Surface Plasmon Dynamics in Silver Nanoparticles Studied by Femtosecond Time-Resolved Photoemission

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Multiphoton photoelectron spectroscopy reveals the multiple excitation of the surface plasmon in silver nanoparticles on graphite. Resonant excitation of the surface plasmon with 400 nm femtosecond radiation allows one to distinguish between photoemission from the nanoparticles and the substrate. Two different previously unobserved decay channels of the collective excitation have been identified, namely, decay into one or several single-particle excitations.

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The nonlinear optical response due to the surface plasmon in metal nanoparticles, a collective oscillation of the conduction electrons, has attracted considerable interest and initiated many theoretical and experimental studies. Recently, multiple plasmon excitation has been observed in fragmentation and ionization of fullerenes [1] and in size selected clusters [2]. The lifetime of the surface plasmon in silver and alkali nanoparticles was determined to be in the range of 10 fs using time-resolved second and third harmonic generation [3–6]. From linewidth measurements of the surface plasmon resonance of a single gold nanoparticle a value of 8 fs was obtained [7]. However, the fundamental issue of the relevant decay channels of the surface plasmon has yet only been addressed theoretically. Theory predicts a very fast photoelectron emission within the first plasmon oscillation period, Landau damping, and electron-electron scattering [8–11].

Time-resolved two-photon photoemission spectroscopy is a powerful technique to investigate electronic relaxation processes [12–17] and the role of coherence in multiphoton excitation [16]. Up to now this method has successfully been applied to homogeneous surfaces, since the different contributions to the photoemission from a heterogeneous surface are difficult to distinguish. Here we demonstrate that this is not a general limitation. The resonant excitation of the surface plasmon in Ag nanoparticles grown on highly oriented pyrolytic graphite (HOPG) allows us to distinguish the different contributions. In Ag nanoparticles on HOPG the surface plasmon mode oriented normal to the substrate couples only weakly to the HOPG because of the low conductivity of graphite perpendicular to the basal plane [18]. Silver nanoparticles on graphite therefore are an ideal model system to investigate the electron dynamics in a confined electron gas. Additionally, since metal nanoparticles on substrates are widely used as model catalysts (e.g., [19]), it is essential to understand their electronic behavior. Our approach also allows one to study other metal nanoparticles with controlled size and distribution characterized by scanning tunneling microscopy (STM) [20]. The experiment presented here opens up a wide range of systematic studies probing the effect of particle size and surface modification on the electronic dynamics in metal clusters and also the cluster substrate interaction.

The preparation of the nanoparticles follows the procedure described in [20]. HOPG is damaged by Ar ion bombardment (1 keV, 10^{11} cm^{-2}) and oxidized in air (530 °C) resulting in the formation of pits in the topmost layer of the graphite. Silver is evaporated on the sample and condenses into the pits forming particles of 3 ± 1 nm height and an average separation of about 30 nm. Stable STM topographies are obtained (Fig. 1), which allow one to estimate the surface coverage to be 2%. Because of the convolution of particle shape and tip shape we can give only an upper limit of the particle width of 5 ± 3 nm. For excitation we use a home-built femtosecond 100 kHz chirped pulse amplifier system whose output is frequency doubled and tripled (intensity on the sample $<10^9$ W/cm^2, incident angle 35°). The pulse duration of the 400 and 267 nm laser pulses was controlled by a compression unit and was 50 and 70 fs, respectively, in most experiments. The energy resolution of the electron spectrometer (acceptance angle ±10°, at 2 eV kinetic energy) has been determined to be 60 meV for an electron of 1.5 eV kinetic energy. Details about the experimental apparatus are published elsewhere [21].

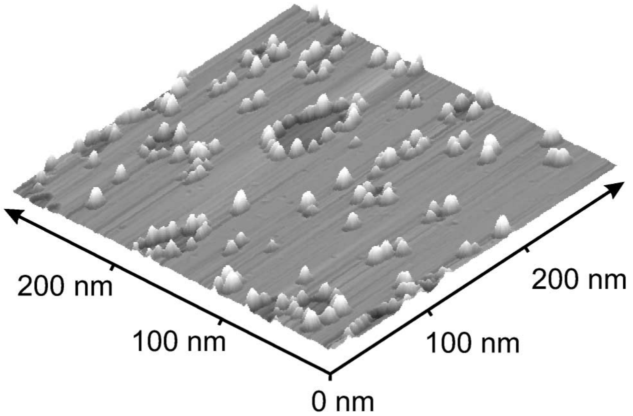

FIG. 1. Topography of silver nanoparticles on HOPG recorded with an *in situ* UHV STM ($U_{\mathrm{tip}} = -0.3$ V, $I_{\mathrm{tunnel}} = 25$ pA).

Photoelectron spectra have been recorded using a sample of which only one half of the HOPG substrate was covered with Ag nanoparticles allowing a quantitative comparison of spectra of HOPG with pits only and of HOPG covered with Ag nanoparticles. If 267 nm light (4.7 eV) is used for excitation, the electron spectra (Fig. 2a) are dominated by a peak below 0.5 eV which is due to one-photon photoemission. From this a work function of about 4.2 eV for both HOPG with and without Ag nanoparticles is obtained. In the two-photon regime (>0.5 eV) the photoelectron spectra from HOPG with and without Ag nanoparticles are almost identical. This indicates that in both cases the photoemission signal is dominated by the contribution from the graphite.

In reflection spectroscopy using p-polarized light of an Xe arc lamp we find that the surface plasmon resonance in Ag nanoparticles on HOPG extends from 3.0 to 3.5 eV. However, when using s-polarized light, we did not find a similar resonance. Figure 2b shows that for resonant excitation with p-polarized 400 nm laser pulses the photoelectron yield from HOPG with Ag nanoparticles is 2 orders of magnitude higher than that from HOPG with pits only. Whereas the spectrum from the semimetal HOPG reflects its vanishing density of states at the Fermi energy [22,23], the spectrum from the Ag nanoparticles on HOPG exhibits a clear edge at an electron energy of 2 eV reflecting the finite density of states at the Fermi energy in Ag. For larger intensities of the 400 nm radiation we even observe another edge at about 5 eV indicating three-photon excitation. When the polarization of the 400 nm light is rotated, the modulation of the total photoelectron yield from the nanoparticles follows a $\sin^4$ dependence. The same dependence has been measured in the total photoemission current. It shows that both photons are absorbed by a dipol resonance oriented perpendicular to the surface. The resonant enhancement of the photoelectron yield, the difference in spectral shape, and the polarization dependence prove that we excite the surface plasmon resonance in the nanoparticles with 400 nm light twice.

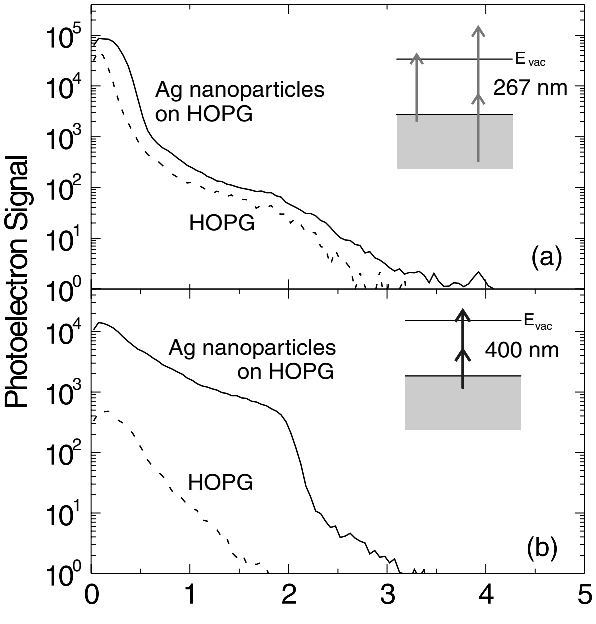

FIG. 2. Photoemission spectra of HOPG with pits and Ag nanoparticles on HOPG. The excitation wavelengths are (a) 267 nm (4.7 eV) and (b) 400 nm (3.1 eV).

Two different excitation processes are possible, either sequential excitation or coherent double excitation of the surface plasmon. In the sequential (i.e., incoherent) process, the excited plasmon decays into a single-particle excitation which is no longer coherent with the exciting light field. This excited electron is then photoemitted by the decaying second surface plasmon. Petek *et al.* have shown that the role of coherence in multiphoton excitation can be studied recording the time-resolved photoelectron signal with interferometric resolution [16]. The excitation process of two-photon photoemission via an intermediate state with finite lifetime can be modeled by the optical Bloch equations. The coherent double excitation of the surface plasmon is described by a three level system with population decay times $T_1^{\mathrm{pl}} = 6$ fs [6] and phase relaxation times $T_2^{\mathrm{pl}} = 2T_1^{\mathrm{pl}}$. The sequential process is described by a two level system ($T_1^{\mathrm{pl}} = 6$ fs, $T_2^{\mathrm{pl}} = 2T_1^{\mathrm{pl}}$) representing the excitation of a single surface plasmon which is coupled by population transfer to the intermediate level of a three level system assuming instantaneous dephasing of the single-particle state ($T_1^{\mathrm{eh}} = 13$ fs, $T_2^{\mathrm{eh}} = 0$ fs). The value of T_1^{eh} corresponds to the known population decay times of 10 to 17 fs for intermediate states 1 to 1.5 eV above the Fermi energy in bulk Ag [14]. Figure 3 displays the time-resolved 400 nm photoelectron signal (thin solid line) and the envelopes of the simulation curves for coherent excitation (solid line) and incoherent excitation (dashed line), both for a pulse duration of 42 fs. The

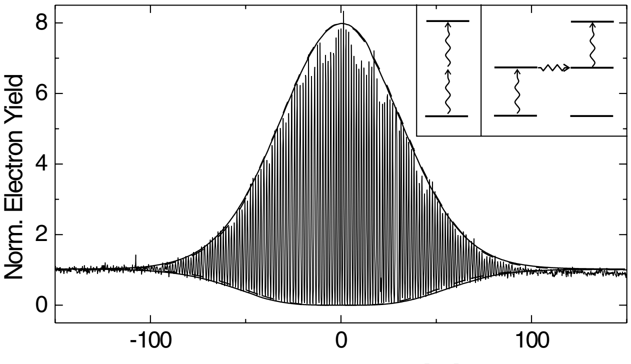

FIG. 3. Interferometric time-resolved pump-probe signal of the total photoelectron yield from Ag nanoparticles on HOPG when exciting with 400 nm fs laser light (thin solid line). The envelopes show a simulation of a coherent (solid line) and an incoherent excitation process (dashed line). Inset: direct (left) and sequential (right) excitation schemes.

envelope of the simulation of coherent excitation matches the data slightly better as the one of the incoherent process. However, neither the differences of the envelopes or of the phase averaged signal nor the differences of the envelopes of the different frequency components are big enough to unambiguously identify the dominating process using our experimental data.

Further evidence is obtained from the relative cross sections of the two excitation processes. The surface plasmon of a spherical particle can be treated as a collective oscillation of the particle's free electrons in the harmonic potential of the positive background charge. For a harmonic oscillator, the dipol matrix element for the excitation of the next higher level is independent of the quantum number of the initial state. Therefore the excitation probability of the doubly excited plasmon can be approximated by the square of the probability of the excitation of the surface plasmon. For the sequential process this probability is multiplied by the probability that a collective excitation couples to the already excited single-particle state. Under the assumption that every free electron has the same chance to be excited in the decay of a collective excitation, which can be approximated by the inverse of the number of free electrons, we estimate the relative strength of the sequential process to about 10^{-3}. In addition, the photoemission signal obtained for higher laser intensities of the 400 nm radiation shows an additional edge at about 5 eV reflecting the electronic occupation close to the Fermi energy in a three-photon process. In the case of sequential excitation this edge should be obscured due to scattering within the intermediate states. From the qualitative discussion of the relative cross sections and the observation of multiple edges in the photoemission spectrum we conclude that the coherent double excitation of the surface plasmon is the dominating excitation process. The observation of a multiple excitation of the plasmon mode is consistent with the interpretation of earlier experiments [1,2]. The edge at 2 eV in the 400 nm spectrum reflecting the Fermi energy gives strong evidence that a substantial part of the multiply excited plasmons transfer their total excitation energy to a single photoelectron. This proves that photoemission is an important decay mechanism for multiply excited plasmons as predicted theoretically [8,11].

Figure 4 displays the result of a time-resolved two-color experiment with 267 and 400 nm radiation. The temporal response from the HOPG essentially shows the cross correlation of the laser pulses, whereas the signal obtained from the nanoparticles on HOPG additionally exhibits a slow decay on a picosecond time scale. The 400 nm probe mainly generates electrons from the Ag nanoparticles and therefore the pump-probe signal reflects the relaxation dynamics in the Ag nanoparticles. In a two-photon probe process, a kinetic electron energy of 2.15 eV corresponds to an intermediate state 0.15 eV above the Fermi energy (see inset of Fig. 4.) From transient absorption measurements it is known that the excited electronic system in metallic nanoparticles loses energy via electron-phonon coupling on a picosecond time scale [24–26]. After thermalization of the electron gas, this coupling is seen in two-photon photoemission only at energies close to the Fermi energy. Therefore the picosecond decay constant observed at 2.15 eV energy can be explained by the cooling of the electron gas in the Ag nanoparticles. This interaction is probed by absorption of two 400 nm photons exploiting the doubly excited surface plasmon. A single 400 nm photon probes intermediate states located at least 1 eV above the Fermi energy. The corresponding fast relaxation processes (for bulk Ag see [14], for HOPG [22]) appear in the initial fast decay of the pump-probe signal and are not resolved in our experiment. A recent two-photon photoionization study on gold and palladium nanoparticles showed that electronic relaxation times in the metal nanoparticles are similar to the bulk values [27]. An explanation for the picosecond relaxation process by a one-photon probe process would therefore require a surface-state-like electronic reservoir originating from the interaction of metal and HOPG. However, no surface state has ever been observed to have such a long lifetime. We therefore rule out that the observed picosecond pump-probe effect is due to a one-photon probe process.

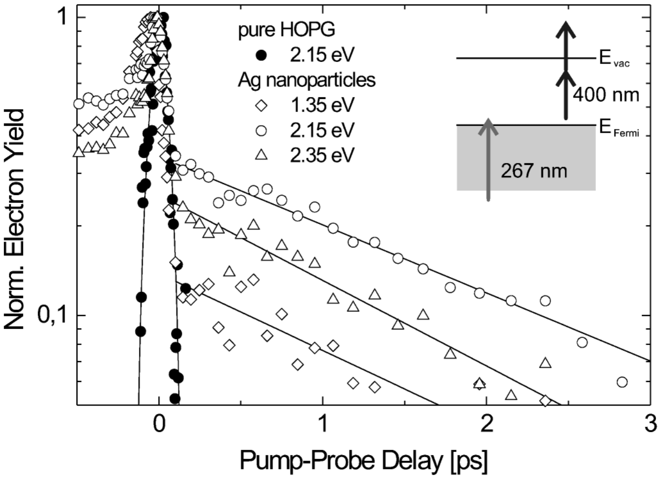

FIG. 4. Normalized photoelectron yield for different kinetic electron energies (background subtracted). The closed symbols represent photoemission from HOPG with pits, the open symbols photoemission from Ag nanoparticles on HOPG. The lines represent fits to a single exponential decay. The inset shows the energy diagram of the pump-probe process.

Surprisingly, the decay constant shows essentially no energy dependence. We find relaxation times of 1.7 ± 0.3, 2.0 ± 0.1, and 1.6 ± 0.2 ps for kinetic electron energies of 1.35, 2.15, and 2.35 eV, respectively. Whereas cooling of the electron gas can quantitatively explain these time constants for the 2.15 eV and for the 2.35 eV energies, it cannot account for the picosecond decay time obtained for 1.35 eV energy. Assuming that the total energy of the doubly excited surface plasmon is transferred to a single photoelectron, a kinetic electron energy of 1.35 eV corresponds to an intermediate state 0.7 eV below the Fermi energy. However, the corresponding occupied states cannot give rise to a positive pump-probe signal. In the following, we want to give a preliminary explanation. Note, the absorption of the two 400 nm probe photons occurs by coherent excitation of the doubly excited surface plasmon. The information of the intermediate state energy is lost in the probe process if this collective excitation also decays by coupling to more than one single-particle excitation which shares the plasmon energy. The existence of this decay channel has recently been demonstrated theoretically [9]. Hence, the emitted photoelectrons from one electronic state are distributed over a range of final state energies and the picosecond relaxation time for electrons close to the Fermi energy can be seen at different kinetic electron energies. Therefore this decay channel can readily account for our experimental results. An alternative explanation is a time-dependent variation of the excitation cross section as observed in [28,29]. In this case, the time-dependent part of the measured electron spectra would be proportional to the electron spectrum obtained with 400 nm excitation only. However, we do not observe this signature in the measured time-dependent electron spectra.

Summarizing, we employed femtosecond time-resolved two-photon photoelectron spectroscopy to study the electronic dynamics of a heterogeneous surface consisting of Ag nanoparticles grown on a HOPG substrate. Nanoparticles and substrate can be probed selectively by tuning in and out of the surface plasmon resonance of the nanoparticles as well as by variation of the polarization. This extends the technique of time-resolved two-photon photoemission spectroscopy to the investigation of heterogeneous surfaces. Our results provide direct evidence for multiplasmon excitation and two of its decay channels. The observation of a clear edge at 2 eV in the 400 nm multiphoton photoelectron spectrum shows that some of the doubly excited surface plasmons transfer their total energy to one single-particle excitation. We even observe an additional edge at about 5 eV similar to above threshold ionization experiments [30]. The observation of a picosecond decay time constant in a two-color pump-probe experiment at intermediate energies 0.7 eV below the Fermi energy indicates that the doubly excited surface plasmon can also decay into at least two single-particle excitations. The understanding of the resulting distribution of excited electrons subsequent to excitation of the surface plasmon will provide valuable information for processes that exploit hot electrons in metal nanoparticles such as photocatalysis.

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