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Photoemission study of metallic nanoparticles passivated by dodecanethiolates: Silver nanoparticles

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Photoemission study of dodecanethiolate-passivated Ag nanoparticles supported on the highly oriented pyrolytic graphite (HOPG) has been carried out in order to investigate their nanoparticle-substrate interactions. It is found that the Fermi-level onset in the photoemission spectrum for the present Ag nanoparticle is not the Fermi edge, with the steep slope being away from the Fermi-level. The observed photoemission spectra are well characterized by a theoretical calculation that takes into account the influence of the photohole left behind in the Ag nanoparticle in the photoemission final-state and nanoparticle-substrate interaction on a femotosecond timescale. From these results, we discuss the nanoparticle-substrate interactions through the surface-passivants of the surface-passivated Ag nanoparticles the HOPG substrates.

Keywords: Photoelectron spectroscopy, Visible/ultraviolet absorption spectroscopy, Silver, Clusters

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1. Introduction

Metallic nanoparticles are recently attracting much interest from the viewpoints of both fundamental and device physics, since they show the distinctive physical properties, such as high catalytic activity [1] and Coulomb blockade [2]. Recently, the surface-passivated metallic nanoparticles have been chemically synthesized in the solution including surfactants [3, 4]. These surface-passivated nanoparticles are suitable to probe their fundamental size-dependent properties, since they are monodisperse and very stable at room temperature. Furthermore, these surface-passivated nanoparticles exhibit the closed-packed nanoparticle self-assemblies [5, 6], therefore, such materials could be important constituents of nanostructured devices, such as a single electron device, catalyst, and ultra highly density memory. In order to elucidate their physical properties and to develop the future devices, it is indispensable to understand their electronic structures and interactions with the substrates supporting the nanoparticles. In this work, we have carried out a photoemission study for dodecanethiolate-passivated Ag nanoparticles supported on the highly oriented pyrolytic graphite (HOPG) substrates. From these results, we discuss the nanoparticle-substrate interactions through the surface-passivants of dodecanethiolate-passivated Ag nanoparticles on the HOPG substrates.

2. Experimental

Dodecanethiolate-passivated Ag nanoparticles were synthesized by a two-phase (water-toluene) reduction method [3]. An aqueous silver ion solution ($AgNO_3$) was mixed with a toluene solution of phase transfer catalyst ($(C_8H_{17})_4NBr$) and then the silver salt is transferred into the toluene phase. The toluene phase was subsequently corrected, and a dodecanethiol ($C_{12}H_{25}SH$) and an aqueous sodium borohydride ($NaBH_4$) were added as a surface-passivants and reducing catalyst, respectively. After stirring, the toluene/nanoparticle-rich phase was corrected, evaporated in a rotary evaporator, and washed three times with ethanol to remove the phase transfer catalyst, excess dodecanethiol, and reaction byproducts. The crude product was redispersed in toluene, annealed at 353 K with dodecanethiol, and washed three times again with ethanol to remove the excess dodecanethiol. After that, the product was redispersed in toluene, and finally size-selective precipitation using toluene/ethanol as the solvent/nonsolvent pair was performed by centrifugation to narrow the size distribution. The size distribution and shape of the synthesized dodecanethiolate-passivated Ag nanoparticles were obtained by direct observation with a JEM-2000EXII (JEOL Co.) transmission electron microscope (TEM). The samples for TEM observations were prepared by drying the dispersion of Ag nanoparticles on amorphous carbon coated copper grid. As a further characterization, the measurements of the optical spectra were performed using V-570 (Jasco Co.) spectrometer.

The thus-prepared dodecanethiolate-passivated Ag nanoparticles were supported on the HOPG substrates by evaporating the solvent (toluene) from the dispersion of Ag nanoparticles on the HOPG cleaved-surface in a nitrogen-filled glove bag connected to the ultrahigh vacuum system. The samples were then transferred into the photoemission analysis chamber without exposure to air. The cleanliness of the HOPG substrates and nanoparticle samples were checked by *in-situ* Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS). The thus-prepared samples show no AES and XPS signals from the contaminants. Photoemission measurements were performed using ARUPS10 (VG Microtech Co.) with the He I resonance line ($h\nu$=21.2 eV) as the excitation source. The total energy resolution was about 75 meV. All measurements were performed at 40 K. The spectra showed no change in the course of the measurements.

3. Results and Discussion

Figure 1 shows the TEM micrographs and the size distributions obtained by the direct TEM observations for the dodecanethiolate-passivated Ag nanoparticles used in this work. From these size distributions, it is found that the mean diameters (and standard deviations σ) of the present dodecanethiolate-passivated Ag nanoparticles are 3.8 nm (σ=0.58 nm), 4.2 nm (σ=0.69 nm), and 5.3 nm (σ=0.47 nm). As shown in Fig. 1, the present dodecanethiolate-passivated Ag nanoparticles show the homogeneous and spherical shape. An important point to note is that each nanoparticle is well separated from its neighboring nanoparticles, indicating that the present Ag nanoparticles are well surface-passivated by dodecanethiol molecules.

Figure 2 shows the photoemission spectra in the vicinity of the Fermi-level measured for dodecanethiolate-passivated Ag nanoparticles supported on the HOPG substrates with various diameters. For a reference, the photoemission spectra of bulk Ag polycrystalline evaporated film and that of HOPG substrate are also shown in Fig. 2. As shown in the top spectrum of Fig. 2, the photoemission spectrum of bulk Ag shows a usual Fermi-edge. However, the photoemission spectra of the present Ag nanoparticles exhibit the distinct deviations from that of bulk Ag, that is, the Fermi-level onsets in the photoemission spectra are not the usual metallic Fermi edge, with the steep slope being away from the Fermi-level. Furthermore, it is found that the slope of the leading edge becomes smaller with decreasing the nanoparticle diameter. Since the photoemission spectrum in the vicinity of Fermi-level of HOPG substrate exhibits the featureless shape, reflecting the vanishing semimetallic density of states toward the Fermi-level, the observed spectral features of dodecanethiolate-passivated Ag nanoparticles on the HOPG substrates are not caused by the HOPG substrates but are characteristic of Ag nanoparticles. The rising intensity for binding energies higher than about 200 meV originates from the photoemission of the uncovered region of HOPG substrate. The photoemission spectra directly reflect the change in the electronic structure (initial-state effect) and are also affected by the final-state effect originating from the positively charged photohole created by photoionization [7, 8]. From the consideration in the Kubo criterion [9], the metal-insulator (semiconductor) transition with decreasing the nanoparticle diameter is not reasonable for the present diameter regime. Of course, we cannot recognize the size-dependent spectral features originated from the quantum size effects on the *sp*- and *d*-states in the overall valence-band photoemission spectra. Moreover, the optical extinction spectra of the present dodecanethiolate-passivated Ag nanoparticles exhibit the distinctive size-dependent Mie plasmon resonance around 3 eV photon energy for all diameters, indicative of normal metallic electronic structures. These discussions suggest that the observed spectral features are not due to the initial-state effect originating from the change in the electronic structure. Therefore, it is considered that the present spectral features originate from the final-state effect due to the photohole left behind in the nanoparticles during the photoemission process. The positively charged photohole left behind in the nanoparticles during the time scale relevant to photoemission process will cause an energy-shift of photoelectron through the Coulomb interaction. In the low-dimensional materials, such as the nanoparticles, the localized positive charge is considered to enhance this final-state effect responsible for unusual spectral feature. Thus, although the relaxation response within the nanoparticle may otherwise proceed normally, there will remain an excess positive charge in the nanoparticle and this significantly induces this final-state effect in the photoemission. In fact, the final-state effects in the photoemission originating from the remaining positive charge have been reported for the free nanoparticles [8] and even for the nanoparticles supported on the substrates [10, 11]. Therefore, it is considered that the observed deviations from the usual Fermi edge also originate from this final-states effect due to the photohole left behind in the nanoparticle during the photoemission process. It is considered that the final-state effect would play a more important role in the present surface-passivated Ag nanoparticles on the substrates, since the surface-passivated nanoparticle weakly couple with the substrates through the surface-passivants.

In order to describe these observations theoretically, we calculated the photoemission spectra using a dynamic final-state effect model [10, 11] that takes into account the Coulomb interaction between the photoelectron and the photohole during the photoemission process and nanoparticle-substrate interaction. The probability of photohole neutalization is expressed by $P(t)dt=(1/\tau)\exp(-t/\tau)dt$ using a tunneling time τ that is determined from the nanoparticle-substrate interaction. The Coulomb potential acting on the photoelectron due to the photohole is expressed by $W(r)=\alpha e^2/4\pi\varepsilon_0(1/R-1/r)$, where R is a radius of nanoparticle, r is the distance from the center of nanoparticle, and $\alpha=0.41$ [8] for Ag nanoparticles. Since the present Ag nanoparticles have the spherical shapes as shown in Fig. 1, this expression is considered to be reasonable. When the photohole left behind in the nanoparticle is neutralized after a time t, the energy shift for the photoelectron with a velocity v is described by $W(R+vt)$. The observed photoemission spectra average over a large number of photoelectrons at different times t, therefore, this leads to the distribution of energy shifts given by,

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

where $C=(R/vt)$ and $W_{\max}=\alpha e^2/(4\pi\varepsilon_0 R)$. This means that this dynamic final state effect induces to an energy-shift distribution of photoelectron even if all the nanoparticles are monodispersed and identically interact with the substrates. Here the parameter $W_{\max}$ corresponds to maximum energy shift due to the dynamic final-state effect and is identical to the energy-shift for a free nanoparticle with an infinite photohole lifetime. The photoemission spectrum in the vicinity of Fermi-level at low temperature, $S(E_B, R)$, for nanoparticle with a radius of R can be described by the convolution of Fermi-Dirac function (step function at low temperature where the thermal broadening is negligibly small) with the energy-shift distribution function $P(W)$, as a function of binding energy E_B. In the case of $C<<1$, the photoemission spectrum $S(E_B, R)$ is the Fermi-level onset shifted by $W_{\max}$, which corresponds to photoemission spectrum of a free nanoparticle with an infinite photohole lifetime, i.e. the case of static charging. On the other hand, in the case of $C>>1$, the photohole is immediately neutralized, therefore, the photoemission spectrum $S(E_B, R)$ shows no energy shift and is almost identical to Fermi-edge observed for usual bulk metal. In the case of intermediate regime, the Fermi-level onset in the photoemission spectrum is not the usual Fermi-edge, with the steep slope being away from the Fermi-level, and the slope of leading edge depends on the value of C [10]. The experimental photoemission spectra $I(E_\mathrm{B})$ include the contribution from the inhomogeneous width due to the size distribution as shown in Fig. 1, since the photoemission spectrum $S(E_\mathrm{B}, R)$ depends on the nanoparticle radius. Furthermore, the photoemission spectra observed in the present experiment include the contributions from a finite instrumental width and the other intensity from the uncovered region of HOPG substrate. Therefore, the observed spectra in the present experiments are expressed by,

$$I(E_B) \propto [S(E_B, R) \otimes D(R)] \otimes G(E_B) + B(E_B), \tag{2}$$

where $D(R)$ is a Gaussian size distribution determined from the direct TEM observation (Fig. 1), $B(E_\mathrm{B})$ is the photoemission intensity from the HOPG substrate, and $G(E_\mathrm{B})$ is an instrumental Gaussian function derived from a fit to experimental Fermi-edge of bulk Ag. We have carried out a fit to the experimental spectra by the least-squares method using the expression of $S(E_\mathrm{B}, R)$ and Eq. (2). The fitting lines to the experimental spectra are shown in Fig. 2. As shown in Fig. 2, the calculated results reproduce the experimental ones for all nanoparticle diameters fairly well. This indicates that the observed spectral features for the dodecanethiolate-passivated Ag nanoparticles on the HOPG substrates can be explained with the dynamic final-state effect model. From these calculations, the obtained parameters τ of the present dodecanethiolate-passivated Ag nanoparticles on the HOPG substrates are 0.20×10^{-15}, 0.21×10^{-15}, and 0.25×10^{-15} sec for the mean nanoparticle diameters of 3.8, 4.2, and 5.3 nm, respectively. It is concluded that the observed spectral features reflect the nanoparticle-substrate interactions through the surface-passivants (dodecanethiolates) on a femotosecond timescale. In the previous analyses for the photoemission spectra of evaporated Ag clusters by Hovel *et al.* [10, 11], they need a modified value of $W_{\max}$ compared to that with α=0.41, given in the work for free Ag nanoparticles [8], in order to reproduce their experimental data. On the other hand, in our analyses, we can reproduce the experimental spectra fairly well by the calculations using α=0.41 in $W_{\max}$, within the theoretical framework of the above dynamic final-state model. As described above, this model treats the case of perfectly spherical particle. As shown in Fig. 1, our dodecanethiolate-passivated Ag nanoparticles have the spherical shapes, but the previous evaporated Ag clusters have the nonspherical shapes. Therefore, the effect due to the nonspherical particle shape might contribute to the deviation of $W_{\max}$ in the previous analyses. On the other hand, the obtained lifetimes τ directly correspond to the tunneling times through the surface-passivants of dodecanethiolates. From the analogy of single electron tunneling, these lifetimes τ can be estimated to τ=R_TC_S, where R_T is the tunneling resistance between the nanoparticle and substrate through the surface-passivants, and C_S is the self-capacitance of the nanoparticle. Therefore, the present discussions will provide the knowledge about the single electron tunneling in the nanoparticle/tunneling-gap (surface-passivant)/substrate system. However, in order to quantitatively discuss the single electron phenomena from these final-state effects on photoemission, a more rigorous calculation, detailed size-dependence, and the detailed comparison with the microscopic tunneling experiments would be necessary. Moreover, up to now, the nanoparticles passivated by other alkanethiolates and other organic molecules [12] have been synthesized, therefore, it would be possible to investigate the nanoparticle-substrate interaction more rigorously by controlling the nanoparticle-substrate configurations with the surface-passivants.

4. Conclusions

We have performed a photoemission study for dodecanethiolate-passivated Ag nanoparticles supported on the HOPG substrates. In the photoemission spectra for the present Ag nanoparticles on the HOPG substrates, the Fermi-level onset is not the Fermi edge, with the steep slope being away from the Fermi-level. From a comparison with the theoretical calculations that take into account the influence of the photohole during the photoemission process (final-state effect) and the nanoparticle-substrate interaction, it is found that the calculated results reproduce well the present experimental ones for the present dodecanethiolate-passivated Ag nanoparticles on HOPG substrates. This indicates that the observed photoemission spectra give a direct evidence of nanoparticle-substrate interaction through the surface dodecanethiolates on a femotosecond timescale.

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Figure captions

Fig. 1. TEM micrographs and size distributions of dodecanethiolate-passivated Ag nanoparticles with mean diameters and standard deviations of (a) 3.8 nm, σ=0.58 nm (b) 4.2 nm, σ=0.69 nm and (c) 5.3 nm, σ=0.47 nm.

Fig. 2. Photoemission spectra in the vicinity of the Fermi-level measured for dodecanethiolate-passivated Ag nanoparticles supported on the HOPG substrates at 40 K with the He I resonance line ($h\nu$=21.2 eV). The mean diameter is indicated on each spectrum. Solid lines show the theoretical calculations that take into account the final-state effect (see text). The top spectrum shows the Fermi-level onset observed for bulk Ag for reference. The photoemission spectrum of HOPG substrate is also shown for a comparison.