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Tanaka, Akinori
Takeda, Yuitsu
Imamura, Masaki
Sato, Shigeru

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Femtosecond dynamic final-state effect in photoemission of surface-passivated metallic nanoparticles on graphite substrates

Akinori Tanaka,[*] Yuitsu Takeda, Masaki Imamura, and Shigeru Sato
Department of Physics, Graduate School of Science, Tohoku University, Aoba-ku,
Sendai 980-8578, Japan

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We have carried out systematic photoemission studies of alkanethiolate-(AT-) passivated metallic (Ag and Au) nanoparticles supported on the highly oriented pyrolytic graphite (HOPG) substrates. The Fermi-level onsets in the photoemission spectra of AT-passivated Ag nanoparticles on the HOPG substrates are not the metallic Fermi-edge, and depend on the nanoparticle diameter and surface-passivant molecules. Furthermore, the core-level photoemission spectra also depend on the nanoparticle diameter. We attribute these unusual spectral features to the dynamic final-state effect in photoemission, indicative of the interaction between the nanoparticle and substrate through the surface-passivants on a femtosecond timescale.

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Keywords: Surface-passivated metallic nanoparticle, Photoemission spectroscopy, Dynamic final-state effect, Nanoparticle-substrate interaction, Single-electron phenomena

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[*] To whom correspondence should be addressed.
Department of Physics, Graduate School of Science, Tohoku University, Aoba-ku,
Sendai 980-8578, Japan
Phone: +81-22-217-6418, Fax: +81-22-217-6419,
E-mail: a-tanaka@srpe.phys.tohoku.ac.jp

1. Introduction

Metallic nanoparticles are attracting much interests, since they show the distinctive physical and chemical properties found in neither bulk nor molecular/atomic systems. Recently, surface-passivated metallic nanoparticles have been chemically synthesized in the solution including surfactants [1, 2]. These surface-passivated nanoparticles are monodisperse and stable at room temperature, and exhibit closed-packed nanoparticle self-assemblies on the single-crystalline substrates [3, 4]. Therefore, it is considered that they could be important constituents of the future nanostructured devices. In order to elucidate their intriguing properties and to develop the future devices, it is indispensable to understand the interactions with the substrates supporting the nanoparticles as well as their electronic structures.

In this work, we have carried out systematic photoemission studies of various alkanethiolate- (AT-) passivated noble-metal (Ag and Au) nanoparticles supported on the highly oriented pyrolytic graphite (HOPG) substrates. The final-state effect in the photoemission (static charging effect) due to the photohole created by photoionization has been reported in the previous photoemission studies [5-11]. In this work, we will discuss the final-state effects on the photoemission spectra of AT-passivated metallic nanoparticles on the HOPG substrates, which originate from the nanoparticle-substrate interactions *with a finite tim*e through the surface-passivants of AT molecules.

2. Experiment

The AT-passivated Ag and Au nanoparticles were synthesized by a two-phase reduction method [1]. The dodecanethiol ($C_{12}H_{25}SH$) and octadecanethiol ($C_{18}H_{37}SH$) were used as the AT surface-passivant molecules. The size distributions and shapes of the synthesized dodecanethiolate- (DT-) and octadecanethiolate- (ODT-) passivated nanoparticles were characterized by *ex-situ* observations with transmission electron microscope (TEM). The detailed experimental procedures are described elsewhere [12-14]. Ultraviolet photoemission (UPS) measurements were performed at 40 K with the He I resonance line ($h\nu$=21.2 eV) as the excitation source at Tohoku University. Synchrotron-radiation photoemission measurements were performed at BL-5A of UVSOR Facility, Institute for Molecular Science. Synchrotron-radiation photoemission measurements were performed with the incident photon energy of 180 eV at room temperature.

3. Results and Discussion

Figure 1 shows the photoemission spectra in the vicinity of Fermi level (E_F) of DT-passivated Ag nanoparticles with a mean diameter d_m of 4.2 nm and ODT-passivated Ag nanoparticles with d_m=4.4 nm on the HOPG substrates, compared with that of bulk Ag polycrystalline evaporated film. The photoemission spectrum of bulk Ag shows the usual metallic Fermi-edge. However, the Fermi-level onsets in the photoemission spectra of AT-passivated Ag nanoparticles on the HOPG substrates are not the usual metallic Fermi-edge observed for bulk Ag, with the steep slope being away from the Fermi level, and moreover depend on the nanoparticle diameter. We have concluded in our previous paper [13] that these spectral features originate from the final-state effect due to the photohole left behind in the nanoparticles during the photoemission process. When the high photon-energy light excites a photoelectron, the photohole left behind in the nanoparticles during the time scale relevant to photoemission process will lower the kinetic energy of photoelectrons through the Coulomb interaction. Although the relaxation response within the nanoparticle may otherwise proceed normally, an excess positive charge left behind in the nanoparticle induces the final-state effect in the photoemission. From the static viewpoint, this kinetic-energy shift of photoelectron is give by $\Delta E=e^2/2C_s$, where $C_s=4\pi\varepsilon_0 R$ is the self-capacitance of the nanoparticle with a radius of R. On the other hand, an exact calculation shows that this energy shift is given by $\Delta E=\alpha e^2/4\pi\varepsilon_0 R$ with α=0.41 for Ag nanoparticle [5]. In the literature [5-9], the energy shifts of the experimental core-level spectra for supported and free nanoparticles have been explained with this *static* charging effect. In the case of photoemission, the nanoparticles are limited to have only positive charge (photohole), but the origin of this final-state effect on the photoemission process should be same as that of single-electron tunneling. Therefore, the investigations of the final-state effect on the photoemission process will provide information about the single-electron phenomena. Moreover, we have reported in our previous paper that the photoemission spectra in the vicinity of E_F of DT-passivated Ag nanoparticles on the HOPG substrates are well characterized by the dynamic final-state effect model that takes into account the Coulomb interaction between the photoelectron and photohole with a *finite* lifetime during the photoemission process [13]. In this model, the probability of photohole neutralization is described by $P(t)dt=(1/\tau)\exp(-t/\tau)dt$, with a charactertic time τ that determined by the coupling strength between the nanoparticle and substrate. While the photohole created by photoionization is remaining in the nanoparticle, the Coulomb interaction between the photoelectron and photohole induces the energy shifts of photoelectrons. The Coulomb potential acting on the photoelectron due to the photohole from the nanoparticle to infinity is expressed by $W(r)=\alpha e^2/4\pi\varepsilon_0(1/R-1/r)$, where r is the distance from the center of the nanoparticle. When the photohole is neutralized after a time t, the energy shift of photoelectron with a velocity v is described by $W(R+vt)$. The observed photoemission spectra average over a large number of photoelectrons at the different times t, therefore, this leads to the distribution of energy shifts given by,

$$P(W)dW = \frac{CW_{\max}}{(W_{\max}-W)^2}\exp\left(-\frac{CW}{W_{\max}-W}\right)dW, \tag{1}$$

with $C=R/v\tau$ and $W_{\max}=\alpha e^2/4\pi\varepsilon_0 R$ with $\alpha=0.41$ for Ag. This means that this dynamic final-state effect induces to an energy-shift distribution of photoelectrons even if all nanoparticles are monodisperse and identically interact with the substrates. In Eq. (1), $W_{\max}$ corresponds to the maximum energy shift of photoelectron and is identical to the energy shift for a nanoparticle with an infinite photohole lifetime. The photoemission spectrum $S(E_B,R)$ in the vicinity of E_F for nanoparticle with a radius of R can be described by the convolution of Fermi-Dirac function at a relevant temperature and the energy-shift distribution function $P(W)$, as a function of binding energy E_B. Our experimental photoemission spectra $I(E_B)$ include the contributions from the inhomogeneous width due to the size distribution, finite instrumental width, and photoemission intensity from the uncovered region of HOPG substrate. Therefore, our experimental spectrum is expressed by $I(E_B)\propto[S(E_B,R)\otimes D(R)]\otimes G(E_B)+B(E_B)$, where $D(R)$ is a Gaussian size-distribution function determined from the TEM observation, $B(E_\mathrm{B})$ is the photoemission intensity from the HOPG substrate, and $G(E_\mathrm{B})$ is an instrumental Gaussian function. Using $I(E_B)$ with $S(E_\mathrm{B},R)$, we have performed a fit to the experimental spectrum of DT-passivated Ag nanoparticles on the HOPG substrate by the least-squares method. As shown in Fig. 1, the fitting line shown by solid line in Fig. 1 reproduces the experimental spectrum fairly well. From this calculation, the obtained parameter C of DT-passivated Ag nanoparticles with d_m=4.2 nm on the HOPG substrates is 4.2, which corresponds to τ=0.21×10^{-15} sec.

Especially, it is found in the present paper that the spectral feature in the vicinity of E_F depends on the surface-passivant AT molecules. That is, the slopes of leading edges are significantly different among the DT- and ODT- passivated Ag nanoparticles in spite of almost same diameters. We have also performed a fit to the experimental spectrum of ODT-passivated Ag nanoparticles on the HOPG substrate based on the dynamic final-state effect model by the same procedures as the DT-passivated nanoparticles, and have compared to the result of DT-passivated Ag nanoparticles. It is found that the fitting line shown by a solid line in Fig. 1 also reproduces the experimental spectrum of ODT-passivated Ag nanoparticles fairly well. The obtained parameter C of ODT-passivated Ag nanoparticles with d_m=4.4 nm is 1.6, which corresponds to τ=0.58×10^{-15} sec. It is concluded that the spectral features of ODT-passivated Ag nanoparticles on the HOPG substrates can be also explained with the dynamic final-state effect model. The obtained lifetimes τ directly correspond to the tunneling time through the surface-passivants of AT molecules. From the analogy of single-electron tunneling, these lifetimes τ can be estimated to be $\tau=R_TC_s$, where R_T is the tunnel resistance between the nanoparticle and substrate through the surface-passivants, and C_s is the self-capacitance of the nanoparticle as described above. Therefore, the present discussions will provide the knowledge about the single-electron tunneling in the nanoparticle/[tunneling-gap (surface-passivant)]/substrate system. The tunnel resistance will scale exponentially with separation between the contacts: $R_T=R_0\exp(\beta s)$, where s is the interelectrode separation defined by the surface-passivant AT molecular length in the present cases. The self-capacitances of the present DT- and ODT-passivated nanoparticles are almost same, since the diameters of both nanoparticles are almost same. As a result, the photohole tunneling-time in this comparison is determined by only tunnel resistance through the surface-passivants between the nanoparticles and substrate. Therefore, the difference of photoemission spectral features in the vicinity of E_F among the DT- and ODT-passivated Ag nanoparticles, that is, the difference of obtained lifetimes τ, reflects the tunnel resistance between the nanoparticle and substrate through the surface-passivants determined by the AT surface-passivant molecular length. However, in order to quantitatively discuss the single-electron phenomena from these final-state effects on photoemission, a more rigorous calculation and the detailed comparison with the tunneling microscopic experiments would be necessary.

Figure 2 shows the Au $4f_{7/2}$ core-level photoemission spectra of DT-passivated Au nanoparticles on the HOPG substrates with that of bulk Au polycrystalline evaporated film. Figure 2 also shows the results of line-shape analyses for Au $4f_{7/2}$ core-level spectra. The detailed procedure of these line-shape analyses have been described elsewhere [14]. As previously well established, Au $4f$ core-level photoemission spectrum of bulk Au crystallite is represented by two components, which originate from the Au atoms in the bulk and topmost surface Au layer. The components with higher binding energy (solid line in the top spectra of Fig. 2) and lower binding energy (dashed line in the top spectra of Fig. 2) are bulk and surface components, respectively. On the other hand, we have reported in the previous paper that Au $4f$ core-level spectra of DT-passivated Au nanoparticles on the HOPG substrates are also represented by two components [14]. We have concluded that the components with lower binding energy and higher binding energy in the Au $4f$ core-level spectra of DT-passivated Au nanoparticles originate from the inner Au atoms of Au nanoparticles (bulk component) and the surface Au atoms of Au nanoparticles bonded to surface-passivants of DT molecules (surface component), respectively. In our previous paper [14], we have only discussed the chemical states of DT-passivated Au nanoparticles from the chemical shifts of surface components. In the present work, it is found that the bulk components in Au $4f$ core-level photoemission spectra of DT-passivated Au nanoparticle shifts to higher binding energy relative to the bulk Au crystallite and this energy shift increases with decreasing the nanoparticle diameter. From the analogy of photoemission spectra in the vicinity of E_F, these higher-binding-energy shifts of bulk components in the DT-passivated Au nanoparticles are considered to originate from the final-state effect. Since the chemical states of both bulk components in the Au 4*f* core-level spectra observed for bulk Au crystallite and DT-passivated Au nanoparticles are considered to be equivalent, the bulk components in the DT-passivated Au nanoparticles on the HOPG substrates correspond to the shifted ones of bulk component observed in the bulk Au crystallite due to the dynamic final-state effect. Therefore, in order to analyze the Au 4*f* core-level spectra of DT-passivated Au nanoparticles on the HOPG substrates, we apply the dynamic final-state model to Au 4*f* core-level spectra again. UPS spectra in the vicinity of E_F of DT-passivated Au nanoparticles can be also reproduced by the above dynamic final-state effect model. Using the fitting results for UPS spectra in the vicinity of Fermi level, we have transformed the parameter C_{4f} in the Au 4*f* core-level photoemission with $h\nu$=180 eV excitation, and then have calculated the energy-shift distribution function $P_{4f}(W)$. The bulk component in the Au 4*f* core-level spectrum of DT-passivated Au nanoparticle on the HOPG substrate can be theoretically described by the convolution of bulk component observed for bulk Au crystallite with the energy-shift distribution function $P_{4f}(W)$. Figure 3 shows the comparison of experimental bulk component in the Au $4f_{7/2}$ core-level spectrum of DT-passivated Au nanoparticles of d_m=3 nm on the HOPG substrate and calculated one from the experimental bulk component of bulk Au crystallite using dynamic final-state effect model. It is found that the calculated bulk components reproduce the experimental ones fairly well. Therefore, it is concluded that the core-level photoemission spectra of the DT-passivated Au nanoparticles on the HOPG substrates can be also characterized by the dynamic final-state effect model that takes into account the nanoparticle-substrate interaction on a femtosecond timescale.

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Figure captions

Fig. 1. Photoemission spectra in the vicinity of Fermi level of dodecanethiolate-(DT-) passivated Ag nanoparticle with a mean diameter d_m of 4.2 nm and octadecanethiolate- (ODT-) passivated Ag nanoparticle with d_m=4.4 nm supported on the HOPG substrates at 40 K measured with the He I resonance line ($h\nu$=21.2 eV). The top spectrum shows the Fermi-level onset observed for bulk Ag polycrystalline evaporated film for a comparison. The solid lines show the calculated spectra based on the dynamic final-state effect model (see text).

Fig. 2. Au $4f_{7/2}$ core-level photoemission spectra of dodecanethiolate- (DT-) passivated Au nanoparticles supported on the HOPG substrates at room temperature measured with photon energy of $h\nu$=180 eV. The mean diameter d_m is indicated on each spectrum. The top spectrum shows the Au $4f_{7/2}$ core-level spectrum observed for bulk Au polycrystalline evaporated film for a comparison. The observed spectrum of bulk Au crystallite is decomposed into bulk (solid line) and surface (dashed line) components, and those of DT-passivated Au nanoparticles on the HOPG substrates are decomposed into bulk components (solid lines) and surface components bonded to surface DTs (dotted lines).

Fig. 3. Comparison of the calculated result based on the dynamic final-state effect model with the experimental bulk component of DT-passivated Au nanoparticle with mean diameter of 3 nm on the HOPG substrate. The top spectra show the experimental spectrum (open circle) and the corresponding decomposed components (solid line: bulk component, dashed line: surface component) of bulk Au crystallite. The middle spectra show the experimental spectrum (open circle) and the corresponding decomposed components (solid line: bulk component, dotted line: surface component) of DT-passivated Au nanoparticle with mean diameter of 3 nm on the HOPG substrate. The bottom spectrum shows the calculated bulk component based on the dynamic final-state effect model (see text). Arrow indicates the energy shift due to the dynamic final-state effect.

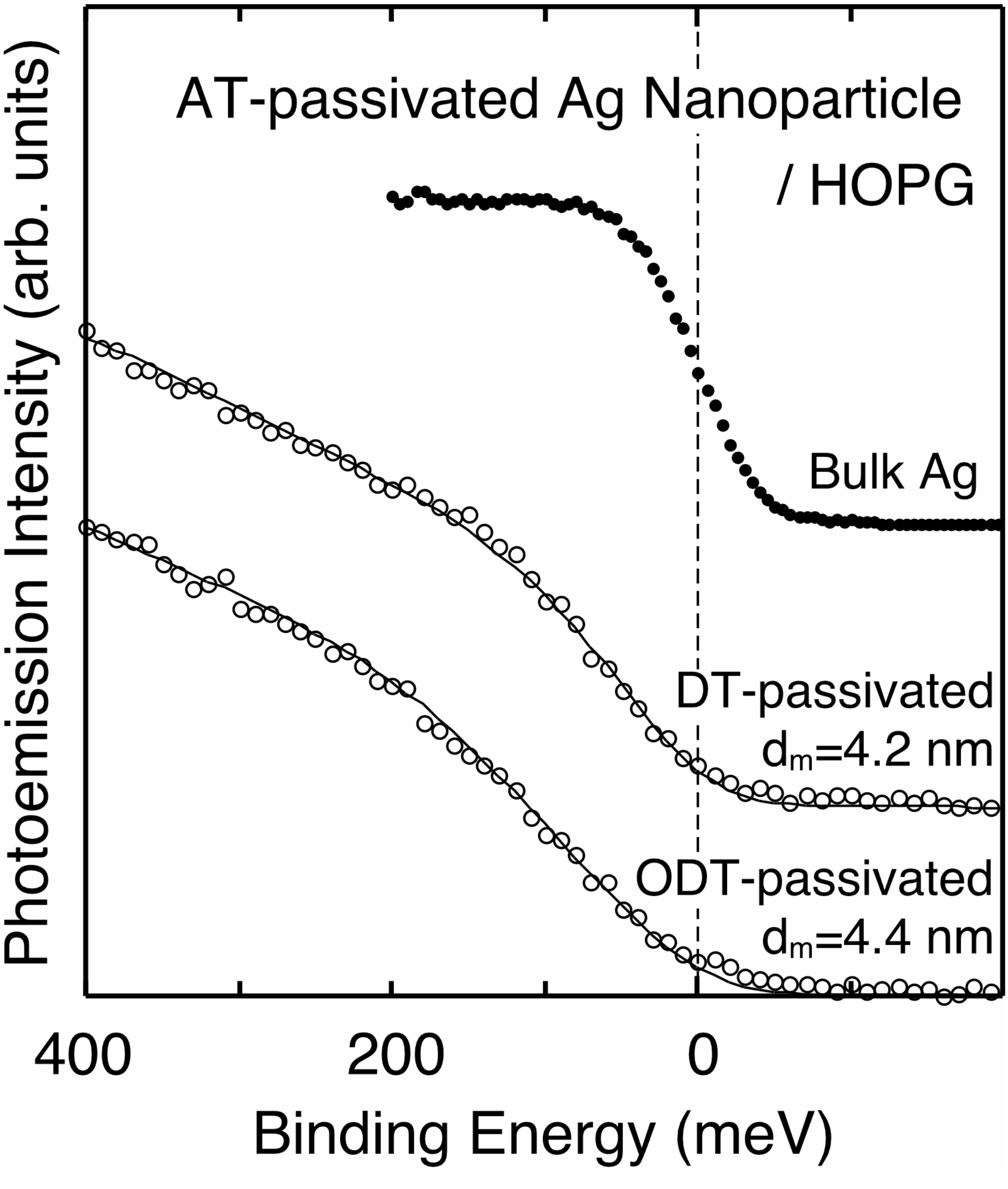

Fig. 1. A. Tanaka *et al.*

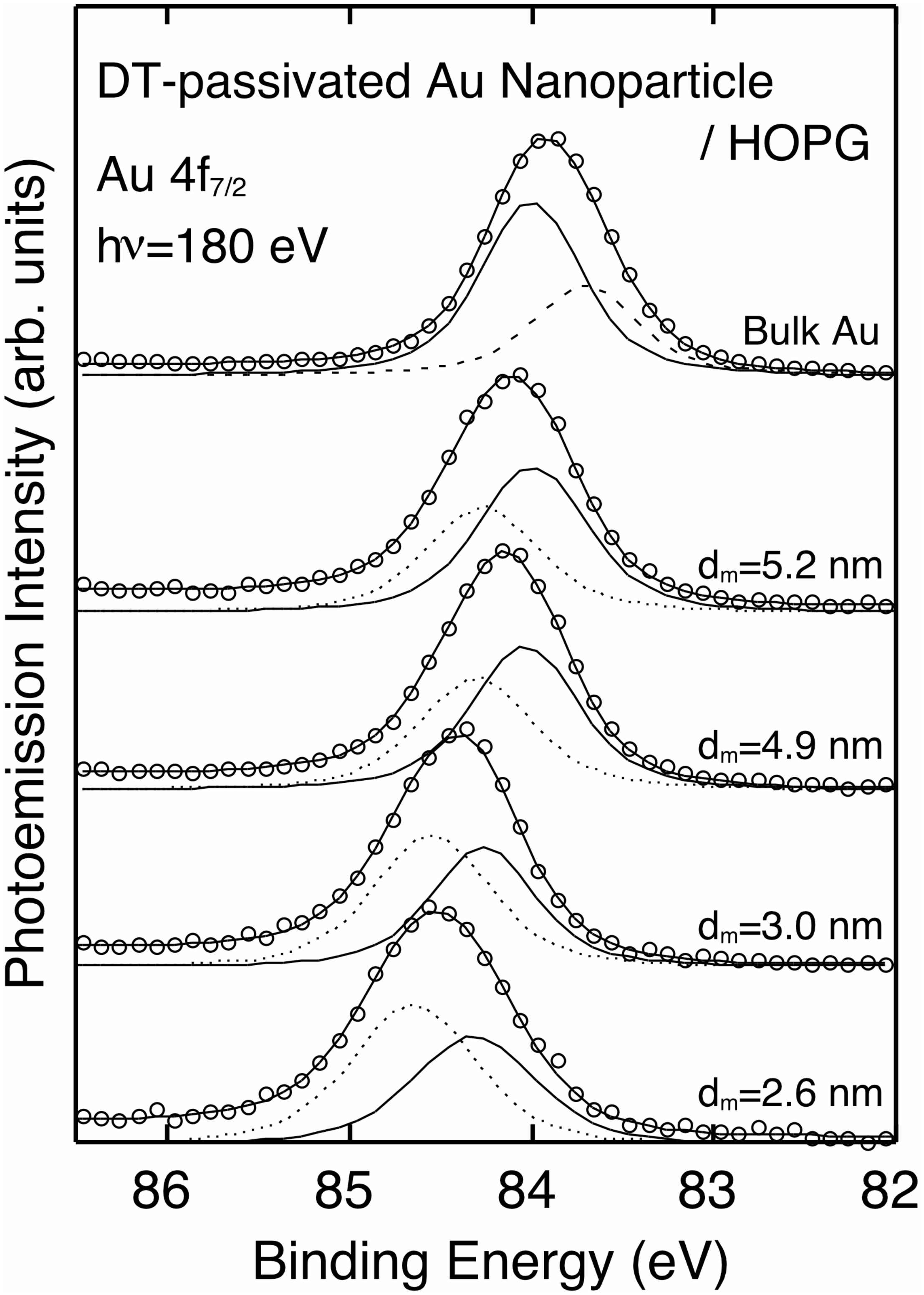

Fig. 2. A. Tanaka *et al.*

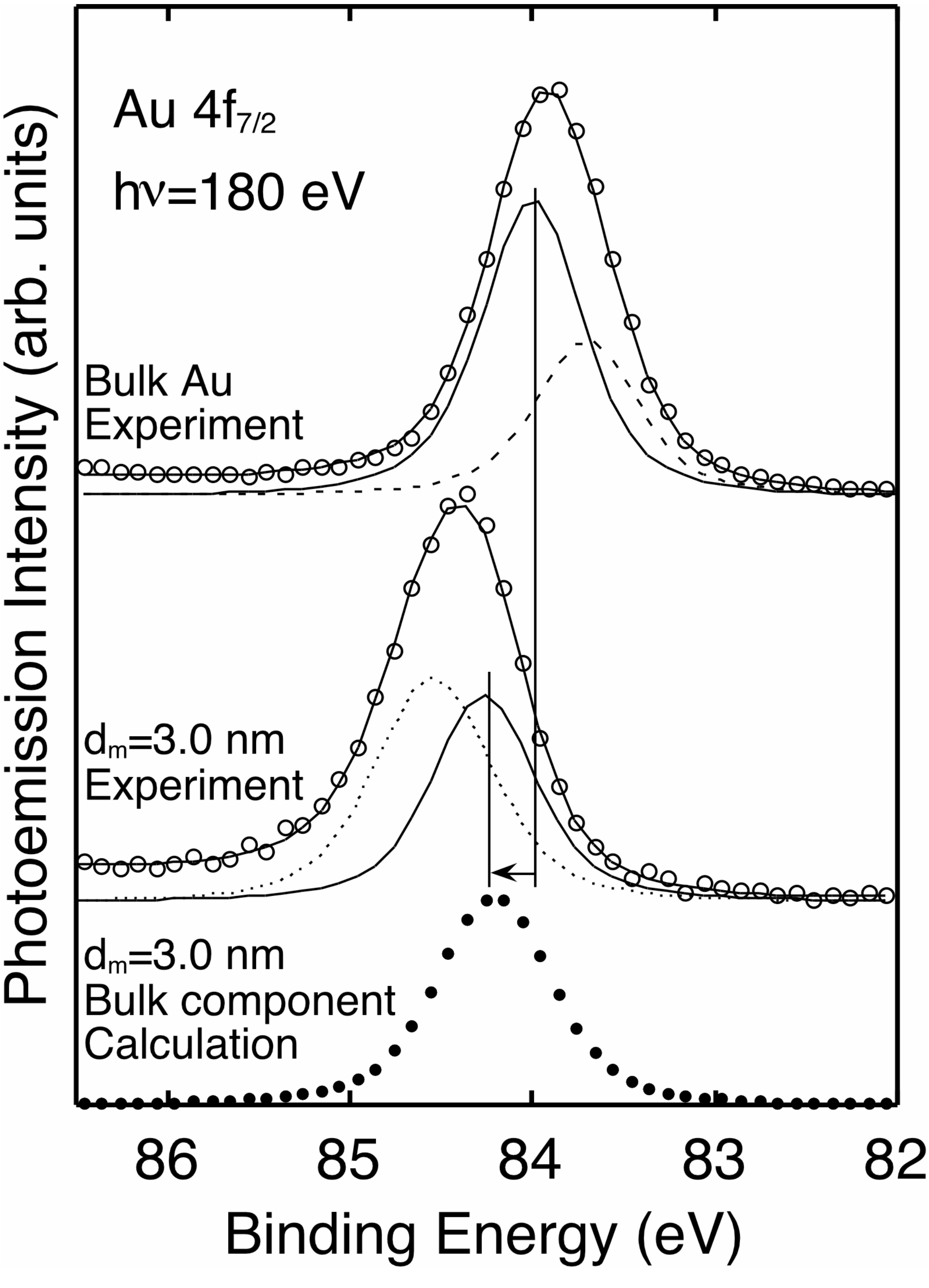

Fig. 3. A. Tanaka *et al.*