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Plasmon emission in photoexcited gold nanoparticles

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Light emission at the particle plasmon frequency is observed in optically excited spherical gold nanoparticles. We find a photoluminescence efficiency of 10^{-6}, which is essentially independent of particle size and four orders of magnitude higher than the efficiencies determined from metal films. Our experimental findings are explained with a process in which excited *d*-band holes recombine nonradiatively with *sp* electrons, emitting particle plasmons. These plasmons subsequently radiate, giving rise to the photoluminescence observed in the experiment. We determine the quantum efficiencies involved in this process.

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Optically excited metal surfaces show no or very little luminescence. For instance, smooth gold films have photoluminescence (PL) efficiencies of $\sim 10^{-10}$ following excitation of electron transitions from the 5*d* to the 6*sp* bands.[1] In other words, only one photon is emitted per each 10^{10} electron-hole pairs excited. One likely reason for this low PL efficiency is that nonradiative energy relaxation processes of photoexcited carriers in metals, such as Coulomb carrier-carrier scattering, are much faster than radiative electron-hole recombination, thus quenching the photoluminescence.

A unique exception from the rule of low PL yields in metals are *noble-metal nanoparticles*. For instance, PL efficiencies on the order of 10^{-4} have recently been observed in gold nanorods.[2] This is a giant enhancement with respect to $\sim 10^{-10}$ efficiency of smooth gold films. The origin of this effect is as yet unclear. Conceivably, the enhancement may have two different causes, either of which would shift the branching ratio of the competing radiative and nonradiative channels: (a) a *slowing of the nonradiative relaxation* of excited carriers, or (b) an *acceleration of the radiative process* in the nanoparticles as compared to the bulk. The first explanation certainly holds for molecular gold clusters. They show very high PL efficiencies of up to 41%, due to the size-induced opening of gaps in their electronic density of states (DOS), which slow down relaxation.[3,4] However, this explanation cannot apply to nanoparticles of sizes greater than 2 nm, which have DOS sufficiently bulklike.[5] Of the processes leading to carrier relaxation in such nanoparticles, carrier-phonon scattering in these nanoparticles is as fast as in the bulk.[6] Coulomb scattering is even faster in metal nanoparticles than in bulk metals, due to size-dependent screening effects which accelerate electron-electron scattering[7] and lead to emission by hot carriers of particle plasmons (PPs), i.e., collective oscillations of the conduction electrons.[8,9] This implies that the PL enhancement in noble-metal nanoparticles cannot be due to a slowing of nonradiative relaxation.

In Refs. 2 and 10, it was argued, based on a phenomenological model by Boyd *et al.*,[11] that the light emission from the radiative recombination of *sp*-band electrons with *d*-band holes is enhanced by the local field associated with the PP oscillation. This would imply possibility (b), i.e., an acceleration of the radiative process. However, in the present paper, we find a PL enhancement inconsistent with the model of Refs. 2, 10, and 11. The PL efficiency which we measure on near-spherical gold nanoparticles of various sizes is far too high to be explained in this way. In contrast, our experimental findings are explained with a process in which excited *d*-band holes recombine nonradiatively with *sp* electrons, emitting PPs. These plasmons subsequently radiate, giving rise to the PL observed in the experiment. We determine the quantum efficiencies involved in this process.

The experiment is performed as follows: The frequency-doubled output (3.3 eV photon energy) of a Kerr-lens mode-locked titanium-sapphire laser (120 fs pulse duration, 76 MHz pulse repetition rate) is used to excite *d-sp* interband transitions in the gold nanoparticles. The excitation beam with a time-averaged power of 17.8 mW is focused into a cuvette containing size-selected gold nanoparticles in aqueous solution. The diameter of the focused laser beam is 500 μm. The luminescence is collected under an angle of 90° with respect to the excitation beam, spectrally dispersed by a grating spectrometer (Chromex IS250), and subsequently time-resolved in a streak camera (Hamamatsu C 5680) operating in the 3.2 ps time-resolution regime. The spectra are corrected for background, for extinction of excitation light and luminescence due to nanoparticles outside the focal volume, and for instrumental response. The size-selected nanoparticles are stabilized by optically inert citric acid,[12] are near spherical in shape and have size dispersions below 15%. Particles with radii *R* between 1 and 30 nm are studied. Prior to the luminescence measurement, the particle solutions are characterized by measuring their optical densities in a VIS photospectrometer.

The black solid line in Fig. 1 shows the result of the

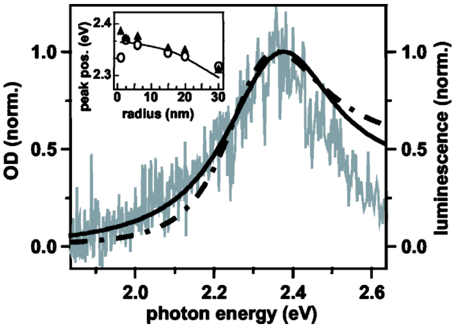

FIG. 1. Optical density (OD, black line) of and photoluminescence (PL, grey line) spectra from gold nanoparticles of 6 nm radius. The dashed-dotted line shows an extinction spectrum calculated using Mie theory. The peak positions of all spectra coincide, indicating the plasmonic nature of the PL. The inset shows the peak positions of OD (triangles) and PL (open circles) spectra from gold nanoparticle solutions of different radii. The solid line represents maxima calculated using Mie theory. The peak positions of the PL closely follow the particle plasmon resonance position.

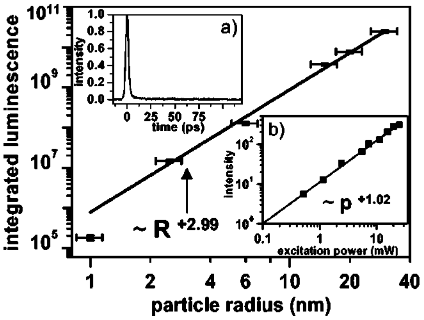

FIG. 2. Spectrally integrated PL intensity from gold nanoparticles of different radii R. The PL is normalized to a common particle concentration of 1.66 μM. Particles from $R=2.5$ nm to 30 nm are considered for the line fit. The error bars reflect the width of the particle-size distribution. Inset (a) shows a temporally resolved PL spectrum from $R=6$ nm particles. The peak width resembles the time resolution of the streak camera mode (3.2 ps). Inset (b) shows the PL from $R=6$ nm particles versus excitation power. The gradient of the fitted line is 1.02.

optical density measurement for a particle radius of $R=6$ nm. The PP resonance, which is caused by the collective oscillation of conduction electrons, is observed as an extinction peak at a photon energy of 2.37 eV. At higher energies the slope of the peak is less steep than at the low-energy side, due to the onset of interband transitions between the 5*d* and 6*sp* bands near the *L* point of the band structure.[5] The grey line shows a PL spectrum from the same nanoparticle solution, integrated over the first 15 ps after pulsed excitation. Except in the interband transition region, the PL spectrum is in good agreement with the optical density spectrum. Both spectra also coincide well with the extinction spectrum calculated using Mie theory[5] for $R=6$ nm gold nanoparticles in aqueous solution as shown by the dashed-dotted line. In particular, the widths of the experimental and calculated extinction peaks are in good agreement, which indicates a low inhomogeneous broadening consistent with the known particle-size dispersion ($<15\%$). The inset shows the peak positions determined from the optical density spectra (triangles), photoluminescence (open circles), and Mie theory calculations (solid line) as functions of R. Good agreement between experimental and calculated positions is found. The slight redshift of the PP peak positions for larger particle sizes is due to a polaritonic effect.[13] The fact that the PL spectrum and the PP peak position shift alike excludes the possibility that the PL spectrum simply reflects the joint density of states of *d* band holes and *sp* band electrons.[1,11] If that was indeed the case, no redshift of the PL spectrum would be observed when the nanoparticle radius is increased. Similarly to our observations, Mohamed*et al.* have shown that for 25 nm-sized gold nanospheres and nanorods of two different aspect ratios the PL spectra peak at the same energy as the extinction spectra.[2,10] We find no shift of the PL peak position when the excitation wavelength is varied. We conclude that the PL peak is associated with the PP resonance.

Inset (a) of Fig. 2 shows a PL trace spectrally integrated over the PP resonance, from nanoparticles with 6 nm radius. Rise and decay of the signal appear to be limited by the 3.2 ps time resolution of the Streak camera. It is therefore not possible to determine the decay time of the PP PL with the present setup. We note that for particles less than 6 nm in radius we also observe a long lived luminescence emission at 440 nm, with a decay time of ~10 ns; this emission is probably due to surface states.[14] Because of the large difference in lifetime we can easily correct the PL spectra for this 440 nm contribution.

Inset (b) of Fig. 2 shows that the emitted intensity, which is spectrally integrated over the PP band, depends linearly on the excitation intensity. This precludes supercontinuum generation or two photon excited PL[15] and thermal radiation[16] of the photoexcited nanoparticles as explanations for the emission observed here, since both phenomena should depend nonlinearly on the excitation intensity. The main part of Fig. 2 shows the PP PL from gold nanoparticles of different radii R. The PL is normalized to a common particle concentration of 1.66 μM. The emitted intensity is proportional to the particle volume. This indicates that the emission at the PP frequency cannot be due to PL involving surface states, since the intensity of such luminescence is expected to depend on the surface area or the surface/volume ratio rather than be proportional to the volume itself. Instead, the volume dependence is easily explained by the fact that the absorption cross section of noble-metal nanoparticles in the interband absorption region is directly proportional to the particle volume. The average number of radiated photons per photoexcited electron-hole (*e*-*h*) pair, i.e., the PL efficiency, appears to be essentially independent of the particle size. We determine the PL efficiency, $\eta_{eh\rightarrow ph}$, quantitatively by comparing the absorbance and PL intensity of the gold nanoparticles with those of Rhodamine 6-G. $\eta_{eh\rightarrow ph}$ is plotted in Fig. 3 as a function of R. Apart from the smallest particle radius, $R=1$ nm, the PL efficiency is close to 10^{-6}, independent of the particle size. This value is four orders of magnitude higher than the PL efficiency of 10^{-10} observed on smooth gold films.

In the following, we will discuss the origin of the PL enhancement in our gold nanoparticles. El-Sayed and co-workers[2] argued that the light emission from the radiative

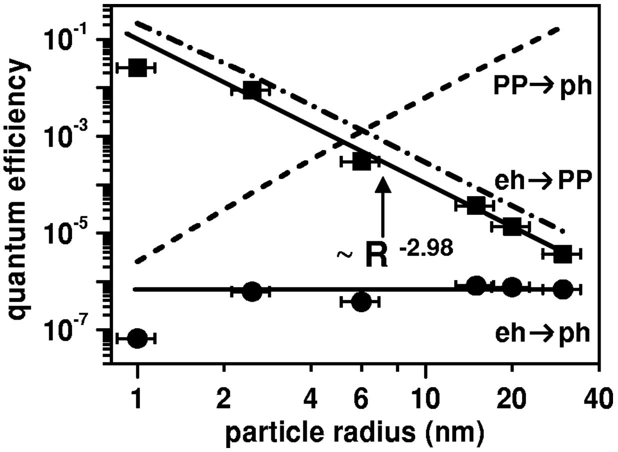

FIG. 3. Quantum efficiencies of various processes versus particle radius R as discussed in the text. Circles, experimental PL efficiency ($eh \rightarrow ph$); solid line, fit to the data for $R > 1$ nm. Dashed line, calculated radiative quantum efficiency of the PP according to Mie theory ($\mathrm{PP} \rightarrow ph$). Squares, plasmon emission efficiency derived from the experiment ($eh \rightarrow \mathrm{PP}$). Straight line, fit to the squares for particle radii >1 nm. Dashed-dotted line, efficiency of resonant plasmon emission as deduced from theory.

recombination of *sp*-band electrons with *d*-band holes is enhanced by the local field associated with the PP oscillation. However, we expect no local-field enhancement in the excitation process in our experiment, since only interband transitions and no PP resonance are excited in our spherical nanoparticles at the excitation photon energy of 3.3 eV. Regarding the emission process, the enhancement of the local field associated with the PP of a spherical gold nanoparticle is on the order of 10 (see, e.g., Ref. 17) and decreases with increasing particle radius due to enhanced radiation damping.[18] It is not possible that the emitted intensity in a linear process such as photoluminescence could be amplified by four orders of magnitude by a mere tenfold local-field enhancement at the emission frequency. This argument suggests that a different mechanism is responsible for the PL enhancement in our experiments.

We propose that the dominant contribution to the PL originates from PPs emitted by excited *d*-band holes. It is known that highly excited carriers in or near metal nanoparticles may relax nonradiatively by emitting plasmons.[8,9,19] For instance, recent pump-probe experiments on copper nanoparticles have given evidence for emission of PPs by Coulomb scattering of *d*-band holes into conduction-band states below the Fermi energy, E_F.[8] Furthermore, electron injection studies have shown that tunnelling electrons with sufficient excess energy may relax by emitting interface and particle plasmons.[19–21] Once the particle plasmons have been generated, they may decay either radiatively by emitting photons, or nonradiatively via transformation into excited *e*-*h* pairs.[17] In our experiment, the photoexcited electrons have an excess energy of no more than 0.9 eV with respect to E_F, which means that they cannot emit any 2.4 eV PPs.[9] In contrast, the photoexcited *d*-band holes have excess energies of up to 3.3 eV. They can therefore relax to *d*-band states from where an energy- and momentum-conserving emission of PPs is possible. Such relaxation of holes within the *d* band is known to be extremely fast, with scattering time of some 10 fs.[22] We thus ascribe the PL observed in our experiment to a three-step process (Fig. 4): a photoexcited *d*-band hole relaxes within the *d* band, then scatters to the conduction band via emission of a PP, which subsequently decays radiatively.

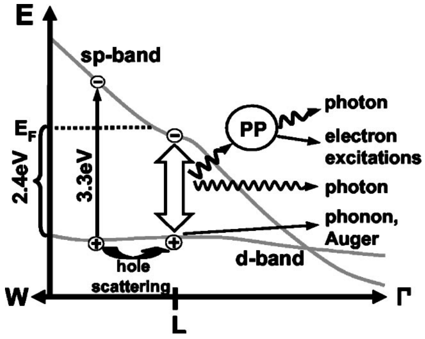

FIG. 4. Schematic representation of $d \rightarrow sp$ interband excitation and subsequent hole relaxation close to the L point of the band structure of gold. A photon with 3.3 eV energy promotes electrons from the *d* band into the *sp* band well above the Fermi level. The holes in the *d* band undergo Auger scattering and hole-phonon scattering. Direct radiative recombination of a *d*-band hole with an electron in the *sp* band below the Fermi surface or emission of a particle plasmon (PP) may occur. The PP subsequently decays either radiatively or nonradiatively.

In the following, we will analyze whether this scenario is consistent with our experimental results. The overall PL efficiency of the three-step process may be written as

$$\eta_{eh \rightarrow ph} = P_{h \rightarrow h'} \cdot \eta_{h' \rightarrow \mathrm{PP}} \cdot \eta_{\mathrm{PP} \rightarrow ph}, \tag{1}$$

where $P_{h \rightarrow h'}$ is the probability of a photoexcited hole to relax to a *d*-band state suitable for PP emission, $\eta_{h' \rightarrow \mathrm{PP}}$ is the quantum efficiency for resonant PP emission by that hole, and $\eta_{\mathrm{PP} \rightarrow ph}$ is the radiative efficiency of the PP. $\eta_{\mathrm{PP} \rightarrow ph}$ can be expressed as $\eta_{\mathrm{PP} \rightarrow ph} = C_{\mathrm{sca}}(\omega_{\mathrm{PP}})/C_{\mathrm{ext}}(\omega_{\mathrm{PP}})$, where $C_{\mathrm{sca}}(\omega_{\mathrm{PP}})$ and $C_{\mathrm{ext}}(\omega_{\mathrm{PP}})$ are the light-scattering and extinction cross sections at the PP resonance frequency, respectively.[23] We use Mie theory[5] to calculate these two cross sections from the dielectric constant of water and the dielectric function of gold, ε.[24] ε includes an added contribution from surface damping for small particle sizes.[5] The resulting radiative efficiency is plotted versus the particle radius R in Fig. 3 (dashed line). $\eta_{\mathrm{PP} \rightarrow ph}$ shows a size dependence close to R^3. This can be understood considering that $\eta_{\mathrm{PP} \rightarrow ph} = \gamma_{\mathrm{PP} \rightarrow ph}/(\gamma_{\mathrm{PP} \rightarrow ph} + \gamma_{\mathrm{nonrad}})$, where $\gamma_{\mathrm{PP} \rightarrow ph}$ and γ_{nonrad} are the radiative and nonradiative decay rates of the PP, respectively. For spherical gold nanoparticles in the size regime studied here, $\gamma_{\mathrm{PP} \rightarrow ph} \ll \gamma_{\mathrm{nonrad}}$ and $\gamma_{\mathrm{PP} \rightarrow ph} \propto R^3$ (see, e.g., Ref. 19), and thus $\eta_{\mathrm{PP} \rightarrow ph} \propto R^3/\gamma_{\mathrm{nonrad}}$. In other words, spherical metal nanoparticles become more efficient radiators with increasing size, due to an increase of the PP polarizability. In a next step, we combine the calculated radiative efficiency $\eta_{\mathrm{PP} \rightarrow ph}$ and the measured PL efficieny $\eta_{eh \rightarrow ph}$ to determine the product $P_{h \rightarrow h'} \cdot \eta_{h' \rightarrow \mathrm{PP}}$ from Eq. (1). This product, which represents the probability, $P_{eh \rightarrow \mathrm{PP}}$, that the photoexcitation of an *e*-*h* pair leads to the emission of a PP, is plotted versus R in Fig. 3 (squares). $P_{eh\to \mathrm{PP}}$ shows a R^{-3} dependence, except at the smallest radius studied here (1 nm). This dependence agrees well with the theoretical prediction of Refs. 8 and 9. In this model, each excited *d*-band hole polarizes the nanoparticle and thus triggers, via the screening motion of the conduction electrons, a collective electron oscillation such that a PP is emitted. The energy required for the PP emission is provided by the hole, which scatters to the conduction band; this scattering process is vertical in k space[8,9] (Fig. 4). The smaller the particle, the more easily it is polarized by the hole, resulting in a R^{-3} dependence of the rate for resonant PP emission, $\gamma_{h'\to \mathrm{PP}}$. We calculate $\gamma_{h'\to \mathrm{PP}}$ according to Eq. (12) of Ref. 8 and from $\gamma_{h'\to \mathrm{PP}}$, the theoretically expected plasmon-emission efficiency $\eta^{(\mathrm{theor})}_{h'\to \mathrm{PP}} = \gamma_{h'\to \mathrm{PP}}/(\gamma_{h'\to \mathrm{PP}} + \gamma_{h',\mathrm{rel}})$. Here $\gamma_{h',\mathrm{rel}}$ is the overall rate of hole scattering processes competing with PP emission, such as Auger scattering, and is assumed to be $(40\ \mathrm{fs})^{-1}$ for holes at the top of the *d* bands of gold.[22] The result of the calculation, which is plotted versus R in Fig. 3 (dashed-dotted line), reproduces the R^{-3} dependence of the experimental $P_{eh\to \mathrm{PP}}$. This agreement confirms the validity of the model proposed here. The remaining discrepancy (approximately a factor of 5) indicates that only a portion of $P_{h\to h'} \approx 20\%$ of all photoexcited holes relax to a *d*-band state from where the resonant emission of a PP is possible (Fig. 4). The other 80% presumably suffer Auger and phonon scattering to the conduction band.

We have thus arrived at a microscopic explanation for the enhanced PL observed from gold nanoparticles. The good agreement between the experimental results and the theory of Ref. 8 indicates that the dominant contribution to the PL originates from PPs resonantly emitted by *d*-band holes, rather than from direct radiative recombination of interband *eh* pairs. The reason for the dominance of the PP-mediated PL over that from direct *eh* interband recombination lies in the much greater polarizability and thus radiative decay rate of the PP as compared to an individual *eh* interband pair. This PP polarizability increases with particle diameter and therefore counterbalances the weakening of PP emission with increasing radius. It is remarkable that the R^{-3} dependence of the PP emission rate $\gamma_{h'\to \mathrm{PP}}$ precisely compensates the R^3 dependence of the radiative PP decay rate $\gamma_{\mathrm{PP}\to ph}$, resulting in a size-independent PL efficiency of 10^{-6} in spherical gold nanoparticles larger than approximately 2 nm. Based on our model, still higher PL efficiencies may be expected for metal nanorods due to their greater polarizability (per unit volume) as compared to nanospheres. This expectation is confirmed by recent experiments on gold nanorods, which have shown PL efficiencies between 10^{-4} and 10^{-3}, depending on rod length.[8] Finally, we note that for plasmon emission by excited *electrons*, size dependencies that are significantly different from R^{-3} have been predicted theoretically.[9,19] We expect that in cases where the plasmon-emission mechanism requires clarification,[25–27] the size dependence of its efficiency should allow an identification of the dominant emission process.

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