IMaSS
Institute of Materials and Systems for Sustainability

時間分解顕微法の開発とオペランド時空間解析への応用

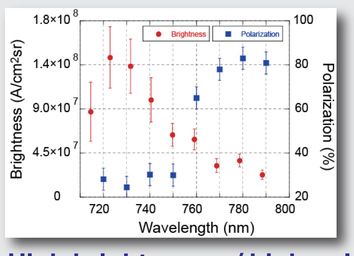
Development of time-resolve microscopy and its application to operando spatiotemporal analysis

桑原研究室, 桑原真人, 小川智史, 岩清水千咲, 唐龍樹, 石田裕一
Advanced Measurement Technology Center, Kuwahara Lab.

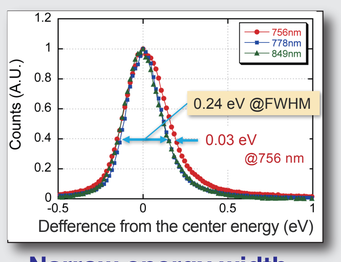
The temporal evolution of phenomena occurring in nanomaterials provides important information on phase transitions, optical coupling, and energy relaxation. Ultrafast measurements in electron microscopy using pulsed electron beams is a promising method for investigating high-speed phenomena on the nanoscale. Furthermore, the use of a high-brightness pulsed beam in transmission electron microscopy (TEM) is expected to enable one-shot electron imaging in projection mode, allowing observations of organic materials or biological specimens without electron-beam damage.

High-quality pulsed beam

A GaAs-type photocathode having a negative electron affinity surface (NEA-PC) was applied to the electron source to generate a picosecond pulse electron beam with high brightness.
We have developed a spin-polarized pulse-TEM (SPTEM) system, which comprises an NEA-PC as a polarized electron source and a 30-keV transmission electron microscope. Evaluation of this system showed that it was capable of producing a highquality electron beam with a high brightness, a high spinpolarization, a long coherence length, a picosecond response time and a narrow energy width.



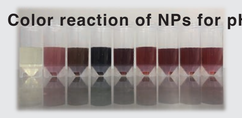
High brightness w/ high pol.

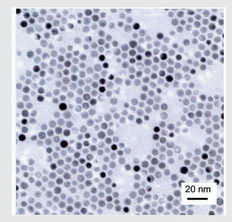


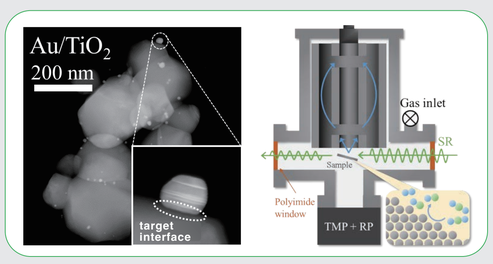
Narrow energy width

Nano particles, XAFS

We synthesized metal nano-particles (NPs) with solution plasma process (SPP) method which can realize arbitrary composition of metals without surface modifications.
Our group uses X-ray absorption fine structure (XAFS) analysis to clarify the chemical information of the NPs, which is similar to TEM-EELS but high precise analysis method. XAFS of NPs revealed atomic distances and the valence information.
Development of high-voltage CMA was started to analyse interface of NPs, which contributes to improve the photocatalytic reaction.

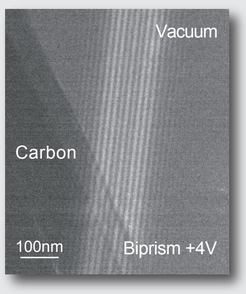




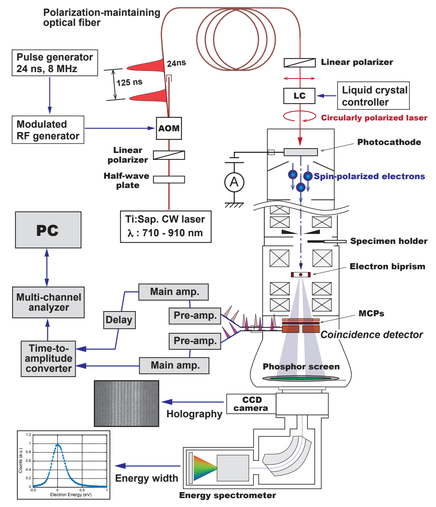


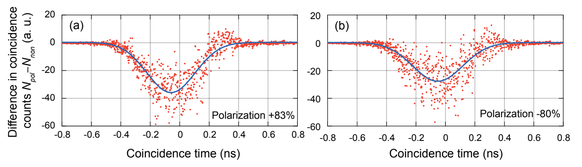
Coherence w/ spin polarized

The first-order interference was clearly observed in the SPTEM, which showed long coherence length was realized by the NEA-PC. The intensity interference between pairs of electrons, second-order intergerence, was investigated using a spin-polarized electron beam having a high polarization and a narrow energy width. Spin-dependent antibunching was observed, demonstrating that the antibunching was associated with fermionic statistics. The coherent spin-polarized electron beam facilitated the extraction of intrinsic quantum interference.



Coherent wave





$$g^{(2)}(\tau_c, P) - g^{(2)}(\tau_c, 0) \approx \frac{1}{2} P^2 \frac{\tau_c}{\tau_d} \exp\left\{-\frac{t^2}{2(\tau_c^2 + \tau_d^2)}\right\}$$

Spin-dependence in antibunching effect

parameter	Pol. +83%	Pol. -80%
Amplitude I_s	-37±2	-28±2
Width τ_s (ps)	165±7	171±9
$\lvert I_s/N_{non}\rvert$	$(3.4 \pm 0.2)\times10^{-4}$	$(2.6 \pm 0.2)\times10^{-4}$
$\frac{1}{2}P^2\tau_c/\tau_s$	$(2.3 \pm 0.9)\times10^{-4}$	$(2.0 \pm 0.7)\times10^{-4}$

M. Kuwahara et al., *Phys. Rev. Lett.* **126**, 125501 (2021).

Time-resolved measurement

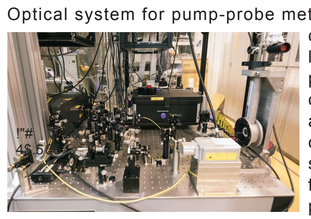
We have developed a time-resolved TEM (TRTEM) system by combining an NEA-PC with a 100-kV TEM instrument. Combination of the pulsed electron beam with electron energy-loss spectroscopy (EELS) in TRTEM realized a transient EELS (TEELS) technique with a temporal resolution of 8 ps and an energy resolution of 0.38 eV. Ultrafast phenomena in gold nanotriangles (AuNTs) stimulated by a pulsed laser beam were investigated using the TEELS technique. Coincidentally, an increment in the energy loss in the EEL spectrum is observed at approximately 0 s. The TEELS data showed two decay processes with a time constant of 7.8 ps and longer than 100 ps. The results indicate that excited electrons on the surface and in the bulk underwent the same relaxation processes during both electron-phonon and phonon-phonon interactions.

A semiconductor with an NEA surface is equipped in the photocathode-type e-gun. The extra-high vacuum and high acceleration field in the electron gun was realized simultaneously.

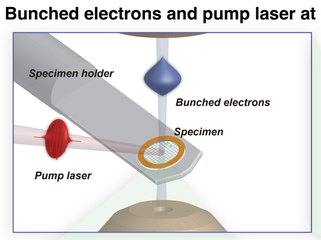
Stroboscopic measurement (cw ~ few ps)
- **Time-resolved TEM imaging**
- **Time-resolved EELS**
- **Ultrafast-Electron-Diffraction**
- **Time-resolved STEM imaging**

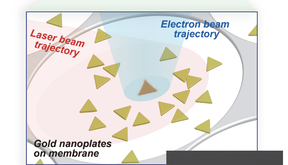
Single-shot measurement
- **Single-shot TEM imaging (> 500 ns)**
- **Single-shot UED (> 100 ns)**

Optical system for pump-probe method in TRTEM, which consists of a mode-locked Ti:Sapphire laser, pulse picker, power control system with EO, and a delay system.We can select the free space path or optical fiber path for driving the photocathode.



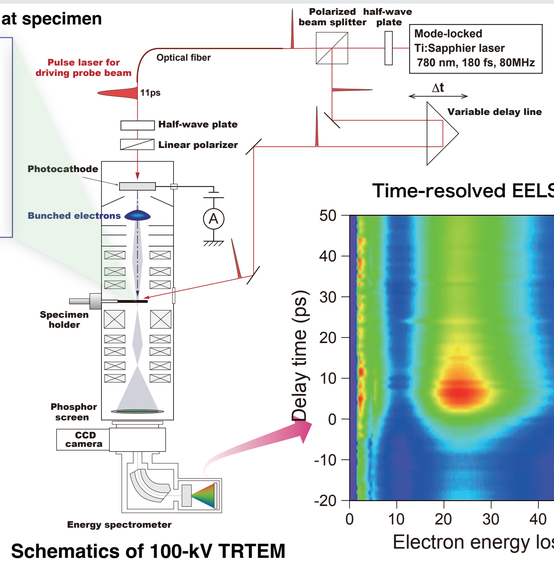
Bunched electrons and pump laser at specimen





NPs on membrane

ADF STEM image



Schematics of 100-kV TRTEM

M. Kuwahara et al., *Appl. Phys. Lett.* **121**, 143503 (2022).

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