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# Propagating Surface Plasmon Induced Photon Emission from Quantum Dots

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**ABSTRACT**

**We investigate the interaction between propagating surface plasmons in silver nanowires and excitons generated in quantum dots. We show propagating surface plasmons can excite excitons, which results in quantum dot emission. In this process, the energy is directly transferred from the propagating surface plasmons to the excitons without converting to photons. Furthermore, we demonstrate the reverse process where the decay of excitons generates surface plasmons.**

Surface plasmons (SPs) are collective electronic excitations evanescently confined along the interface of a conductor and a dielectric. SP resonance-based research and its applications has emerged as a very active field (generally referred to as "plasmonics").[1,2] SPs can propagate in metallic structures with dimensions much smaller than the wavelength of light and, thus, possess great potential for nano-optics and optical interconnects.[3−5] Recently, the propagation of SPs in Ag nanowires (NWs) has received increasing attention.[6−8] Propagating SPs can be launched at the discontinuities of the NWs, such as at the tips or at kinks. Also, nanoparticles adsorbed on Ag NWs can facilitate the coupling between photons and SPs. More recently, extremely sensitive remote excitation of surface-enhanced Raman scattering at the single molecule level was demonstrated via propagating SPs in Ag NWs.[9] In a different system of a metal nanoparticle chain, Maier et al. showed that fluorescent nanospheres could be excited via remote excitation of propagating SPs about 0.5 $\mu$m away.[10]

Owing to the potential key roles of quantum dots (QDs) in quantum information and nanophotonics,[11−14] interactions of SPs and QDs represent a topic of great interest. Both experimental and theoretical investigations show that the emission properties of QDs can be significantly modified near the metallic nanostructures. Depending on the details of the configurations, either enhancement or quenching has been observed.[15−20] Recent investigations have further extended into the regime of interactions of quantum emitters such as QDs and propagating SPs. For example, Fedutik and co-workers studied the exciton−plasmon−photon conversion in a Ag NW/CdSe QD system.[21] Akimov and co-workers reported on the coupling of a single exciton in a QD and propagating SPs.[22] These studies bring about an exciting possibility to create a technology platform which integrates SP-based passive elements and QD-based active elements. However, these studies primarily focused on the conversion of QD excitons into SPs. The reverse process—conversion of SPs into exciton excitations in QDs—to the best of our knowledge, has not yet been realized.

In this Letter, we demonstrate that propagating SPs in Ag NWs can excite QDs. The propagating SPs interact with the QDs and result in QD emission, in which process the energy is directly transferred from the propagating surface plasmons to the excitons. Moreover, the excited QDs can also induce the generation of propagating SPs in the Ag NW. In other words, the interaction between QDs and SPs in NWs is bidirectional.

The Ag NWs were prepared by a wet-chemical method.[23] The synthesized Ag NW colloid was washed via centrifugation in acetone and ethanol separately and redispersed in ethanol for future use. These Ag NWs were about 100 nm in diameter and a few to tens of micrometers in length with single crystalline structure. A typical scanning electron microscope (SEM) image of the NWs is shown in Figure 1a. A drop of the dilute solution of Ag NWs in ethanol was

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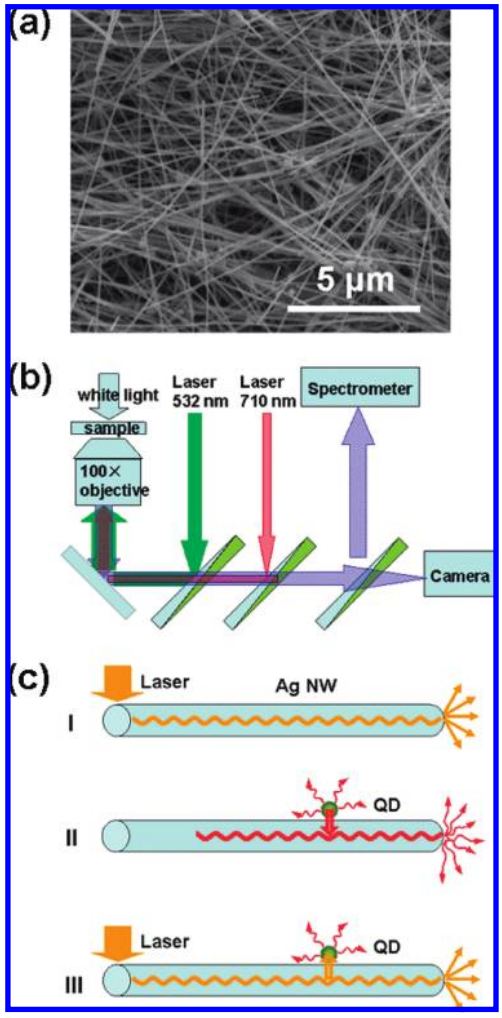


**Figure 1.** (a) SEM image of the Ag NWs. (b) Sketch of experimental setup. (c) Schematic illustration of the processes of the studied system.

placed on a clean glass substrate and dried naturally. Then $SiO_2$ of thickness 25 nm was deposited on the NWs using plasmon depositions to prevent the quenching of QD emission by the Ag NWs. QDs (fluorescence emission centered at ~800 nm) with a CdSeTe core and a ZnS shell of concentration 8 $\mu$M (Invitrogen, SKU# Q21371MP) were diluted to 8 nM with deionized water. Then a drop of 8 nM QD solution was spin-coated on the $SiO_2$-coated Ag NWs at 3000 rpm for 60 s.

The schematic shown in Figure 1b illustrates the experimental setup. White light was used as the illuminating source in transmission mode to find the Ag NWs on the sample. A continuous-wave laser at 532 nm was used for wide field excitation of the QDs, while a mode-locked Ti:sapphire laser (pulse width ~200 fs) centered at 710 nm was used to launch propagating SPs in Ag NWs and excite QDs. A long working distance, 100× objective (NA = 0.7) was used to focus the laser on the sample. The scattered light and fluorescence light from the sample were collected with the same objective and directed to a room temperature CCD camera for imaging or to a spectrometer with a liquid nitrogen cooled CCD for spectral measurements. For imaging, a band-pass filter (Chroma, HQ800/30) centered at 800 nm with a 30 nm spectral width was employed to select the emission from the QDs. For spectral measurements, a long pass filter (Thorlabs, FEL0750) with a 750 nm cutoff wavelength was used to block out the laser.

There are three processes, illustrated in Figure 1c, which are relevant to this study. When the 710 nm laser is focused on the NW end, the SPs are launched and propagate in the NW. At the discontinuities of the NW, the propagating SPs couple out as photons. This process is labeled as process I. The second process (labeled II) entails the excitation of QDs near the Ag NWs whose exciton decay can generate propagating SPs in the NWs. This process is what was investigated in both Fedutik and Akimov's work.[21,22] The third process (labeled III) involves launching the SPs at the discontinuity of NWs, the interactions of the SPs with the QDs which generate excitons, and the radiative decay of excitons which are detected as photons. The focus of this Letter is on the third process. It should be noted, in the middle of process III, the exciton decay can also transfer its energy into generation of propagating SPs, thus reverting to process II. In our study, we have observed all these processes.

In Figure 2a, a Ag NW with a kink is shown. The 710 nm wavelength laser light was focused on the bottom end of the NW to launch propagating SPs. Figure 2b shows that bright spots were detected at both the wire kink and the upper tip where the propagating SPs coupled out as photons, which is process I in Figure 1c. The spectra of the laser and the light coupled out are shown in Figure 2c. It can be seen that the spectrum stays almost the same when the laser propagates in the NW and couples out at the discontinuities. The small deviation at the shorter wavelength edge can be attributed to stronger SP damping at shorter wavelengths which has been demonstrated by Fedutik et al.[24] Figure 2d shows the wide-field excitation QD emission image, using the 532 nm laser as the excitation source and a band-pass filter (800/30 nm) to allow direct imaging of QD emissions. The wide-field excitation image shows that while there is strong emission of the QDs near the shorter segment of the NW probably due to the higher QD concentration, there is very little QD emission near the longer segment of NW.

In Figure 2e, the image was acquired with the same band-pass filter but with the 710 nm excitation source focused on the bottom NW tip. In this case, while the excitation is at a remote location (the bottom tip of the NW), QD emission can be observed along the NW. Also shown in Figure 2f are spectra of the QDs measured through a 750 nm long pass filter (black curve) and an 800/30 nm band-pass filter (red curve). It should be emphasized that the QD emission is excited by the propagating SPs directly. Since the propagating SPs can only couple out as photons at the wire kink and tip, the emission at the upper part of the wire is the result of direct interaction between SPs and QDs.

Figure 3 shows that the excited QDs can also launch the SPs in the Ag NW, which propagate in the NW and finally couple out at the NW tips (process II in Figure 1c). In Figure 3b, we show the wide field excitation QD emission image by using the 532 nm laser as the excitation source. The corresponding Ag NW image is shown in Figure 3a. When

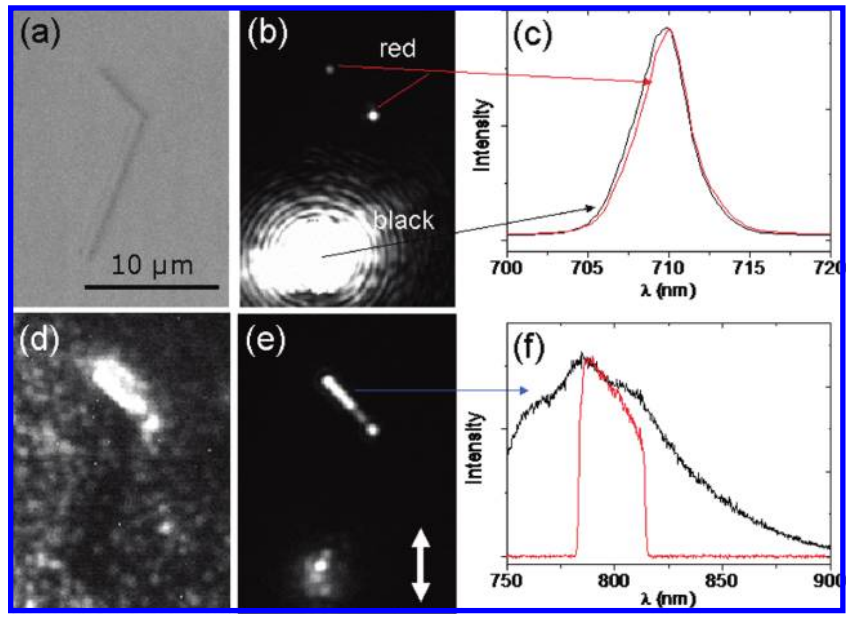


**Figure 2.** (a) White light transmission image of an Ag NW. (b) Optical image with 710 nm laser focused on the bottom NW tip. (c) Spectra of laser (black) and light coupled out (red). (d) QD emission image with wide-field excitation by a 532 nm laser. (e) Image of QD emission induced by propagating SPs in the Ag NW using an 800/30 nm band-pass filter. The 710 nm laser power is about 200 $\mu$W, and exposure time is 5 s. (f) Spectra measured at the bright part of the NW remotely excited in (e) with 750 nm long pass filter (black) and 800/30 nm band-pass filter (red), respectively. Scale bar is the same for all images. The white arrow in (e) indicates the polarization of the 710 nm laser.

the 710 nm laser was focused on a spot in the middle of the straight NW (red circle), no light is coupled out at the two ends of the NW, as shown in Figure 3c. This is consistent with the notion that one cannot launch the SPs directly at this location.[7,8] Nevertheless, as the laser can excite excitons in QDs at this location, there exists a decay channel for these excitons into propagating SP excitations (process II in Figure 1c). Indeed, such exciton−SP conversion can be seen in Figure 3d when we inserted the band-pass filter and increased the laser intensity. The direct excitation leads to QD emission at the focused spot while the exciton−SP conversion is reflected by the photon emission at two ends of the NW. Spectra from the two ends of the wire are similar as Figure 2f, which confirm the exciton−SP conversion process.

On the other hand, if we focus the 710 nm laser light at one end of the NW, we can launch the propagating SPs. The propagating SPs then interact with QDs on the NW and excite the excitons whose radiative decay can be directly observed in the QD emission image shown in Figure 3e (and Figure 3f when SPs are launched at the other end). These two images thus correspond primarily to the SP−exciton conversion process (process III). It should be noted that in these two images, the bright spots at the opposite ends of the launching spots are actually due to the exciton−SP−photon conversion.

Govorov et al. studied theoretically the exciton−plasmon interaction in semiconductor−metal nanoparticle systems.[19,25−27] On the basis of these studies, an energy level scheme shown in Figure 4 can be employed to provide a general picture for the interaction between the propagating SPs in the Ag NW and the excitons in QDs. First, the laser launches the propagating SPs in the Ag NW (process A in Figure 4). Then the SPs interact with the nearby QDs, and some energy is transferred to the QDs (process B in Figure 4), which are excited thereby. After the QDs near the Ag NW are excited, there are three channels to decay, i.e., emission as photons (process C in Figure 4), conversion into heat due to damping (not shown), and the generation of SPs in the Ag NW (process D in Figure 4). Certainly process D can occur by direct excitation of QDs. However, the ability to remotely excite them provides great flexibility in designing functional plasmonic structures.

In our experiment, these individual processes have been clearly distinguished. These include (i) the straightforward excitation of propagating SPs in the NW and then detecting them via conversion to photons (Figure 2b); (ii) direct excitation of QDs whose exciton decay gets converted to propagating SPs and then detected as photons at the discontinuities of the NW (Figure 3d); (iii) excitation of propagating SPs whose interactions with the QDs results in QD emission (Figures 2e, 3e, and 3f); and (iv) the back action of process iii where exciton decay results in SPs which are then converted to photons at the end of the NW (Figure 3, parts e and f).

These processes can potentially form basic building blocks for several technological platforms. For example, propagating SPs inducing QD emission may have potential applications in QD-based bioanalysis. As is known, one important application for colloidal semiconductor QDs is bioanalysis.[28−31] The high photostability and bright emission make QDs a powerful substituent for organic fluorophores. Combined with the remote excitation technique, new excitation and detection approaches may be developed. Moreover, combining the metallic nanostructure based SP waveguide as the passive component with nanoscale emitters (e.g., QDs) as the active component forms a potential new platform for nanoscale photonics.

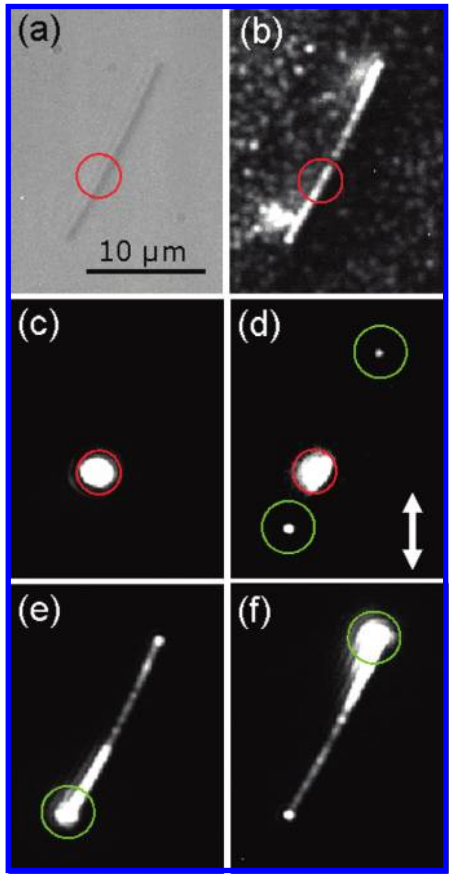


**Figure 3.** (a) White light transmission image of an Ag NW. (b) QD emission image with wide-field excitation. (c) The image with 710 nm laser focused on the position marked with a red circle as in (a) and (b). (d) Emission image acquired using an 800/30 nm band-pass filter and with an excitation wavelength of 710 nm. The laser is focused on the same position as in (c) but with a higher power level of 200 $\mu$W. The exposure time is 5 s. The white arrow indicates the polarization of the laser. (e) and (f) QD emission images obtained by focusing a 710 nm wavelength laser on the wire ends marked with green circles.

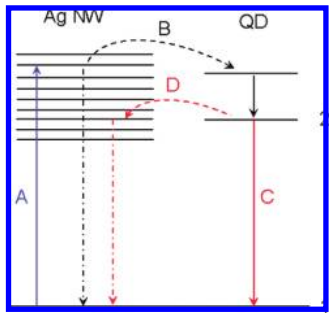


**Figure 4.** Energy structure of the Ag NW−QD system. The arrows show the transitions.

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**Supporting Information Available:** Examples showing the QDs were excited by the SPs in Ag NWs and QDs excited by a laser at different wavelengths. This material is available free of charge via the Internet at http://pubs.acs.org.

## References

(1) Barnes, W. L.; Dereux, A.; Ebbesen, T. W. *Nature* **2003**, *424*, 824–830.
(2) Ozbay, E. *Science* **2006**, *311*, 189–193.
(3) Lal, S.; Link, S.; Halas, N. J. *Nat. Photonics* **2007**, *1*, 641–648.
(4) Bozhevolnyi, S. I.; Volkov, V. S.; Devaux, E.; Laluet, J. Y.; Ebbesen, T. W. *Nature* **2006**, *440*, 508–511.
(5) Oulton, R. F.; Sorger, V. J.; Genov, D. A.; Pile, D. F. P.; Zhang, X. *Nat. Photonics* **2008**, *2*, 496–500.
(6) Ditlbacher, H.; Hohenau, A.; Wagner, D.; Kreibig, U.; Rogers, M.; Hofer, F.; Aussenegg, F. R.; Krenn, J. R. *Phys. Rev. Lett.* **2005**, *95*, 257403.
(7) Sanders, A. W.; Routenberg, D. A.; Wiley, B. J.; Xia, Y. N.; Dufresne, E. R.; Reed, M. A. *Nano Lett* **2006**, *6*, 1822–1826.
(8) Knight, M. W.; Grady, N. K.; Bardhan, R.; Hao, F.; Nordlander, P.; Halas, N. J. *Nano Lett* **2007**, *7*, 2346–2350.
(9) Fang, Y. R.; Wei, H.; Hao, F.; Nordlander, P.; Xu, H. X. *Nano Lett.* **2009**, *9*, 2049–2053.
(10) Maier, S. A.; Kik, P. G.; Atwater, H. A.; Meltzer, S.; Harel, E.; Koel, B. E.; Requicha, A. A. G. *Nat. Mater.* **2003**, *2*, 229–232.
(11) Imamoglu, A.; Awschalom, D. D.; Burkard, G.; DiVincenzo, D. P.; Loss, D.; Sherwin, M.; Small, A. *Phys. Rev. Lett.* **1999**, *83*, 4204–4207.
(12) Ulrich, S. M.; Strauf, S.; Michler, P.; Bacher, G.; Forchel, A. *Appl. Phys. Lett.* **2003**, *83*, 1848–1850.
(13) Hanson, R.; Kouwenhoven, L. P.; Petta, J. R.; Tarucha, S.; Vandersypen, L. M. K. *Rev. Mod. Phys.* **2007**, *79*, 1217–1265.
(14) Schlamp, M. C.; Peng, X. G.; Alivisatos, A. P. *J. Appl. Phys.* **1997**, *82*, 5837–5842.
(15) Shimizu, K. T.; Woo, W. K.; Fisher, B. R.; Eisler, H. J.; Bawendi, M. G. *Phys. Rev. Lett.* **2002**, *89*, 117401.
(16) Kulakovich, O.; Strekal, N.; Yaroshevich, A.; Maskevich, S.; Gaponenko, S.; Nabiev, I.; Woggon, U.; Artemyev, M. *Nano Lett.* **2002**, *2*, 1449–1452.
(17) Pons, T.; Medintz, I. L.; Sapsford, K. E.; Higashiya, S.; Grimes, A. F.; English, D. S.; Mattoussi, H. *Nano Lett.* **2007**, *7*, 3157–3164.
(18) Ueda, A.; Tayagaki, T.; Kanemitsu, Y. *Appl. Phys. Lett.* **2008**, *92*, 133118.
(19) Govorov, A. O.; Bryant, G. W.; Zhang, W.; Skeini, T.; Lee, J.; Kotov, N. A.; Slocik, J. M.; Naik, R. R. *Nano Lett.* **2006**, *6*, 984–994.
(20) Lee, S. Y.; Nakaya, K.; Hayashi, T.; Hara, M. *Phys. Chem. Chem. Phys.* **2009**, *11*, 4403–4409.
(21) Fedutik, Y.; Temnov, V. V.; Schops, O.; Woggon, U.; Artemyev, M. V. *Phys. Rev. Lett.* **2007**, *99*, 136802.
(22) Akimov, A. V.; Mukherjee, A.; Yu, C. L.; Chang, D. E.; Zibrov, A. S.; Hemmer, P. R.; Park, H.; Lukin, M. D. *Nature* **2007**, *450*, 402–406.
(23) Sun, Y. G.; Xia, Y. N. *Adv. Mater.* **2002**, *14*, 833–837.
(24) Fedutik, Y.; Temnov, V.; Woggon, U.; Ustinovich, E.; Artemyev, M. *J. Am. Chem. Soc.* **2007**, *129*, 14939–14945.
(25) Zhang, W.; Govorov, A. O.; Bryant, G. W. *Phys. Rev. Lett.* **2006**, *97*, 146804.
(26) Govorov, A. O.; Lee, J.; Kotov, N. A. *Phys. Rev. B* **2007**, *76*, 125308.
(27) Yan, J. Y.; Zhang, W.; Duan, S. Q.; Zhao, X. G.; Govorov, A. O. *Phys. Rev. B* **2008**, *77*, 165301.
(28) Michalet, X.; Pinaud, F. F.; Bentolila, L. A.; Tsay, J. M.; Doose, S.; Li, J. J.; Sundaresan, G.; Wu, A. M.; Gambhir, S. S.; Weiss, S. *Science* **2005**, *307*, 538–544.
(29) Klostranec, J. M.; Chan, W. C. W. *Adv. Mater.* **2006**, *18*, 1953–1964.
(30) Gill, R.; Zayats, M.; Willner, I. *Angew. Chem., Int. Ed.* **2008**, *47*, 7602–7625.
(31) Resch-Genger, U.; Grabolle, M.; Cavaliere-Jaricot, S.; Nitschke, R.; Nann, T. *Nat. Methods* **2008**, *5*, 763–775.

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