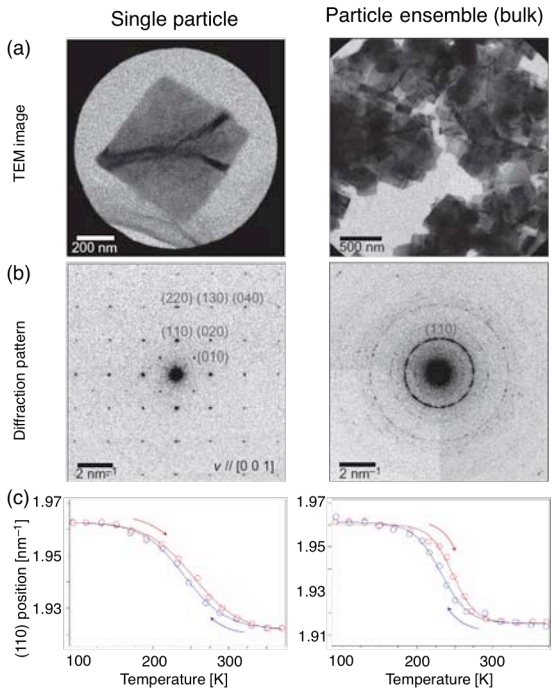

Figure 4. Observation of single particle and its ensemble. (a) TEM image of single particle with selected area aperture (left) and ca. 100 particle ensemble without aperture (right). (b) Diffraction image of (a). (c) Temperature dependence of position of (110) diffraction center. The position of diffraction pattern was determined by Gaussian fitting of the contrast.

2.2. Time-dependent phase transition (Figure 5)

• Laser irradiation
–> Heat jump of ca. 300 K
–> PT & size expansion (Figure 5b)
• Size expansion at < 15–50 ns
–> ca. 75% conversion to HS state
• Partial recovery of LS state within 150 ns & further recovery in ms order
• cf. particle ensemble (Figure 4 right)
–> Size expansion from 29 ± 3 ns & almost complete recovery of LS state within 980 ± 50 ns
–> Slow LS –> HS conversion & fast HS –> LS recovery
• Anisotropic expansion
–> Friction at the contact on substrate hinders parallel motion against substrate.

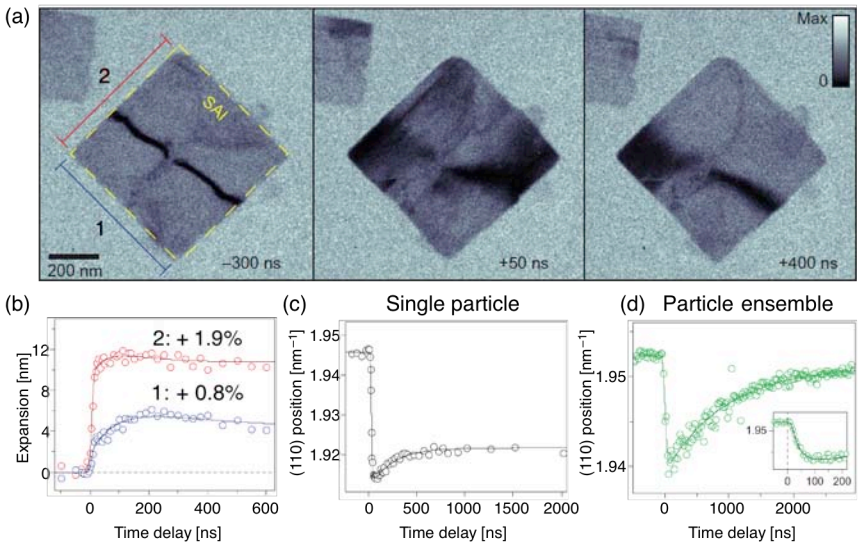

Figure 5. Time-dependent phase transition of single particle. (a) TEM image. (b) Time-dependent expansion of the crystal. (c) Diffraction dynamics of single nanoparticle. (d) Diffraction dynamics of particle ensemble (see Figure 4 right).

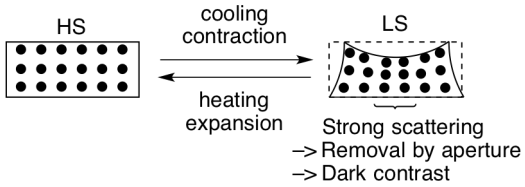

Figure 6. Dark contrast originating from lattice contraction.

◊ Origin of black contrast on crystals (Figure 6):
• Formation of concave surface during cooling the sample from rt
–> Good orientation for strong e^- diffraction.
–> Removal of strongly diffracted e^- by aperture
–> Dark contrast
• Anisotropic line formation
–> Substrate strain & structural anisotropy

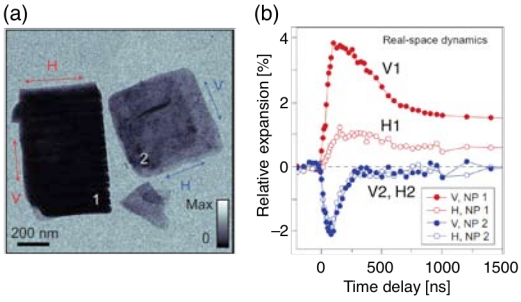

Figure 7. Time-dependent phase transition of crystals with different thickness. (a) TEM image of two particles. (b) Time-dependent relative expansion of crystal.

2.3. Particle-dependent structural change (Figure 7)

- Thick (ca. 100 nm) particle 1 –> Size increase (cf. Figure 5)
- Thin (ca. 10 nm) particle 2 –> Size decrease (appearance: ca. 10%): negative thermal effect [3]
- Laser-induced transverse vibration of CN ligand WITHOUT PT (Figure 8) –> Crystal shrinkage

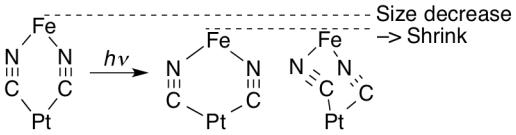

Figure 8. Negative thermal effect induced by laser light.

2.4. Summary of phase transition (Figure 9)

(1) 0 < t < ca. 15 ns:
"Incubation", heating the sample toward LS –> HS PT threshold

(2) 15 < t < 100 ns:
"Crystal growth" of HS state

(3) 100 < t < 200 ns:
Heat release to the substrate (90 K) & HS –> LS PT

(4) 200 ns < t & ca. 200 K < T:
Gradual decreasing in PT rate

(5) T = ca. 90 K :
ms-order HS –> LS (spin forbidden) PT

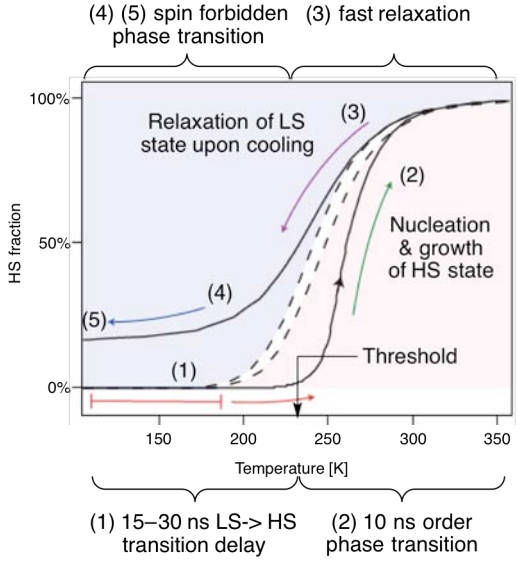

Figure 9. Phase transition behavior against temperature. (1), (2): Heating path by laser irradiation. (3)–(5): Cooling path by contact with substrate.

- Spin forbidden PT time > e^- pulse repetition time –> HS state accumulation at t = 0

–> Single pulse observation is further required.

3. Conclusion

- Difference between single particle & particle ensemble was visualized.
- Time-dependent phase transition was visualized in ns-order time resolution.
- Negative thermal effect was observed in 10% of the particles.

4. References

1. Zewail, A. H.; Thomas, J. M. *4D Electron Microscopy: Imaging in Space and Time,* Imperial College Press: London, 2010.
2. Ohba, M.; Yoneda, K.; Agustí, G.; Muñoz, M. C.; José, A. B.; Real, A.; Yamasaki, M.; Ando, H.; Nakao, Y.; Sakaki, S.; Kitagawa, S. *Angew. Chem. Int. Ed.* **2009**, *48*, 4767–4771.
3. Goodwin, A. L.; Kepert, C. J. *Phys. Rev. B* **2005**, *71*, 140301.