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Surface plasmon polariton-controlled tunable quantum-dot emission

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The unique properties of surface plasmon polaritons, such as strong field confinement and local field enhancement effects, make them ideal candidates to enhance and shape the emission of luminescent nanoparticles. Of these nanoparticles, quantum dots are highly versatile, suitable for vastly different applications due to their size and material tunability. In many cases however, the emission wavelength of the quantum dots is fixed after manufacturing, allowing no control over the *in situ* emission properties. Here, we show fully optical, *in situ* tunability of the emission wavelength of quantum dots, with shifts of over 30 nm, employing surface plasmon polaritons to control the emission wavelength. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4724327>]

The combination of surface plasmon polaritons (SPPs) with emitters, such as dye molecules,^{1–5} rare-earth ions,^{6,7} and quantum dots,⁸ is a heavily studied field of optics. The unique properties of SPPs, such as a strong field confinement, a resonant behavior, and the presence of local field enhancement,^{9,10} explain the broad interest. Of all types of emitters, quantum dots have been shown to be versatile luminescent nanoparticles, suitable for various applications in plasmonics, such as loss compensation and gain,^{11–14} coupling to plasmonic antennas,¹⁵ and imaging of near fields of plasmonic waveguides and bends.¹⁶ Moreover, broader applications like *in vivo* imaging of cells and animals,^{17,18} single emitter studies,^{15,19,20} and fundamental research of quantum effects^{8,20,21} are also possible with quantum dots. The versatility of quantum dots stems from the fact that their absorption and emission properties can be selected by varying the material and size^{22,23} of the individual particles, allowing the particles to be designed to a particular application. However, in many cases, the emission wavelength of the quantum dots is fixed after fabrication, and one has no control over the *in situ* emission properties. Here, we show fully optical, *in situ* tunability of the wavelength of the emission of quantum dots with SPPs as the excitation and wavelength control. The shift in wavelength we obtain with our method is over 30 nm and therefore can be employed with frequency-selective devices to allow, e.g., switchable selective emission redirection.²⁴

Our approach employs basically a classic Kretschmann configuration,⁹ with either a 532 nm frequency-doubled continuous wave (CW) neodymium yttrium aluminium garnet (Nd:YAG) laser for excitation and wavelength control, or a combination of a CW 405 nm diode laser for excitation and a 740–850 nm tunable titanium-sapphire (Ti:Sapph) laser for emission wavelength control. See Figure 1 for a schematic depiction of the setup. Three solutions of quantum dots in toluene were made, each with a different concentration. Subsequently, quantum dots were spin coated onto glass substrates containing a 50 nm thin silver film. The quantum-dot

concentration was 20 μM , 40 μM , and 60 μM , respectively, and the samples in this study are referred to with these concentrations.²⁵

The SPP reflectance minima for p-polarized light with a wavelength of 532 nm were determined for samples with silver and quantum dots applied, as a function of angle. See Figure 2. The minimum in reflectance for the samples with 20 μM , 40 μM , and 60 μM quantum-dot concentrations occurred at $45.6^\circ \pm 0.2^\circ$, $49.2^\circ \pm 0.2^\circ$, and $55.6^\circ \pm 0.2^\circ$, respectively. The plasmonic nature of the interaction of p-polarized light with the sample is clearly visible in Figure 2. In accordance with theory,⁹ for samples with a layer of quantum dots obtained from a more concentrated solution, the plasmon resonance shifts to higher angles due to the effective refractive index of the quantum dots that form the layer, which is greater than that of air.⁸ The inset in Figure 2 shows the reflectance curve of the 60 μM sample for s-polarized light, which indeed does not show any sign of the existence of SPPs: The reflectance is larger than $94\% \pm 3\%$ for all angles of incidence. A similar behavior was observed for the

FIG. 1. Experimental setup to demonstrate SPP-controlled quantum dot emission. (a) Kretschmann setup where a 532 nm laser is used for excitation and wavelength emission control of quantum dots. (b) Kretschmann setup where a 750–850 nm tunable Ti:Sapph laser is used for emission wavelength control and an auxiliary 405 nm diode laser for the excitation of the quantum dots. Here, θ is the angle of incidence.

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FIG. 2. Reflectance minima of glass/silver/quantum dot samples, for p-polarized incident excitation light with a wavelength of 532 nm. The silver layer was 50 nm thick, and the concentration of the quantum dots in solution was 20 μM , 40 μM , and 60 μM . The minimum in reflectance for the 20 μM , 40 μM , and 60 μM samples occurred at $45.6^\circ \pm 0.2^\circ$, $49.2^\circ \pm 0.2^\circ$, and $55.6^\circ \pm 0.2^\circ$, respectively. The inset shows the reflectance curve for s-polarized light for the 60 μM sample, which does not show any sign of the existence of SPPs: the reflectance is larger than $94\% \pm 3\%$ for all angles of incidence. Similar results are obtained for the 20 μM and 40 μM samples (not shown). The lines are guides for the eye.

20 μM and 40 μM samples, but these curves were omitted from the graph for clarity.²⁵

Subsequently, the excitation light (here, 532 nm) was blocked with a 550 nm long pass filter and a spectrometer was used to monitor the emission spectrum of the quantum dots. The emission spectrum of the quantum dots was recorded as a function of angle of the excitation light, and as a function of excitation power. Then, the peak emission wavelength of the quantum dots was determined by fitting a Gaussian curve to the recorded spectrum. In Figure 3, the peak wavelength as a function of angle and power are plotted for the 20 μM , 40 μM , and 60 μM samples. We observe a clear, systematic shift of the peak emission wavelength towards longer wavelengths with increased pumping of the quantum dots, the largest shift in emission wavelength coinciding with the SPP resonance angle of the excitation.

Figure 4(a) shows the shift in the quantum dot emission peak as a function of power of the 532 nm laser, measured at the surface plasmon resonance for that wavelength. Here, a roughly linear behavior is observed for powers of up to approximately 4 W. Then, the curves for the 40 μM and 60 μM samples start to deviate from a straight line, something we attribute to sample degradation, see also below. The maximum shift observed is for the 20 μM sample, of $34.3 \text{ nm} \pm 0.9 \text{ nm}$, corresponding to $99 \text{ meV} \pm 2 \text{ meV}$.

We also show that the shift of the emission wavelength can be controlled independently and is not directly tied to the process of exciting the quantum dots, which is shown by experimental results obtained with the setup as shown in Figure 1(b). The quantum dots are excited by pumping with a 405 nm diode laser at a low power of 1 mW, under near-normal incidence. A tunable Ti:Sapph IR laser is used to induce SPPs in the sample, which are used to control the emission wavelength of the quantum dots, independently of the excitation. The angle of incidence of the IR laser is fixed to the surface plasmon resonance angle at the wavelength of the IR laser. Subsequently, the shift of the emission peak of the quantum dots as a function of IR laser power was measured. The change in emission peak wavelength versus incident IR laser power in milliwatts is shown in Figure 4(b).

FIG. 3. Wavelength shift of quantum dots, for three samples of different concentration, as a function of incident angle of the laser exciting the SPP that pumps the quantum dots: The pumping power of the SPP directly controls the peak in the wavelength of the emission of the quantum dots. As can be seen, the peak emission wavelength shifts towards longer wavelengths with increased pumping power, and the largest shift in emission wavelength coincides with the SPP resonance angle of the excitation. The lines are guides for the eye.

We pose that the tunability in our approach stems from the fact that the band gap of the semiconductor quantum dots depends on the local temperature. The temperature dependence of the band gap of semiconductors and semiconductor quantum dots can be approximated by²⁶

$$E_g(T) = E_{g_0} - \alpha \frac{T^2}{T + \beta}, \quad (1)$$

where E_g is the temperature-dependent band gap, E_{g_0} is the band gap at 0 K, T is the temperature in Kelvin, and α and β are experimentally determined parameters.

The absorbed power by each sample, irradiated upon by the 532 nm laser, is calculated by multiplying the incident power by $1-R$, with R the reflection coefficient as shown in Figure 2. It is assumed that the temperature of the sample and the absorbed power are linearly dependent on each other, and the temperature rise due to the absorbed power is calculated under the assumptions that the prism is at room temperature (293 K) and that heat transfer by convection is

FIG. 4. The quantum dot emission wavelength shifts as a function of the laser power inducing the SPP, both for SPP caused (a) and independent (b) excitation of the quantum dots. (a) Shift of the emission peak of the 20 μM , 40 μM , and 60 μM quantum dot samples as a function of the power of a 532 nm laser, inducing SPPs in the sample while simultaneously exciting the quantum dots in the thin film on top of the silver. With increasing power of the induced SPP, the emission of the quantum dots shifts towards the red. For the 20 μM quantum dot sample, a shift in band gap of $34.3 \text{ nm} \pm 0.9 \text{ nm}$ was observed, or, in electronvolts, a shift of nearly 100 meV. (b) Shift of the emission peak of the 60 μM and 40 μM quantum dot samples as a function of the power of a tunable Ti:Sapph laser, inducing SPPs in the sample. The excitation power of the 405 nm laser is kept constant at 1 mW. This shows that the shift can be controlled independently from the quantum dot excitation power. Data for two samples are shown, each at two wavelengths of the SPP-inducing laser. These 40 μM and 60 μM samples are the same samples as in (a). Lines are guides for the eye.

negligible.²⁵ The change in the emission peak wavelength (in eV) versus the increase in temperature of the sample, both compared to the case of the lowest excitation power (200 mW), is shown in Figure 5, which also contains plots of Eq. (1) with the constants taken from literature.^{27–29} The plots show the minimum and maximum change possible given the constants from literature and their respective error bounds. At temperatures close to the boiling temperature of octadecylamine, the surface group of the quantum dots, the measured data deviate from the theoretical curves. However, for lower temperatures, the overlap of the quantum dot emission wavelength with the theoretical curves is excellent. The likely range of temperature increase, above room temperature, makes this scheme highly attractive for plasmoelectric devices.³⁰

In conclusion, we have shown surface plasmon polariton-controlled emission wavelength control of quantum dots, spin-coated onto a thin silver film. By varying the power of the surface plasmon, we repeatedly and reversibly have shifted the wavelength of the emission of the quantum dots towards longer wavelengths, with observed shifts of up to 34 nm. The control of the emission wavelength is independent from the excitation of the quantum dots, as is shown

FIG. 5. Shift of the emission peak (in eV) of the quantum dot samples as a function of calculated SPP-induced temperature elevation, for quantum-dot concentrations of 20 μM , 40 μM , and 60 μM , respectively. The temperature is calculated from the power absorbed by the sample and involves an estimate of the illuminated area, leading to the error bounds as shown. The shift in emission wavelength is derived from the data shown in Figure 4(a). The solid curves are plots of Eq. (1), where the constants have been obtained from literature (reference a: Pugh-Thomas, Walsh, and Gupta,²⁷ reference b: Valerini *et al.*,²⁸ and reference c: Joshi *et al.*²⁹). The plots show the minimum and maximum change possible given the constants and their respective error estimates. Also shown is the relative location of the boiling point of octadecylamine, the surface group attached to the quantum dots.

by employing two separate lasers: one for the excitation of the quantum dots and one to induce surface plasmon polaritons in the silver film. On the other hand, we have shown that the effect can be realized also with one laser only, providing simultaneously the quantum dot excitation and the emission wavelength control. We pose that the control of the emission wavelength is due to dissipation of power, in the form of surface plasmon polaritons, causing local heating. The rise in temperature consequently shifts the band gap of the quantum dots to lower energetic values. With a model for the heating of the sample due to surface plasmon dissipation, the local temperature elevation is calculated. The measured shift in emission peak wavelength versus temperature shows a considerable overlap with theoretical curves, obtained from literature. Our results demonstrate the power

of SPPs in the control of emitters and introduce an accurate, highly controllable method for *in situ* tuning of the quantum dot emission wavelength.

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