Luminescence of quantum dots by coupling with nonradiative surface plasmon modes in a scanning tunneling microscope

Manuel J. Romero* and Jao van de Lagemaat
National Renewable Energy Laboratory (NREL), 1617 Cole Boulevard, Golden, Colorado 80401-3393, USA
(Received 4 June 2009; revised manuscript received 22 July 2009; published 25 September 2009)

The electronic coupling between quantum dots (QDs) and surface plasmons (SPs) is investigated by a luminescence spectroscopy based on scanning tunneling microscopy (STM). We show that tunneling luminescence from the dot is excited by coupling with the nonradiative plasmon mode oscillating at the metallic tunneling gap formed during the STM operation. This approach to the SP excitation reveals aspects of the SP-QD coupling not accessible to the more conventional optical excitation of SPs. In the STM, luminescence from the dot is observed when and only when the SP is in resonance with the fundamental transition of the dot. The tunneling luminescence spectrum also suggests that excited SP-QD hybrid states can participate in the excitation of QD luminescence. Not only the SP excitation regulates the QD luminescence but the presence of the dot at the tunneling gap imposes restrictions to the SP that can be excited in the STM, in which the SP cannot exceed the energy of the fundamental transition of the dot. The superior SP-QD coupling observed in the STM is due to the tunneling gap acting as a tunable plasmonic resonator in which the dot is fully immersed.

DOI: 10.1103/PhysRevB.80.115432 PACS number(s): 78.60.−b, 07.79.Cz, 78.67.Hc, 73.20.Mf

I. INTRODUCTION

The radiative and nonradiative properties (luminescence and extinction) of quantum dots (QDs) can be controlled by the precise excitation of surface plasmons (SPs) in the local environment of the dot.[1] This is a result of the more general principle that the fluorescence emission rate of a molecule depends on the distribution of the electromagnetic field in its surroundings (Purcell effect).[2] This principle is behind the application of plasmon excitation to the detection of single QDs[3] and other nanoscopic objects such as fluorophores[4] and molecules[5] (either by luminescence or extinction spectroscopies), biosensing,[6] and the exploration of *hybrid metal-semiconductor nanostructures* for optoelectronics,[7] photonics,[8,9] and photovoltaics applications.[10] Although much progress has been made, the coupling between the excited plasmon confined to the metallic nanostructure and the electronic states of the dot is not fully understood, a core issue for all the potential applications described above. The discussion of the results remains controversial because (i) the intimate interaction in the nanoscale (which is the most relevant for this coupling) is very difficult to measure directly and, (ii) from the theory, *ab initio* calculations of the electron density distributions in this coupled system are nearly impossible to accomplish because of the dissimilarities in the theoretical approach to the excited electron states of the plasmon and the electronic states of the dot.

In this contribution, we investigate the intimate nature of the SP-QD interaction by a luminescence spectroscopy based on scanning tunneling microscopy (STM). The high localization of tunneling electrons in the STM enables the controlled excitation of plasmons with nanometer resolution. Highly energetic electrons tunneling across a metallic gap excite plasmon modes. Although such plasmon excitations are inherently nonradiative, the dispersion characteristics at the tunneling gap are affected so dramatically at the tip that the plasmon radiates at optical frequencies (with a maximum energy given by the bias applied to the tip). This SP luminescence has been reported extensively in the literature[11–16] and applied to different systems; from metallic nanoparticles[17] to plasmonic corrals.[18] Thanks to this, the plasmon excitation can be measured using conventional optics and photodetectors.

Here, we use (CdSe)ZnS dots of (core)shell structure to investigate the microscopic nature of the electronic coupling between the localized SP oscillating at the metallic tunneling gap (the *localized mode* of the SP or *LSP*) and the electronic states of one single QD present inside the tunneling gap, which is physically under observation in the STM.

II. EXPERIMENTAL

(Sub)mono and monolayers of self-assembled (CdSe)ZnS dots (Evident Technologies) are prepared by immersion of 1,6-hexanedithiol-covered atomically flat gold substrates. The thiol monolayer insulates the dot from the conductive substrate. The monolayers are labeled by the fluorescence emission (nominal) maximum of their respective solutions in nanometers: 488, 556, and 614 nm. This series covers the visible spectrum.

The STM, specifically designed for these measurements, is based on a *X-Y-Z* nanopositioning platform. For the detection of the tunneling luminescence, the tip is positioned in the focal point of a parabolic mirror providing optimum collection efficiency. The light is guided through a spectrograph equipped with a cryogenic multichannel detector [Roper Scientific Silicon EEV 1340×400 charge-coupled device (CCD)]. *Spectrum imaging* combines *spectroscopy* and *imaging* in one single measurement by acquiring the emission spectrum (the output of the CCD) in synchronization with the scanning of the STM tip. After the acquisition is complete, the resulting *spectrum series* can be processed to reconstruct maps of the photon intensity (resolved in energy), photon energy, or extract the spectrum for a selected area on the STM image. This setup is described in more detail elsewhere.[19]

 ©2009 The American Physical Society

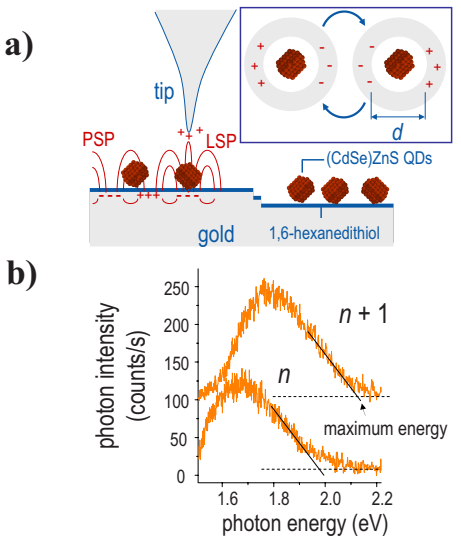

FIG. 1. (Color online). (a) Schematics of the STM measurements. The dots are excited by the localized mode of the plasmon excitation (LSP), which is basically an oscillating dipole aligned with and confined to the tunneling gap. A propagating mode (PSP) also exists. A simplified model for the interpretation of the STM measurements can be represented by a metallic cavity (or shell) in which the dot is inserted (inset illustration). The cavity acts as a tunable plasmonic resonator. (b) SP tunneling luminescence spectrum (raw data) for modes of increasing energy with V_n=2.3 V and V_{n+1}=2.7 V, corresponding to an atomically flat gold substrate showing the conventional (111) reconstructed surface. No dots are present.

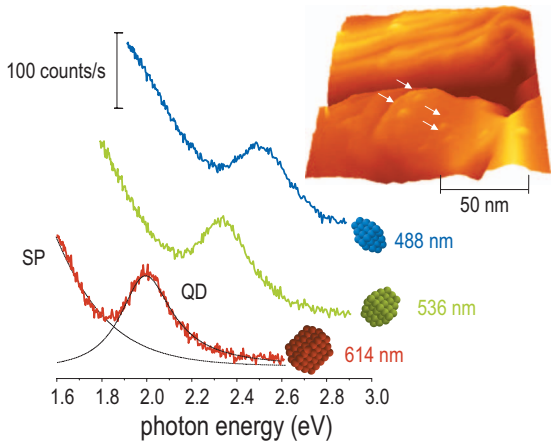

FIG. 2. (Color). Tunneling luminescence from (CdSe)ZnS dots of fluorescence 614, 536, and 488 nm (in solution). The SP and QD contributions to the spectrum are easily differentiated (shown for the 614 nm QD). The STM image corresponds to a 614 nm dot (sub)monolayer where individual dots can be seen. V=+500 mV, I_t=500 pA.

For the STM measurements here described, PtIr tips with controlled geometry are provided by the Evans analytical group (EAG) (nominal radius $r \sim 10$ nm, aspect ratio better than 5:1). The use of these tips with controlled geometry largely reduces the effects of multiple and/or dull tips on the plasmon spectral response.[12] Similar results are obtained with *ultrasharp* ($r \sim 10-20$ nm) *electrochemically etched* tungsten and gold tips, although the stability of the STM operation under the high tunneling current ($I_t \sim 10-20$ nA) needed for the SP excitation is superior for PtIr tips.

III. PLASMON EXCITATION IN THE STM

The discussion of the SP-QD interaction requires first an understanding of the fundamentals of the plasmon excitation in the STM.[20,21] The metallic tunneling gap can be envisioned as a model of a cavity in which the object under observation is embedded (in our case, a single dot)—see illustration in Fig. 1(a). In this configuration the dot is fully immersed in the field of the LSP, an oscillating dipole confined to the tunneling gap, and the SP-QD coupling is expected to be maximized. In the configuration that is more generally proposed, in which the dot is tethered to a metallic nanosphere or nanoshell, the distribution of the plasmon field is obviously very different.

The LSP mode(s) supported by the optical cavity at the tunneling gap are determined by the *optical* radius of the tip r and the tunneling gap itself [expressed by the diameter d in the simplified model of the STM-induced cavity in Fig. 1(a)]. LSP modes of increasing energy can be excited by simply increasing the voltage applied to the tip V (and therefore the energy of the tunneling electrons). These modes are confined at the STM-induced cavity and, therefore, quantized ($n=1,2,3,\ldots$). Figure 1(b) shows the tunneling luminescence spectrum of LSP modes n and $n+1$ when increasing the bias from V_n=2.3 V to V_{n+1}=2.7 V. In these measurements, we operate under constant tunneling current conditions (closed feedback) and therefore, the tunneling gap is adjusted to maintain the tunneling current setpoint when increasing or decreasing the bias. Because the LSP modes at the tunneling gap are most sensitive to the *optical* radius of the tip, these variations only affect slightly the plasmon spectral response.

The spectrum reflects the energy distribution of the radiating plasmon (which is basically equivalent to the energy distribution of the tunneling electrons undergoing inelastic scattering) with a maximum energy corresponding to the most energetic tunneling electron transferring all its energy to the excitation of the LSP mode. This upper limit increases with V but depends on the local tunneling barrier seen by the electron and, therefore, does not coincide with V.

IV. RESULTS AND DISCUSSION

We have succeeded in exciting tunneling luminescence from single (CdSe)ZnS dots when they are embedded in the plasmonic cavity formed during the STM operation. Figure 2 shows the tunneling luminescence spectrum obtained from dots with fluorescence at 614, 536, and 488 nm. The inset corresponds to an STM image of a (sub)monolayer where dots can be resolved. The SP and QD contributions to the spectrum are easily differentiated. Three possible origins can be postulated for the observed luminescence from the quantum dots. The schematics for each process is shown in Fig. 3.

(a) Resonant electron tunneling involving both the HOMO and LUMO of the dot (it can be visualized as a direct

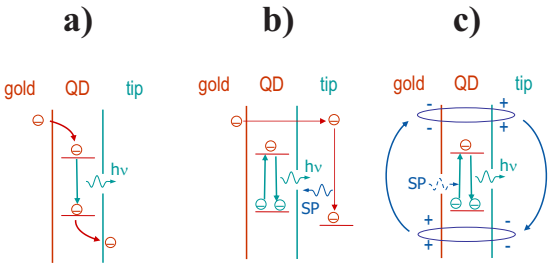

FIG. 3. (Color online) Three possible origins for the tunneling luminescence of the dots. (a) Resonant electron tunneling with LUMO→HOMO recombination. (b) Excitation of the dot by the plasmon radiation and subsequent radiative recombination at the dot (this process is basically photoluminescence). (c) The oscillating dipole associated to the plasmon transfer its energy to the dot without the intervention of a photon (nonradiatively), either directly or through one or a sequence of hybrid SP-QD states. The excited dot relaxes with the emission of a photon.

transfer of an electron and a hole to the dot from each electrode) with radiative LUMO→HOMO recombination. This process will be accompanied by the extinction of the plasmon luminescence.[19]

(b) Electrons tunnel across from one electrode to the other without much perturbation from the presence of the dot, exciting a plasmon mode that recombines with the emission of photons. The photon promotes one electron from the HOMO to the LUMO that subsequently recombines with the emission of a photon from the dot.

(c) The oscillating dipole associated to the plasmon transfers its energy to the dot without the intervention of a photon (nonradiatively), either directly or through one or a sequence of hybrid SP-QD states. The excited dot relaxes with the emission of a photon.

In order to gain insight into the physics of the luminescent dots in the STM and the microscopic aspects of the SP-QD coupling, we performed a comprehensive investigation of spectral time sequences acquired under different settings (voltage applied to the tip V, tunneling current I_t) over multiple locations of each dot monolayer. We observe luminescence from the dot when (and only when) the maximum energy of the plasmon excitation as seen on the spectrum coincides (i.e., is in resonance) with the fundamental (HOMO-LUMO) transition of the dot. This is exemplified by Fig. 4 for the dots with nominal fluorescence of 488 nm. When the maximum energy of the luminescence spectrum associated to the plasmon excitation is below a certain threshold, the dot does not emit, even though the input energy (the applied bias) is sufficient to excite the dot by direct transfer (the postulated process *a*). Only when the plasmon excitation is on the onset of the threshold we do observe luminescence from the dot.

Figure 5 shows a time sequence of the maximum energy of the SP emission spectrum in which V increases from 2.1 to 2.7 V with the tip located over a single dot (nominal fluorescence of 614 nm). In the dot bright state (indicated by vertical lines) the plasmon excitation is in a resonant state with the fundamental transition of the dot. Fluctuations in the tunneling gap during the measurement causes the dot to turn on

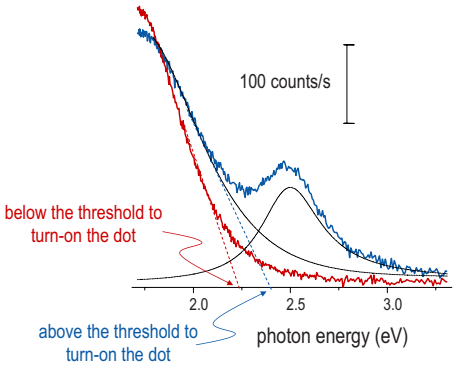

FIG. 4. (Color online) Tunneling luminescence spectroscopy (488 nm monolayer shown). When the energy of the SP is below the fundamental transition of the dot, the dot does not luminescence even though the input energy ($e \times V$) is sufficient for resonant tunneling through the LUMO→HOMO. When the SP resonates with the fundamental transition of the dot, on the other hand, the dot does luminescence with high efficiency.

and off. This is due more to the plasmon excitation falling below the threshold than to the 'blinking' of the (CdSe)ZnS dot. Actually, charge storage in the dot, which is basically responsible for the "blinking," will cause the extinction of the plasmon luminescence. This is something that we observe and depends on the time scale used for the acquisition of the spectra, but is being removed from the time sequences for clarity. Because of the need of energizing the plasmon excitation up to a threshold energy near the fundamental transition of the dot, the number of events of luminescence recorded decreases with the increase in the HOMO-LUMO separation [number of luminescent QDs N, $N(614\ \text{nm}) > N(536\ \text{nm}) \gg N(488\ \text{nm})$].

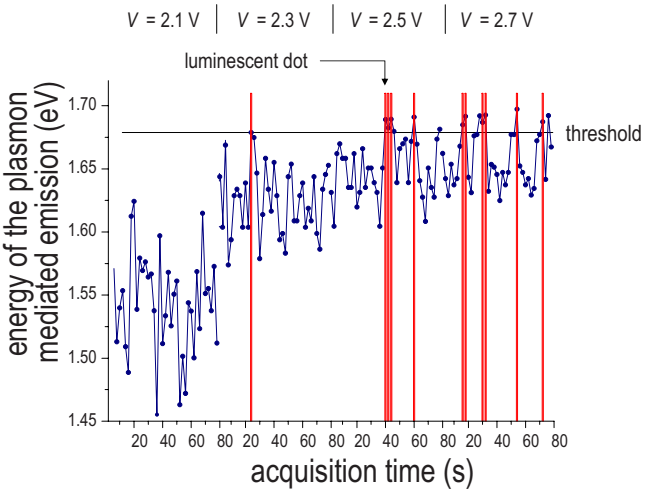

FIG. 5. (Color online). Time sequence representing the maximum energy of the SP emission spectrum in which V increases from 2.1 to 2.7 V with the tip located over a single dot (nominal fluorescence of 614 nm). When luminescence from the dot is observed (indicated by vertical lines) the plasmon excitation is in a resonant state with the fundamental transition of the dot. Clearly, a threshold in the energy of the SP has to be reached to stimulate luminescence from the dot.

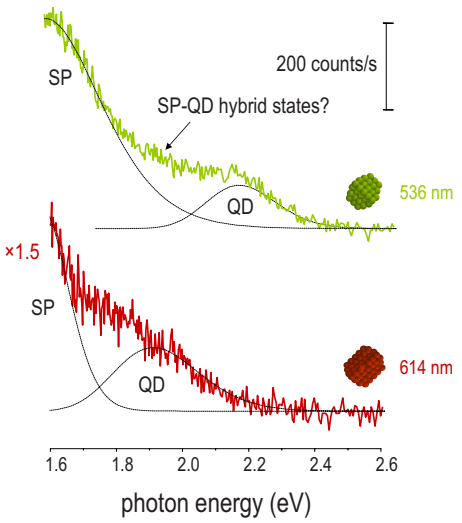

FIG. 6. (Color online). Selected tunneling luminescence spectra (one corresponding to the 614-nm dot and the other to the 536-nm dot) that suggest the participation of one or multiple hybrid SP-QD state(s) in the SP excitation of the dot luminescence: a quasicontinuum of states seems to connect the SP to the QD emission.

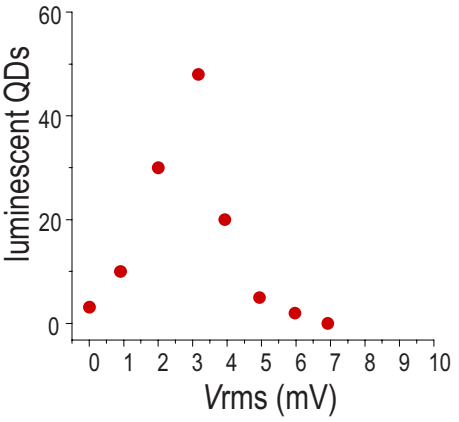

FIG. 7. (Color online) Number of luminescent dots for a given time sequence versus the oscillation voltage of the Z piezo (expressed in mV, V_{rms}). This superimposed mechanical oscillation, which the feedback electronics cannot follow, induces the vibration of the tip up and down above the quantum dot over a short distance. A maximum number of events of luminescence is recorded when an optimum QD-SP coupling is achieved.

On the question of SP-QD hybridization, tunneling luminescence spectroscopy also suggests that an excited SP-QD hybrid state can participate in the excitation of QD luminescence. Figure 6 shows tunneling luminescence spectra (corresponding to dots with nominal fluorescence at 614 and 536 nm) in which a quasicontinuum of states seems to connect the SP to the QD emission. If such transitional states are indeed a consequence of SP-QD hybridization and our assumption of QD luminescence excited through a SP in resonance with the dot fundamental transition holds true then a resonant SP-QD hybrid state (SP like) can be responsible for the excitation of QD luminescence. No evidence of hybridization was found for the 488 nm dots.

To investigate the impact of the strength of the dipole field on the SP-QD coupling we added an oscillating voltage to the Z piezo of a frequency above the time response of the feedback electronics (>2 kHz). Such an escalating voltage causes the tip to vibrate up and down above the quantum dot over a short distance. The strength of the SP dipole field sensed by the dot will oscillate accordingly during the cycle of expansion and contraction of the dipole. Because the dipole is basically aligned with the tunneling gap, the distribution of the dipole field does not significantly change during the oscillation. We have observed that the addition of this nanoscale vibration to the tunneling gap increases the number of bright dots (up to a factor of ten or so) during a given time sequence, suggesting that not only the energy of the plasmon excitation but also the strength of the dipole field in the vicinity of the dot regulates the efficiency of the QD luminescence. This is shown in Fig. 7, where the density of luminescent dots increases with the amplitude of the vibration at the tunneling gap until an optimum QD-SP coupling is attained. On the possibility that this effect can be explained by an easier tuning to resonant tunneling conditions (not to the strength of the dipole field), no QD luminescence is observed when the energy of the plasmon is below the fundamental transition of the dot, although the conditions for resonant electron tunneling through the dot [process a in Fig. 3(a)] must exist. Not only the SP must be present, but the energy and strength of the SP dipole field are critical to the efficient excitation of the QD luminescence.

Finally, we have observed that the presence of the QD imposes restrictions to the maximum energy of the plasmon excitation in the STM. Independent of the input energy (the voltage applied to the tip V) the SP cannot exceed the energy of the fundamental transition of the dot. This is evident from the time sequence in Fig. 5 where the SP energy does not rise above the threshold energy corresponding to the optical transition of the dot. In the absence of QDs, the energy of the SP gradually increases with the applied voltage up to the upper limit imposed by the transition between the Au-d band and the Fermi level (at 2.45 eV) and/or other local factors at the tunneling gap. However, in the case of a dot in the cavity, the fundamental transition becomes an unsurpassable "ceiling" for the plasmon excitation. This self-regulating process can be explained by a fast electron transfer from the electrode to the dot's LUMO; or using a different perspective, by inelastic scattering of the tunneling electron by the dot with the corresponding loss in energy ($E_{f,\mathrm{tip}}-E_{\mathrm{LUMO}}$ for negative tip bias, $E_{f,\mathrm{sub}}-E_{\mathrm{LUMO}}$ for positive tip bias). This is yet additional evidence of the very high SP-QD coupling for this experimental configuration, in which the electronic states of the dot can participate in the electron tunneling and tunneling electrons can undergo inelastic scattering by the dot, thereby affecting the plasmon excitation, which in turn controls the luminescence of the dot.

Based on these results, we suggest that the tunneling luminescence from the dot is caused by coupling with the nonradiative mode of the plasmon excitation (process c, Fig. 3(c)). A luminescent dot is only seen when the energy of the plasmon excitation is in resonance with the fundamental transition of the dot. The spectrum of the radiating plasmon is below this threshold energy when the tip is above the dot

and, therefore, fluorescence of the dots caused by the plasmon radiation seems to be dubious.[22] The fact that the strength of the dipole field is affecting the efficiency of the dot emission supports the nonradiative SP-QD coupling. The naturally occurring fluctuations of the tunneling gap during the STM operation are the reason that QD luminescence is observed even when no vibration is exerted over the tunneling gap. The possibility of SP-QD hybridization as an intermediate state in the excitation of QD luminescence also supports the nonradiative SP coupling scenario. If the process *a* were the most relevant, only conditions ensuring resonant electron tunneling through the dot will be necessary, without the contribution of the plasmon excitation. This is not the case. The SP must be present, its energy should be in resonance with the fundamental transition of the dot, and the strength of the SP dipole field should be optimum for the dot to luminescence with high efficiency. The process *a* might be possible, but its efficiency is not comparable to process *c*.

V. SUMMARY AND CONCLUSIONS

In conclusion, we have investigated the electronic coupling between semiconductor QDs and SPs by a luminescence spectroscopy based on STM. The STM provides both the nanoscale resolution to investigate one single dot and the capability to locally excite and control the plasmon excitation. The SP confined at the tip can be envisioned as an oscillating dipole aligned with the tunneling gap in which the dot is fully immersed. Therefore, the tunneling gap functions as a tunable plasmonic resonator. We have succeeded in exciting luminescence from single dots using the STM SPs. Based on the arguments given in the previous section, we suggest that tunneling luminescence from the dots is excited by coupling with nonradiative surface plasmon modes.

Many open questions remain, especially about the participation of intermediate excited SP-QD hybrid states in the QD luminescence. Low-temperature STM will be needed to better resolve the SP-QD hybrid state(s) and time-resolved spectroscopy will be required to investigate the dynamics of the excitation.

The basic aspects of the SP-QD coupling should be considered in the future development of functional hybrid metal-semiconductor nanostructures. The plasmon modes of the metallic nanostructure should be in resonance with the electronic transition of the photoactive nanosemiconductors (QDs, molecules, or similar), paying special attention to the three dimensional distribution of the SP field and how the active molecules are immersed within.

ACKNOWLEDGMENTS

This work was funded by the Photochemistry and Radiation Research Program of the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Division of Chemical Sciences, Geosciences and Biosciences, under Contract No. DE-AC36-99GO10337 to NREL.

*FAX: (303)384-6604; manuel.romero@nrel.gov

[1] K. T. Shimizu, W. K. Woo, B. R. Fisher, H. J. Eisler, and M. G. Bawendi, Phys. Rev. Lett. **89**, 117401 (2002).
[2] E. M. Purcell, Phys. Rev. **69**, 674 (1946).
[3] J. N. Farahani, D. W. Pohl, H.-J. Eisler, and B. Hecht, Phys. Rev. Lett. **95**, 017402 (2005).
[4] P. Anger, P. Bharadwaj, and L. Novotny, Phys. Rev. Lett. **96**, 113002 (2006).
[5] F. Rossel, M. Pivetta, F. Patthey, and W.-D. Schneider, Opt. Express **17**, 2714 (2009).
[6] K. Aslan, I. Gryczynksi, J. Malicka, E. Matveeva, J. R. Lakowicz, and C. D. Geddes, Curr. Opin. Biotechnol. **16**, 55 (2005).
[7] P. Vasa, R. Pomraenke, S. Schwieger, Yu. I. Mazur, Vas. Kunets, P. Srinivasan, E. Johnson, J. E. Kihm, D. S. Kim, E. Runge, G. Salamo, and C. Lienau, Phys. Rev. Lett. **101**, 116801 (2008).
[8] W. L. Barnes, A. Dereux, and T. W. Ebbesen, Nature (London) **424**, 824 (2003).
[9] N. Yu, J. Fan, Q. J. Wang, C. Pflügl, L. Diehl, T. Edamura, M. Yamanishi, H. Kan, and F. Capasso, Nat. Photonics **2**, 564 (2008).
[10] A. J. Morfa, K. L. Rowlen, T. H. Reilly III, M. J. Romero, and J. van de Lagemaat, Appl. Phys. Lett. **92**, 013504 (2008).
[11] J. K. Gimzewski, B. Reihl, J. H. Coombs, and R. R. Schlittler, Z. Phys. B **72**, 497 (1988).
[12] R. Berndt, J. K. Gimzewski, and P. Johansson, Phys. Rev. Lett. **67**, 3796 (1991); **71**, 3493 (1993).
[13] R. Berndt and J. K. Gimzewski, Phys. Rev. B **48**, 4746 (1993).
[14] A. Downes and M. E. Welland, Phys. Rev. Lett. **81**, 1857 (1998).
[15] A. Downes, P. Guaino, and P. Dumas, Appl. Phys. Lett. **80**, 380 (2002).
[16] N. Nilius, H. M. Benia, C. Salzemann, G. Rupprechter, H.-J. Freund, A. Brioude, and M. P. Pileni, Chem. Phys. Lett. **413**, 10 (2005).
[17] N. Nilius, N. Ernst, and H.-J. Freund, Phys. Rev. B **65**, 115421 (2002).
[18] S. Egusa, Y. H. Liau, and N. F. Scherer, Appl. Phys. Lett. **84**, 1257 (2004).
[19] M. J. Romero, J. van de Lagemaat, I. Mora-Sero, G. Rumbles, and M. M. Al-Jassim, Nano Lett. **6**, 2833 (2006).
[20] S. J. Ushioda, J. Electron Spectrosc. Relat. Phenom. **109**, 169 (2000).
[21] M. J. Romero, J. van de Lagemaat, G. Rumbles, and M. M. Al-Jassim, Appl. Phys. Lett. **90**, 193109 (2007).
[22] We have observed that one single dot can partially absorb light from the radiating plasmon near the fundamental transition of the dot (the process *b*). This is seen as a dip in the emission spectrum of the plasmon (see supporting information). This occurs when the dot is in close proximity to the STM tip but not when the electrons tunnel across the dot. Indeed, this absorption line on the spectrum is never seen for monolayers, where the gold substrate is completely covered by QDs.