Plasmonic Near-Electric Field Enhancement Effects in Ultrafast Photoelectron Emission: Correlated Spatial and Laser Polarization Microscopy Studies of Individual Ag Nanocubes

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Supporting Information

ABSTRACT: Electron emission from single, supported Ag nanocubes excited with ultrafast laser pulses (λ = 800 nm) is studied via spatial and polarization correlated (i) dark field scattering microscopy (DFM), (ii) scanning photoionization microscopy (SPIM), and (iii) high-resolution transmission electron microscopy (HRTEM). Laser-induced electron emission is found to peak for laser polarization aligned with cube diagonals, suggesting the critical influence of plasmonic near-field enhancement of the incident electric field on the overall electron yield. For laser pulses with photon energy below the metal work function, coherent multiphoton photoelectron emission (MPPE) is identified as the most probable mechanism responsible for electron emission from Ag nanocubes and likely metal nanoparticles/surfaces in general.

KEYWORDS: Coherent multiphoton photoelectron emission, single-particle dark field scattering, scanning photoionization microscopy, localized surface plasmon resonance, Ag nanocubes, ultrafast excitation

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Nanotechnology research and development have become prominent subjects in the last few decades, fueled by new fundamental understanding and analytical tools. Plasmonic nanoparticles and nanostructures, in particular, have attracted much attention due to their potential application in fields ranging from medical diagnostics to optical devices and optoelectronic circuits. The phenomenon relevant to such functionality is a localized surface plasmon resonance (LSPR): a light-induced coherent oscillation of the conduction electrons in small metallic particles. In the far-field, the localized surface plasmon manifests itself as enhanced light scattering and absorption by the particle, whereas in the near-field it generally amplifies the incident electromagnetic field (E0) and results in increased electric field (E) near the particle surface. This local electric field enhancement is of particular interest as it increases the effective intensity of the incident electromagnetic radiation, thereby leading to phenomena such as surface enhanced Raman scattering (SERS), improved efficiency of various nonlinear processes, and surface enhanced fluorescence, to name a few. In individual nanoparticles, near-field enhancement factors as large as |E|/|E0| = 105 can be observed, whereas values as high as |E|/|E0| = 106 can be attained in interparticle junctions of specially designed nanostructures.

These large local electric field enhancements have also recently been proposed to underlie more exotic processes, such as the generation of (i) high kinetic energy (up to keV) electrons and (ii) THz radiation upon ultrafast laser illumination of metallic surfaces and metallic nanostructures, respectively. In these cases, the observed phenomena are necessarily accompanied by electron emission—a process poorly understood for metallic nanoparticles and nanostructures irradiated with ultrafast laser pulses at a photon energy (Eph) below the material work function (Φ). In particular, the exact role of the localized surface plasmon in augmenting the electron emission is presently unclear.

Two families of mechanisms are often invoked to explain electron emission from metallic surfaces upon ultrafast excitation with sub-work function photon energies (i.e., Eph < Φ). In thermionic emission models, the laser pulse momentarily heats up the conduction electrons, thus promoting a fraction of electrons in the Fermi–Dirac distribution above the metal work function, whereupon they...
are emitted. Alternatively, the electron emission can be described in terms of a multiphoton photoelectric effect, where a particular electron is emitted after absorbing \( n \times \Phi / E_{ph} \) photons either simultaneously (i.e., a coherent/direct process) or sequentially (i.e., an incoherent/indirect process).\(^{36-40}\) Note that another commonly encountered mechanism, that is, the field emission, is the low frequency/high intensity limit of the same electric field induced electron ejection mechanism, that of field emission, leads to multiphoton photoelectric effect in the high frequency/low intensity regime, where the current experiments operate.

In the current work, we have devised an experiment that distinguishes between the two possible plasmon roles, and consequently the two mechanisms, by studying electron emission from individual, supported Ag nanocubes (edge length, \( d \sim 160 \text{ nm} \)).\(^{41}\) The (i) 4-fold symmetry (nominally \( C_{4v} \) on a substrate), (ii) well-defined positioning on the substrate (i.e., face down), and (iii) relatively simple scattering spectra in the visible spectral range make nanocubes ideal for this experiment. Single Ag nanocubes exhibit two main plasmon resonances as shown in a representative dark experiment. Single Ag nanocubes exhibit two main plasmon resonances as shown in a representative dark experiment. The two prominent peaks correspond to a quadrupolar (\( \lambda = 480 \text{ nm} \)) and a dipolar (\( \lambda = 690 \text{ nm} \)) plasmon resonance. The charge distribution for the two resonances is schematically depicted at the top of the figure for the indicated incident electromagnetic radiation. Inset: TEM image of the Ag nanocube responsible for the shown scattering spectrum.

Figure 1. Dark field scattering spectrum of an individual Ag nanocube (\( d \sim 160 \text{ nm} \)) on a C-Flat substrate. The two prominent peaks correspond to a quadrupolar (\( \lambda = 480 \text{ nm} \)) and a dipolar (\( \lambda = 690 \text{ nm} \)) plasmon resonance. The charge distribution for the two resonances is schematically depicted at the top of the figure for the indicated incident electromagnetic radiation. Inset: TEM image of the Ag nanocube responsible for the shown scattering spectrum.
To differentiate between the two mechanisms, structural, optical, and electron emissive properties of the same single nanoparticles have been studied. Since a specific particle thus needs to be probed by a number of different experimental techniques, particle registration is essential. This is achieved by depositing the sample onto indexed, transmission electron microscope (TEM) grids and has been successfully implemented previously for correlating optical and structural properties of nanoparticles.42 Such correlated dark field microscopy (DFM) and electron microscopy studies have greatly improved our understanding of how particle structure influences plasmonic properties in systems as varied as decahedra53,54 cubes,50,51 cages,55 and flat nanoprism57,58 to name a few. In a similar fashion, we have obtained correlated SPIM, DFM, and high-resolution TEM images to study the properties of supported Ag nanocubes.

The sample data shown in Figures 3 and 4a and the Supporting Information (SI) reveal several interesting features worth noting. For example, the dark field scattering signal from Ag nanocubes at $\lambda = 800$ nm exhibits no significant dependence on polarization (Figure 4a and SI), in agreement with previous observations and calculations as well as with the expectations based on the particle 4-fold rotational symmetry.59 Slight polarization-dependent fluctuations in the scattering signal from nanocubes are observed [average $(I_{\text{max}} - I_{\text{min}})/I_{\text{average}} = 9\%$, standard deviation = 3\%, $N = 20$]; however, their magnitude is substantially smaller than typically observed (>70\%) in the same setup for asymmetric shapes, such as dimers and elongated structures (see SI). While the origin of these variations is presently unclear, they do not correlate with the physical orientation of the cubes (see SI), suggesting that the cause is not intrinsic to the particle structure.

In contrast to the dark field scattering signal, electron emission from Ag nanocubes is observed to strongly depend on the laser polarization, as can be seen in Figure 4a, b for the same cube. Since the electron ejection probability for any linear absorption dependent process should be insensitive to the incident laser polarization (Figure 2c), the results unequivocally rule out a thermionic emission mechanism and instead indicate that the multiphoton photoelectric effect is responsible for the observed electron emission signal. The multiphoton nature of this process is further confirmed by a power law dependence of the electron emission rate on laser intensity at $\lambda$...
= 800 nm, where the expected ensemble-averaged exponent value \( n = 4.0(1) \) has been measured in a sample of \( N = 7 \) cubes (see SI).

Since photoelectron emission is strongly influenced by the local electric field at the particle surface, the electron emission yield would be expected to peak when the laser polarization aligns with the regions of highest electric field enhancement, that is, cube corners.\(^{43,44,49,50,52} \) This is precisely what has been experimentally observed in correlated SPIM-TEM measurements on \( N = 10 \) Ag nanocubes (Figure 5). Note that a similarly marked increase in the SERS signal (i.e., also nonlinearly dependent on local electric field enhancement) had been observed in earlier studies for laser polarization aligned with the nanocube diagonals.\(^{52} \) The present finding of a

Figure 4. (a) Dark field scattering intensity from a single Ag nanocube as a function of the laser polarization angle \( \theta \) (center wavelength, \( \lambda = 800 \) nm), revealing near isotropic behavior anticipated for a 4-fold rotational axis of symmetry. (b) A sequence of electron photoemission images (top) from the same Ag nanocube as a function of laser polarization angle, immediately signaling strongly anisotropic behavior. A polar plot (bottom) of SPIM intensity for a single Ag nanocube as a function of laser polarization angles recorded at a laser intensity \( I = 4.5 \times 10^9 \) W/cm\(^2\). Note the clear four-lobed anisotropy, which for a 4-fold rotational axis of symmetry is qualitatively inconsistent with any linear absorption dependent process such as thermionic emission, but provides strong support for a coherent multiphoton photoemission model.

Figure 5. (a) Polar plots of electron emission rates from two supported, Ag nanocubes (upper left: \( I = 4.5 \times 10^9 \) W/cm\(^2\); bottom left: \( I = 5.6 \times 10^9 \) W/cm\(^2\)) as a function of laser polarization orientation. Corresponding TEM images (right) of the two nanocubes in the same reference frame. Note that the peak electron emission is always observed when the laser polarization aligns with the cube face diagonals (i.e., corners). (b) Quantitative correspondence between (i) direction of the cube corners (\( \theta_{\text{Corner}} \)) and (ii) laser polarization direction resulting in maximum electron emission (\( \theta_{\text{SPIM MAX}} \)) for a sample of \( N = 10 \) Ag nanocubes.
similar polarization-dependent electron ejection propensity further identifies the electric field enhancement induced by the localized surface plasmon resonance as critical for efficient electron emission.

With electron emission from plasmonic nanoparticles established as a multiphoton photoelectric process for ultrafast laser excitation with sub-work function photon energies, the question remains whether the process occurs via a coherent or incoherent absorption of multiple photons. In the latter case, population change in the intermediate states occurs, whereas an in-phase excited state is generated by the radiation field in the former case, with no accompanying change in the intermediate state populations. A general model has been recently proposed by Yalunin et al. that specifically describes coherent MPPE from a surface of a free-electron metal (i.e., perfect electric conductor) upon ultrafast excitation. Since Ag acts as a relatively good free-electron metal in the relevant wavelength range, their theory can be employed to compare the observed experimental photoelectron emission rates from Ag nanocubes with predictions for a coherent process. To include plasmonic excitations into their theory, we treat plasmons classically by assuming that this incident electric field can be scaled by the local plasmon-induced near-field enhancement factor, \(\frac{\|E\|}{\|E_0\|}\). This assumption of a classical limit is justified since multiphoton photoelectron emission under our typical experimental conditions generate plasmon numbers \(N_{pl} \sim 10^6\) orders of magnitude larger than the number \(N_{el} = n = 4\) energetically required for electron ejection.

To implement this theory further, typical electric field enhancement factors of \(\frac{\|E\|}{\|E_0\|} \sim 12\) have been calculated using COMSOL at the corners of a representative cube in vacuum (edge length, \(d = 160\) nm; corner roundness, \(r = 8\) nm) for \(\lambda = 800\) nm excitation. This value is in qualitative agreement with previously reported SERS enhancement factors \(\frac{\|E\|}{\|E_0\|}\) \(\sim 10^4\) to \(10^5\) for Ag nanocubes. If the observable electron emission current is assumed to originate predominantly from the top cube corners, the four-photon photoelectron emission cross-section is predicted to be \(\sigma_{pe}^{(4)} \sim 5.2 \times 10^{-105}\) cm\(^8\) s\(^{-3}\) for circularly polarized \(\lambda = 800\) nm light based on the modified model of Yalunin et al. Circularly polarized light is employed in measuring the electron emission rate as a function of laser intensity to eliminate the signal dependence on the laser polarization direction. The calculated photoelectron emission cross-section compares rather well to the experimental results (see SI) that range from \(\sigma_{pe}^{(4)} \sim 10^{-105}\) to \(10^{-104}\) cm\(^8\) s\(^{-3}\) for different Ag nanocubes. Note that the lower limit is likely to be another order of magnitude smaller (i.e., \(\sigma_{pe}^{(4)} \sim 10^{-106}\) cm\(^8\) s\(^{-3}\)), because signals from many of the nanocubes (~40%) are found to be too small to distinguish from the support film background. Given the simplicity of our assumptions, experimental variations in the electron emissivity of different cubes, and semiquantitative evaluation of the electric near-field enhancement, the observed agreement is extremely good.

We have previously shown that the same approach also predicts the observed electron emission rates in resonantly excited Au nanorods reasonably well. This dual success in describing experimental photoelectron emission rates in two substantially different nanoparticle systems speaks substantially in support of such a coherent multiphoton model. In particular, the results indicate that: (i) coherent multiphoton photoelectron emission is likely a general phenomenon for metallic nanoparticles/nanostructures excited with ultrafast laser pulses with photon energy below material work function, and (ii) the role of nanoparticle plasmons can be effectively included into the coherent MPPE models by simple multiplication of the incident electric field by the near-field enhancement factor \(\frac{\|E\|}{\|E_0\|}\).

In an earlier study of two-photon photoelectron emission from small \((d = 3.6 \pm 0.8\) nm\) Ag nanospheres, the alternative, incoherent MPPE process has been argued to yield \(\sim 10^3\)-fold lower photoelectron current than for a coherent process. Simply stated, this is because the energy (and momentum) of a decaying plasmon has to be transferred to an already excited electron among a much larger number of unexcited conduction electrons. As the particle size and consequently the number of electrons \(N_{el}\) increases, the likelihood for such a process becomes progressively smaller, with the probability scaling as \(P \sim (1/N_{el})^4\). Consequently, the role of incoherent MPPE is anticipated to be negligible compared to the coherent process, particularly as the number of involved photons, and thus intermediate states, increases.

The MPPE signal depends sensitively on the local electric field distribution \([\frac{\|E\|}{\|E_0\|}^4]\) and consequently all factors that affect the electric near-field. For example, local structure can dramatically influence the magnitude of the nanoparticle near-field, suggesting that the MPPE could in principle depend sensitively on tiny differences in topography of the particle surface. Indeed, these nanoparticle-to-nanoparticle variations in structure are likely responsible for observed asymmetries in the four-lobed images of MPPE rate versus excitation laser polarization (Figure S3a), where one diametrically opposed lobal pair is generally stronger than the other by typically 3- to 5-fold. However, for these fourth-order processes, such differences between the adjacent lobes would require only \(\approx 22\%\) (i.e., \(S^{1/8} = 1.22\)) variation in \(\frac{\|E\|}{\|E_0\|}\) for neighboring cube corners, which would in turn be consistent with the slight topological imperfections observed in the HRTEM images.

Since curvature near the cube corners would appear a dominant structural factor influencing the local electric field enhancement, the inferred variation in \(\frac{\|E\|}{\|E_0\|}\) within the same cube implies that the roundness of neighboring corners may slightly differ. Interestingly, we explored the link between observed photoelectron emission rates and the measured corner radii for \(N = 8\) different cubes and found no clear correlation (see SI). This result is surprising and may suggest that only corner features smaller than a typical HRTEM resolution of \(\sim 1\)–\(2\) nm significantly contribute to the overall photoelectron emission. Alternatively, since the corner radius is not measured directly, but rather inferred from the roundness of the corresponding edges, the dominant topological sources contributing to the observed MPPE signal could simply have escaped observation. Indeed, the actual sharpness of the corner topology may be more readily identifiable in HRTEM by tilting the sample, as will be investigated in greater detail in the future.

In summary, spatial and polarization correlated DFM-HRTEM-SPIM studies of individual nanoparticles at high sensitivity and high signal-to-noise offer unique insight into the electron emission process following excitation with high-intensity ultrashort laser pulses. In particular, these studies identify coherent multiphoton photoelectron emission as the most probable mechanism responsible for electron emission from Ag nanocubes, and likely metal nanoparticles in general, when ultrafast excitation with photon energies smaller than the metal work function \((E_{ph} < \Phi)\) is employed. The coherent
MPPE model proposed by Yalunin et al. predicts the experimentally measured absolute photoelectron emission rates reasonably well, with the simple modification that the incident electric field is augmented by the plasmon-induced electric near-field enhancement factor $|E|/|E_0|^{19}$. According to the modified model, the photoelectron emission rate depends sensitively on $|E|/|E_0|$ by scaling approximately with $|E|/|E_0|^{26}$, where $n$ is the minimum number of photons required to overcome the material work function (i.e., $n > \Phi/E_{ph}$). For typical values of $n = 4$, the presence of a plasmon resonance can therefore dramatically enhance the total photoelectron emission yield, even for only relatively modest increase in the incident electric field near the particle surface. In a view toward future directions, this strong sensitivity of MPPE to the local field enhancement factor $|E|/|E_0|$ may dramatically change the present understanding of this important phenomenon.

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