第9回UVSORワークショップ「固体の低エネルギー光電子分光とナノサイエンスの可能性を探る」　March 5-6, 2002　分子研

金属低次元ナノ構造体の光電子分光

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→ フェムト秒時間分解2光子光電子分光

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Outline

- Angle-resolved photoemission study of 2D metallic nanofilms using combined system of MBE-photoelectron spectrometer (Review)
- New target : Surface-passivated nanoparticle
- Photoemission study of dodecanethiolate-passivated Ag nanoparticles
- Femtosecond time-resolved two-photon photoemission study of dodecanethiolate-passivated Ag nanoparticles
- Summary

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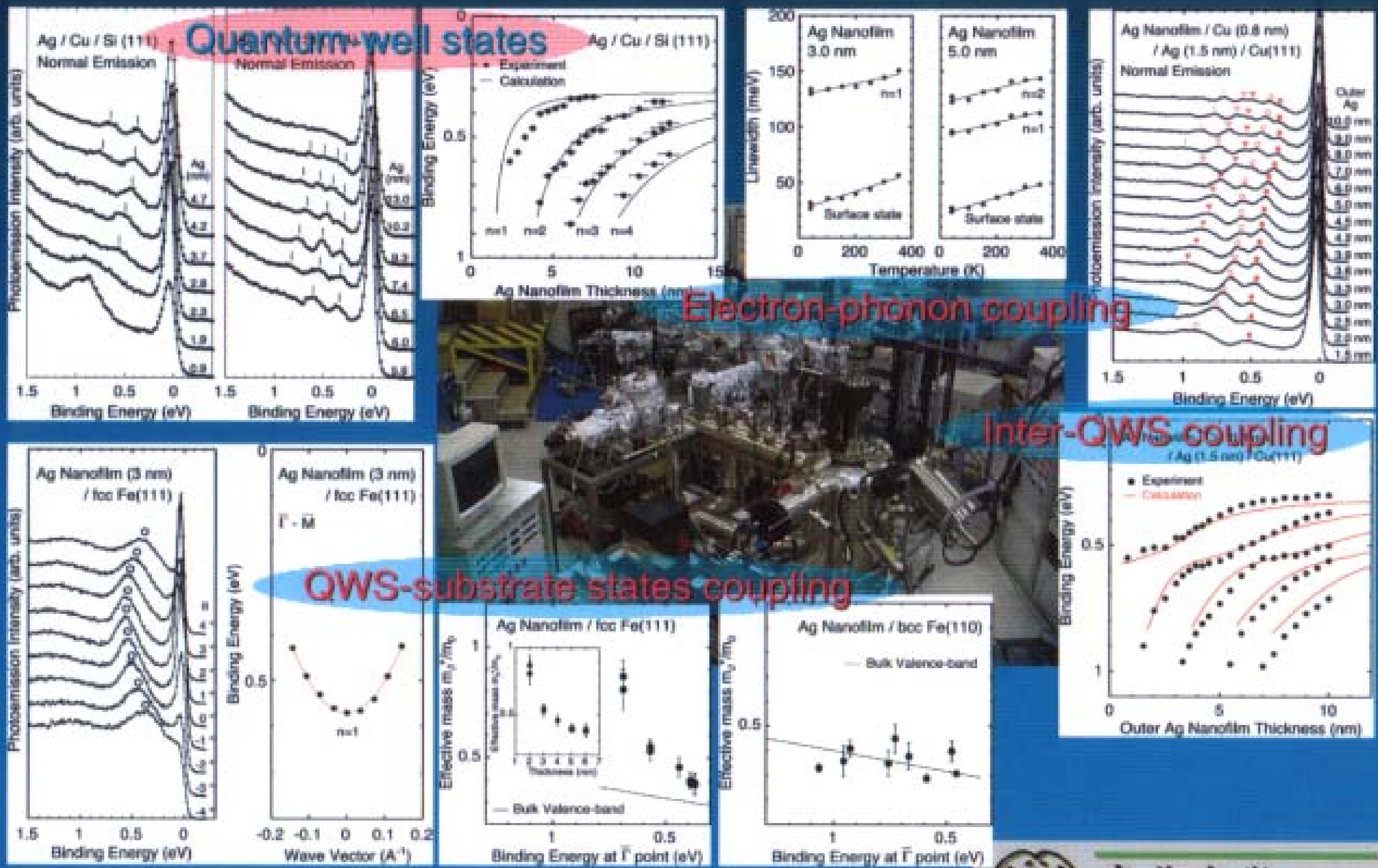
ARPES study of 2D metallic nanofilms using combined system of MBE-photoelectron spectrometer



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New target : Surface-passivated nanoparticle

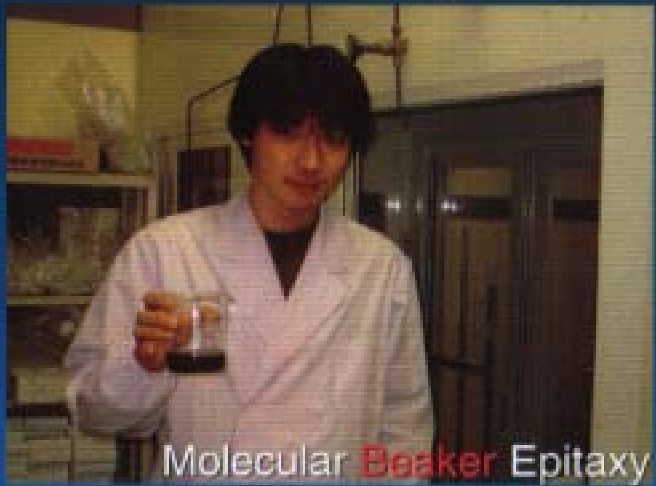
Molecular Beaker Epitaxy vs Molecular Beam Epitaxy

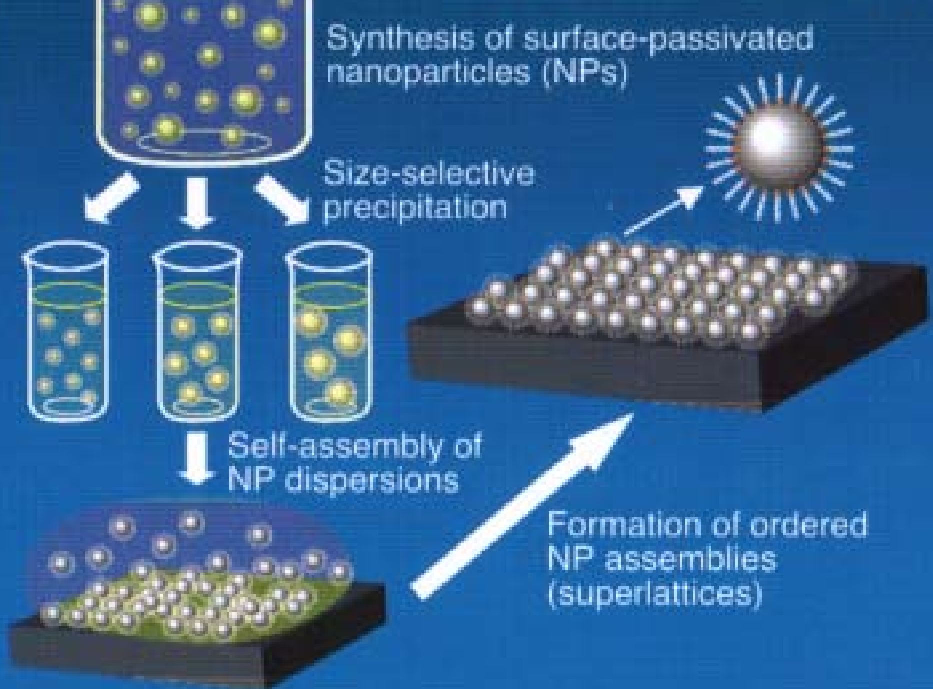
ビーカー中で、 還元 : $M^{+} + e^{-} \rightarrow M$

凝集 : $n\,M \rightarrow (M)_n$

表面修飾安定化 :

$(M)_n + m\,P \rightarrow (M)_n\,(P)_m$





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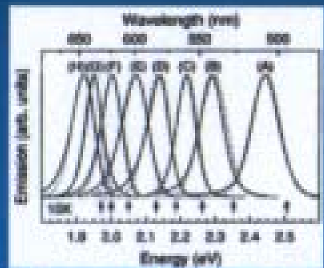
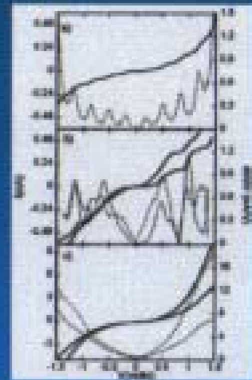
Surface-passivated nanoparticle

- 単分散（サイズ、形状）　■ 安定、凝集しない　■ 大量合成
- 自己組織化によるナノ粒子配列（超格子）構造
- 表面修飾基に依存したナノ粒子配列構造の制御可能
- ナノエレクトロニクスデバイスの基本素子

Co NP



CdSe NP



Ag NP

S. Sun *et al.*, J. Appl. Phys. **85**, 4325 (1999).　D. J. Norris *et al.*, PRB **53**, 16347 (1996).　G. Medeiros-Ribeiro *et al.*, PRB **59**, 1633 (1999).

Self-assembled superlattice　　Full luminescence　　Coulomb blockade

磁気記憶デバイス　　発光、蛍光体デバイス　　単電子デバイス

光電子分光

電子構造、化学状態、ナノ粒子間及びナノ粒子-基板相互作用、励起電子ダイナミクス

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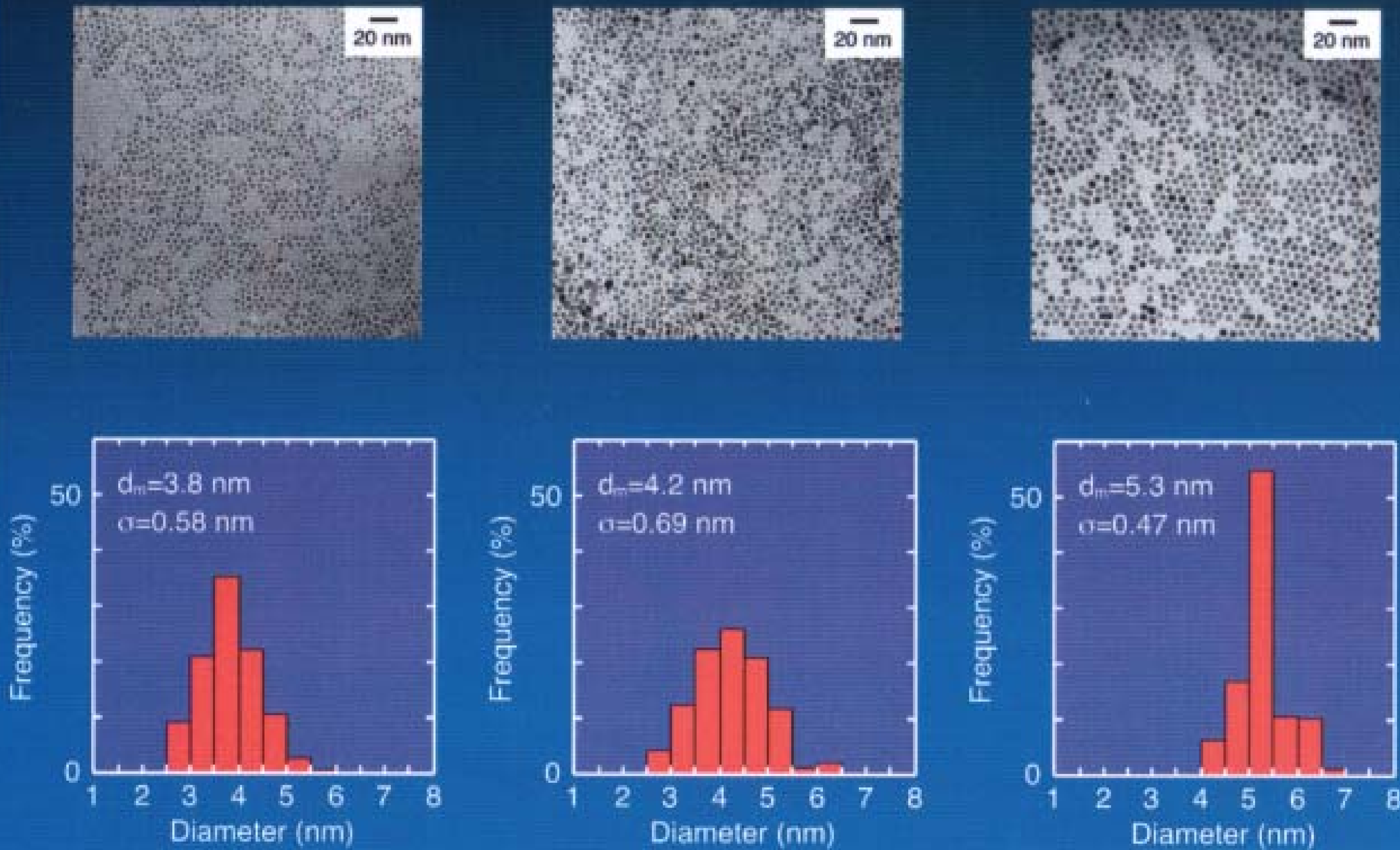
Dodecanethiolate(DT)-passivated Ag nanoparticles



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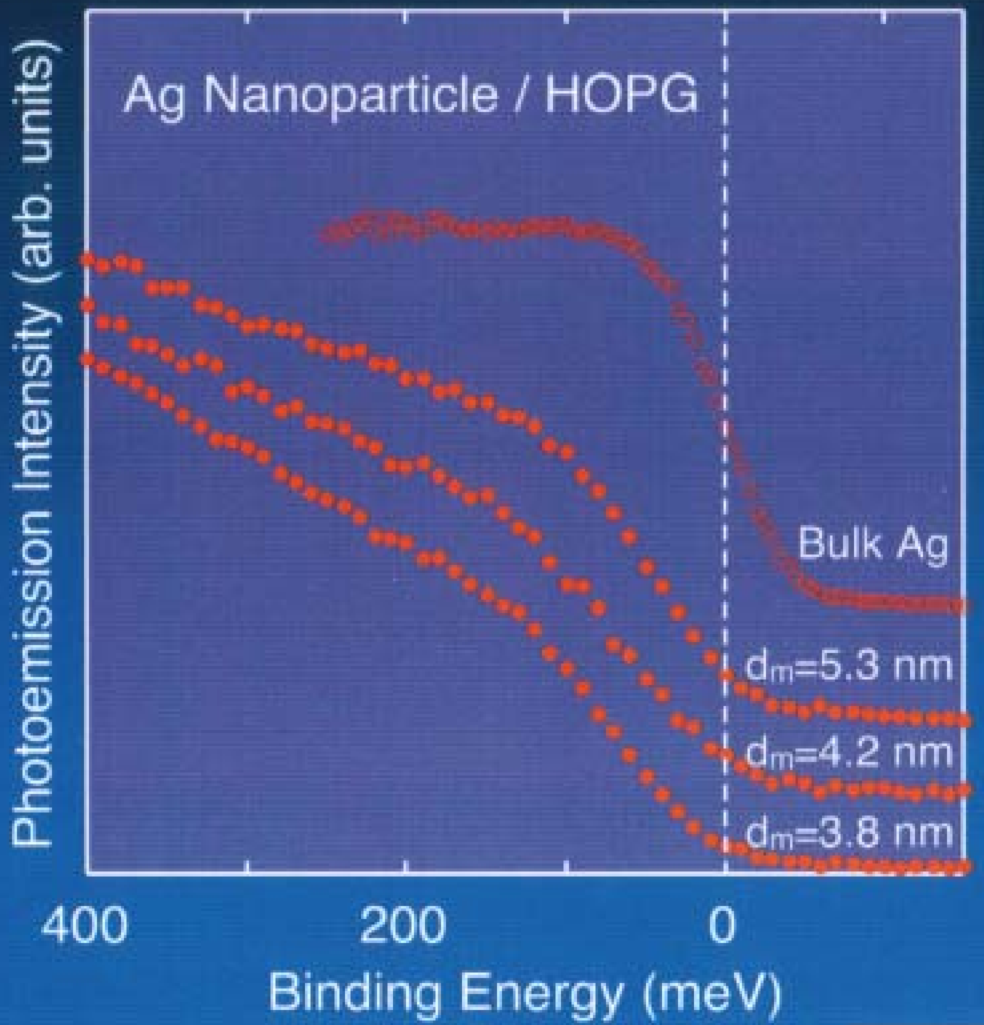
Photoemission spectra in the vicinity of Fermi level of DT-passivated Ag nanoparticle on HOPG substrates



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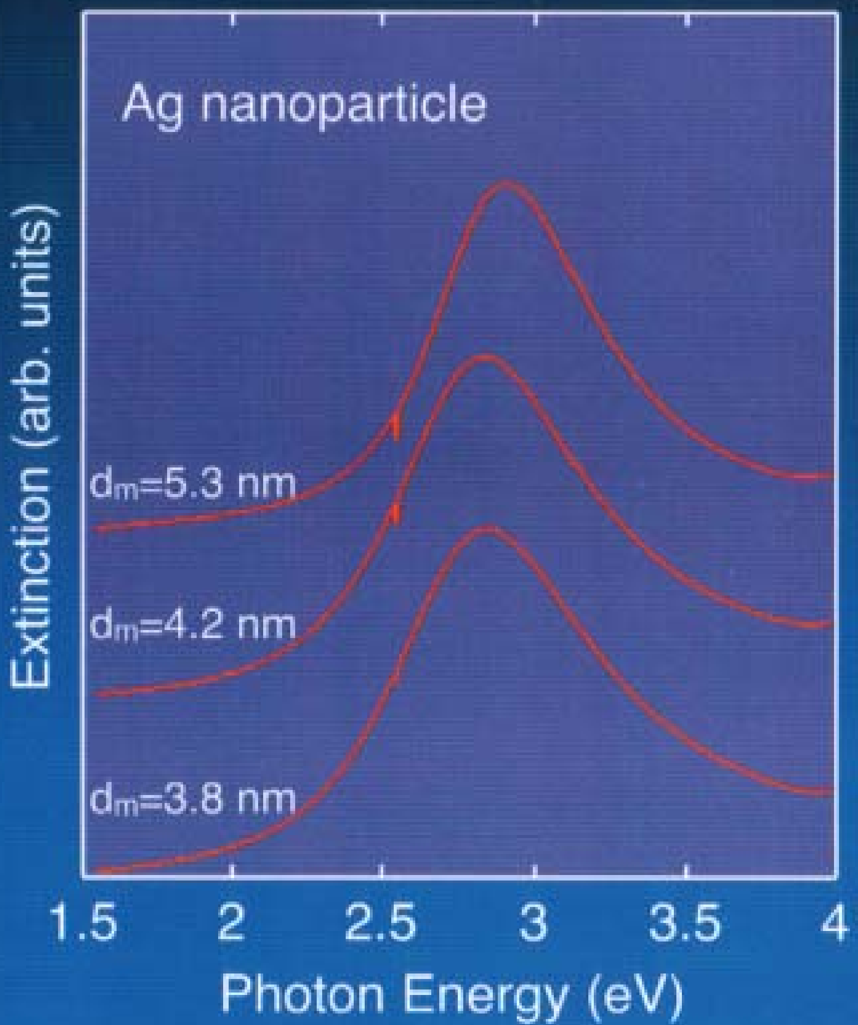
Optical absorption spectra of DT-passivated Ag nanoparticles



Distinct plasmon resonance

↓

Collective motion of *s*-electron typical for a metal

⇓

Initial-state effect = ×

Model for a dynamic final-state effect

After H. Hovel *et al.*, Phys. Rev. Lett. **81**, 4608 (1998).

Positive charge (photohole) remaining in the nanoparticle during the photoemission process → Reducing energy-shift of photoelectron

- For a free nanoparticle (cluster) in vacuum,

  Energy shift $\Delta E \sim$ Difference between the ionization potential of the nanoparticle and work function of bulk materials

  $\Delta E = \alpha e^2 / 4\pi\varepsilon_0 R$ with $\alpha = 0.41$ for Ag

- For a nanoparticle on the substrate,

  Elimination of photohole is described by characteristic time τ.

  Probability that the charge eliminated during $[t, t + dt]$

  $$P(t)dt = (1/\tau)\exp(-t/\tau)dt$$

  Potential acting the electron on its way from nanoparticle to ∞

  $$W(r) = \frac{\alpha e^2}{4\pi\varepsilon_0}\left(\frac{1}{R} - \frac{1}{r}\right)$$

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Model for a dynamic final-state effect (cont'd)

After H. Hovel *et al.*, Phys. Rev. Lett. **81**, 4608 (1998).

Charge in the nanoparticle is neutralized after time t →

Energy shift of the electron = $W(R+vt)$

Measured spectra average over a large number of photoelectrons with different time t

→ Distribution of energy shifts

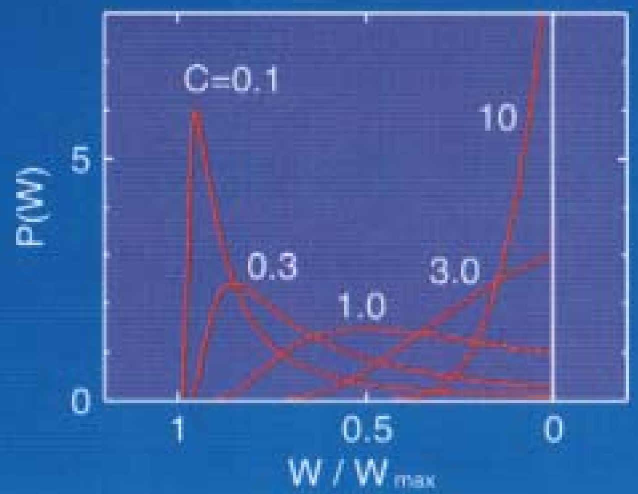
$$P(W)\,\mathrm{d}W = P(t(W))\,(dt/dW)\,dW$$

with $W \in [0, W_{max}]$ and $W_{max}=\Delta E$

$$= \frac{CW_{max}}{(W_{max}-W)^2}\exp\left(-\frac{CW}{W_{max}-W}\right)dW$$

with $C=(R/v\tau)$

v : Photoelectron velocity



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Application of dynamic final-state effect model to Fermi-level onset observed for nanoparticles

Fermi-level onset in the photoemission spectrum at low-temperature

(Thermal broadening ≈ 0)

$$S(E_B) = \int_0^{W_{\max}} P(W)\Theta(E_B - W)dW$$

$$S(E_B) = \begin{cases} 1 - \exp\left(-\dfrac{CE_B}{W_{\max} - E_B}\right) & \text{for } E_B < W_{\max} \\ 1 & \text{for } E_B \geq W_{\max} \end{cases}$$

Experimental photoemission spectrum

$$I(E_B) \propto [S(E_B, R) \otimes D(R)] \otimes G(E_B) + B(E_B)$$

$D(R)$: Size distribution : Gaussian determined by TEM observation

$G(E_B)$: Instrumental Gaussian function

$B(E_B)$: Background

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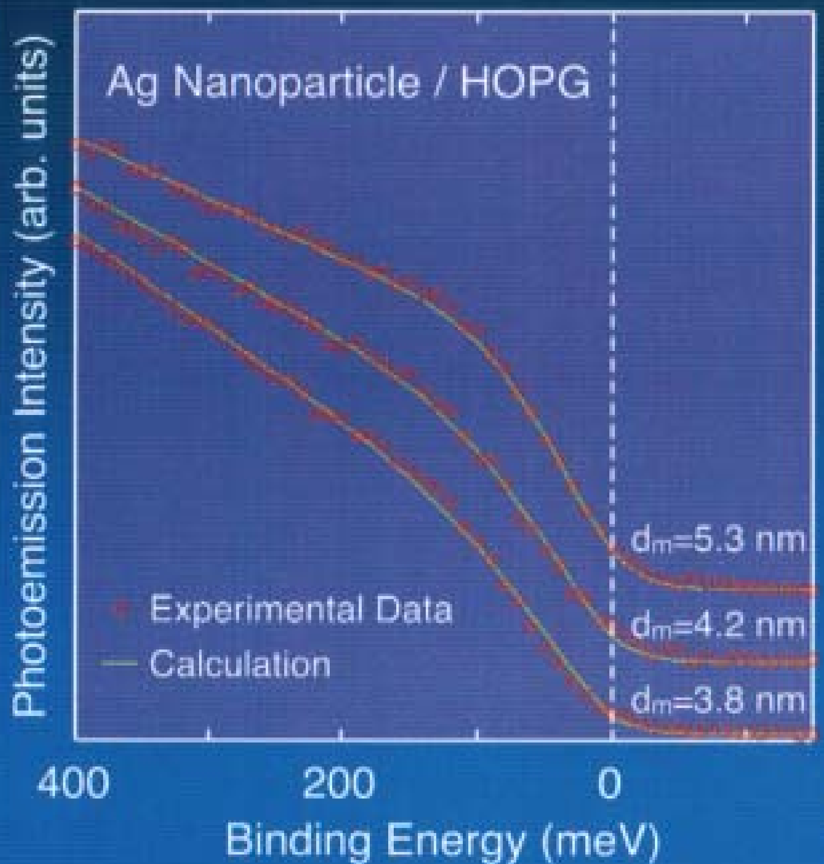
Comparison of experimental results with calculations



d_m	(W_{max})	C
5.3 nm	(0.22 eV)	4.4
4.2 nm	(0.28 eV)	4.5
3.8 nm	(0.30 eV)	4.2

d_m	τ
5.3 nm	0.25×10^{-15} sec
4.2 nm	0.19×10^{-15} sec
3.8 nm	0.19×10^{-15} sec

Nanoparticle-substrate interaction through the surface-passivants on a femtosecond time scale

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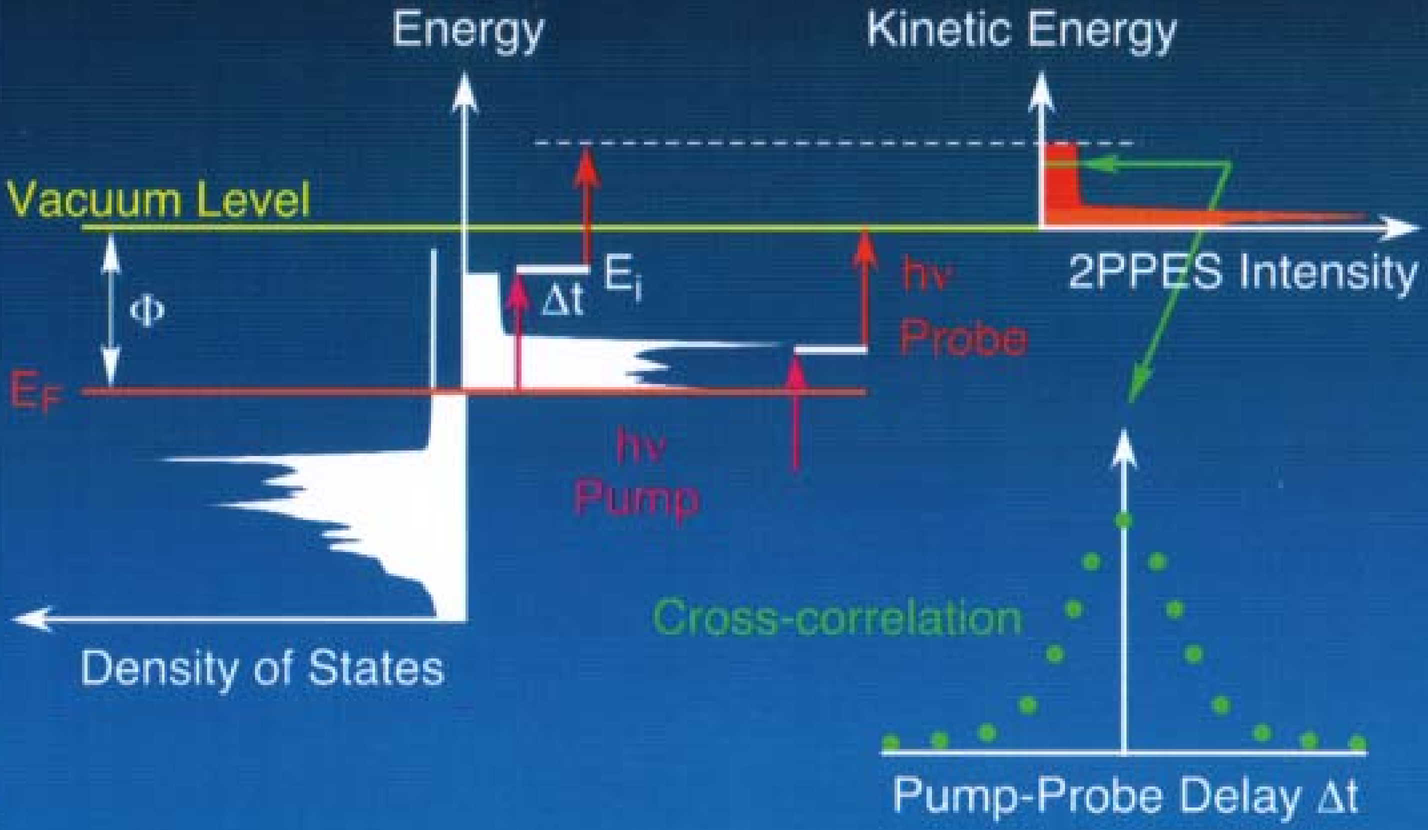
Time-resolved two-photon photoemission spectroscopy (TR-2PPES)



Temporal evolution of hot-electron population

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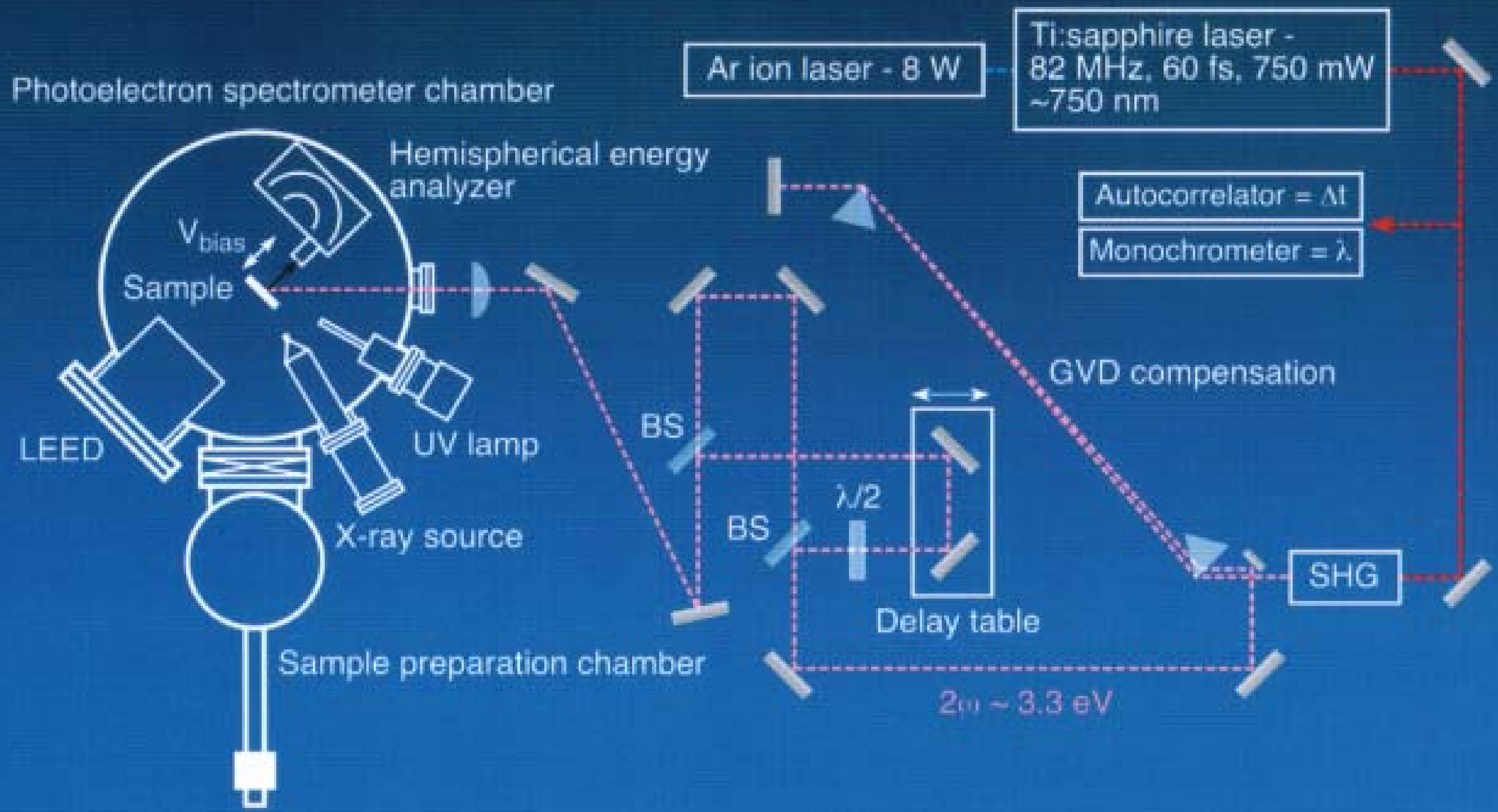
Experimental set-up for femtosecond TR-2PPES



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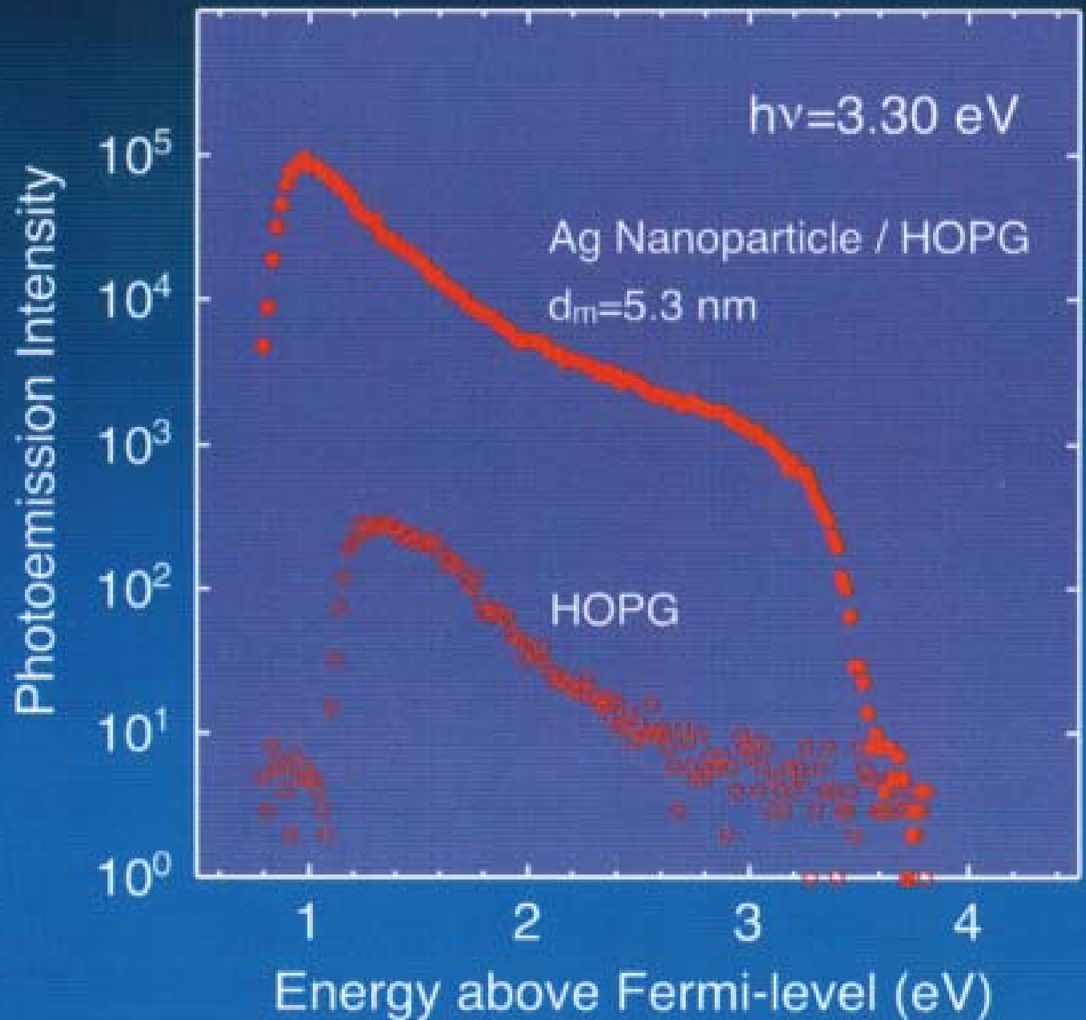
Two-photon photoemission spectra of DT-passivated Ag nanoparticles



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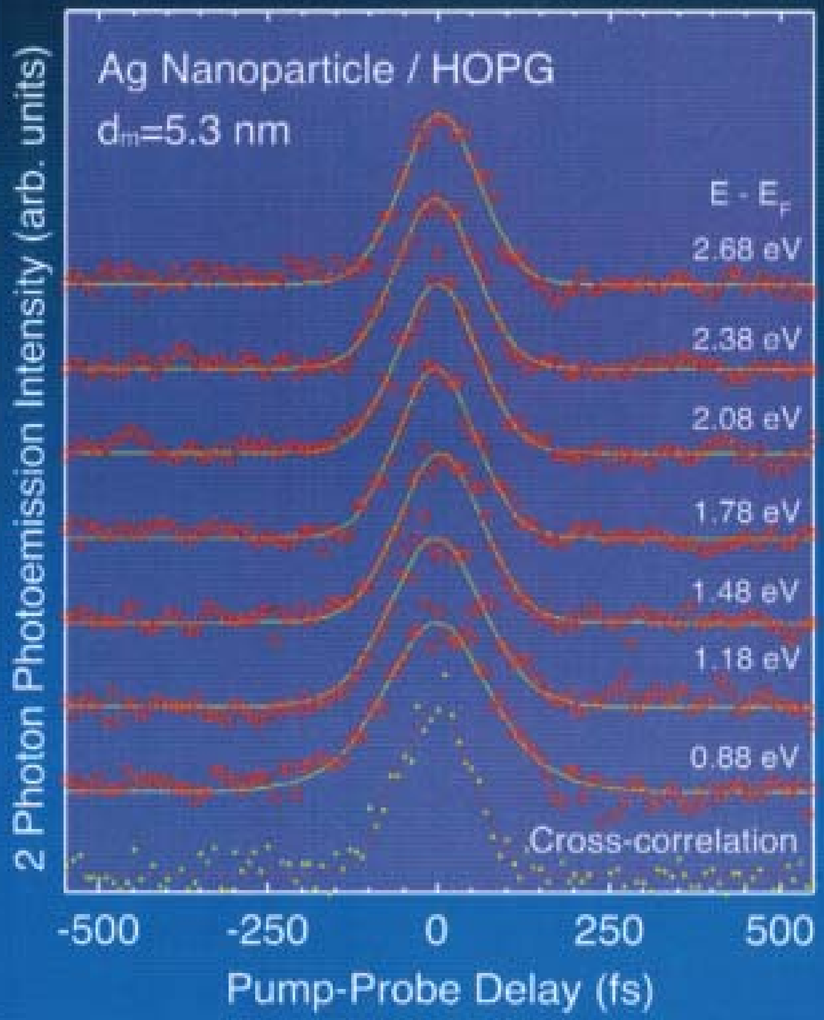
Pump-probe measurements for DT-passivated Ag nanoparticles : TR-2PPES



Photoemission intensity as a function of pump-probe delay time $I(t)$:

$$I(t) \propto R(t) \otimes \exp(-|t|/\tau)$$

$R(t)$: Instrumental response function (Gaussian function)

$\exp(-|t|/\tau)$: Population decay function of excited states

→ Relaxation lifetime τ

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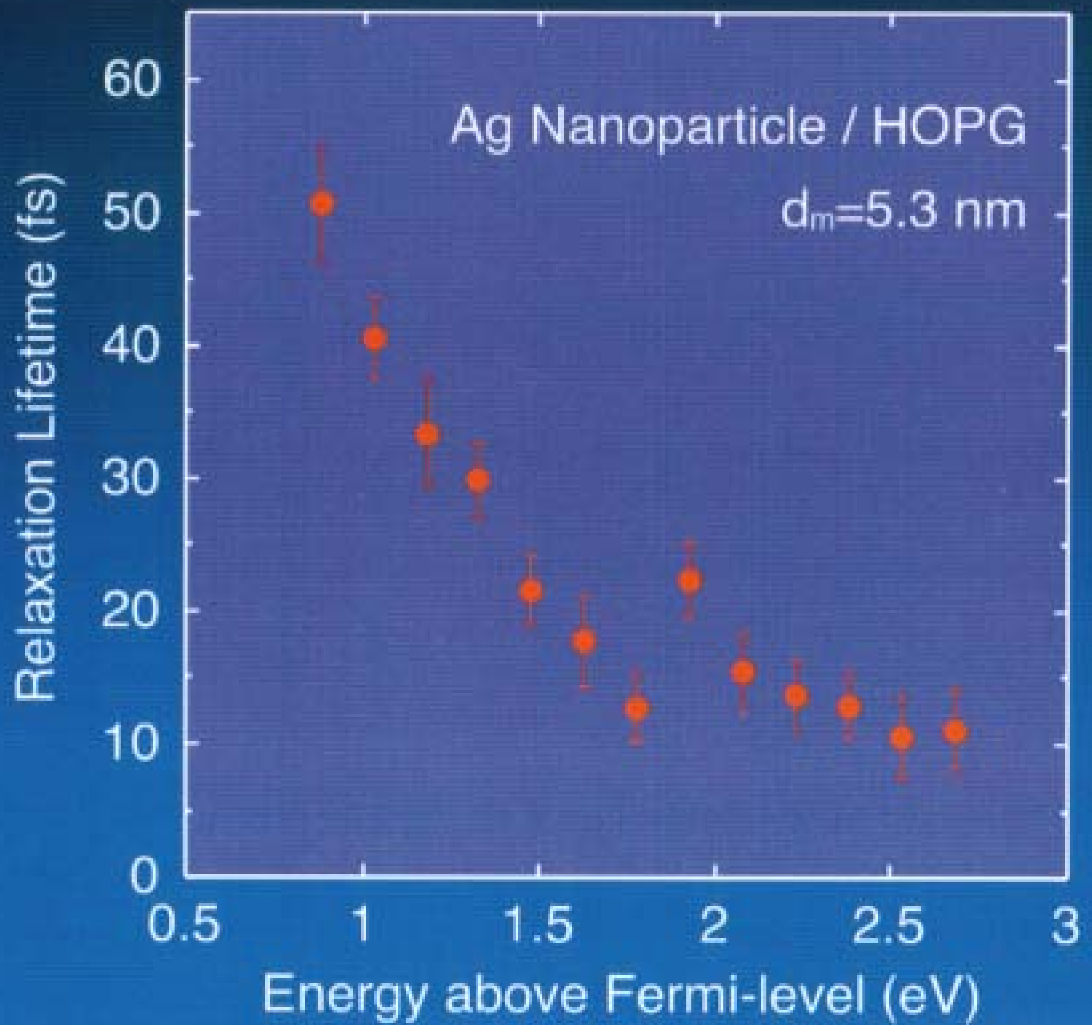
Relaxation lifetime in DT-passivated Ag nanoparticles



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Summary

- 金属2次元ナノ薄膜系（単層ナノ薄膜、二重ナノ薄膜構造）の角度分解光電子分光
  - 量子化電子構造（エネルギー固有値、2次元分散）
  - 電子 - フォノン相互作用
  - 量子化電子準位-基板電子状態相互作用
  - 量子化電子準位間相互作用
- 表面修飾金属0次元ナノ粒子の光電子分光及びフェムト秒時間分解2光子光電子分光
  - ナノ粒子-基板相互作用
  - 励起電子ダイナミクス
  - （電子構造、化学状態）

金属低次元ナノ構造体の低エネルギー光電子分光

⇒ 定常特性 ＋ 動的特性

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