Creating optical anisotropy of CdSe/ZnS quantum dots by coupling to surface plasmon polariton resonance of a metal grating

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Abstract: An efficient method that can be used to control the optical anisotropy of CdSe/ZnS quantum dots by coupling to the surface plasmon polariton resonance of a metal grating has been demonstrated. It is found that the unpolarized emission and Raman scattering signals arising from CdSe/ZnS quantum dots can be manipulated and exhibit a strong anisotropic behavior based upon our strategy. The optical anisotropy is interpreted in terms of the coupling between the directional surface plasmon of metal grating and the emitted light beam of quantum dots. Due to the importance of quantum dots in optoelectronic devices, our new approach should be useful for future application.

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References and links

1. Introduction

Semiconductor quantum dots (QDs) are considered as a novel material of light source, mainly due to their high luminescence efficiency, very narrow and size-tunable spectral emission, chemical stability, easy plasticity, and inherent inorganic qualities [1-3], which make them ideal for a wide spectrum of applications ranging from displays [4] and lasers [5,6] to in vivo biological imaging and therapeutic agents [7]. Especially, the use of a wide-gap semiconductor for overcoating a core made of a narrower-gap material, which allows one to significantly improve emission quantum yields by reducing surface-related nonradiative carrier losses [8,9]. Recently, the mixing of quantum dots and light emitting diodes (LEDs) offers a great prospect for developing low-cost, efficient, bright, color-saturated, and large-area color displays compatible with flexible substrates [10]. Meanwhile, nanowires have also attracted a great deal of interesting. Due to the inherent nature of a large shape anisotropy of a nanowire and the strong refractive index contrast between nanowires and environment, nanowires have been used as polarization dependent emitters and sensors [11-13]. It will be valuable if QDs can also exhibit optical anisotropic behavior.

Surface plasmon (SP) is a fundamental electromagnetic excitation mode of a metal-dielectric interface [14], which decays exponentially with distance from the interface into each of the bounding media and is free to propagate along the metal surface. Polaritons are quasiparticles resulting from strong coupling of electromagnetic waves with an electric or magnetic dipole-carrying excitation. The interaction of light with metals in a periodic structure excites the modes of surface plasmon polariton (SPP) which are useful to store and release energy on the surface. In turn, this behavior offer an excellent possibility to control SP properties for specific application, including enhanced transmission and beaming, waveguides and optoelectronic devices [15-19]. In this report, by combining both of the exciting research fields of quantum dots and surface plasmon, we demonstrate an interesting phenomenon for the creation of polarization anisotropy and intensity enhancement of emission arising from the coupling between semiconductor quantum dots and surface plasmon polaritons. This finding opens up the possibility for the invention of polarization dependent emitters based on semiconductor quantum dots.

2. Experiment

In our experiments, the CdSe/ZnS QDs with a diameter about 3-4 nm were prepared according to previous reports [20]. In brief, a Se injection solution containing 0.079 g of Se (1 mmol) was prepared in a glovebox by dissolving Se powder in 0.3 mL of tri-n-butylphosphine and then diluted with 1.681 g di-n-octylamine. The Se injection solution was then brought out of the glovebox in a vial sealed with a rubber subseal. A mixture of CdO (0.0128 g, 0.10 mmol) and stearic acid (0.114 g, 0.40 mmol) was heated in a three-neck flask to 140 °C under
Ar flow. After CdO was completely dissolved, the mixture was allowed to cool to room temperature. 1.94 g of the tri-n-octylphosphine oxide (TOPO) and hexadecylamine (HDA) was then added to the flask, and the mixture was heated to 320 °C. At this temperature, the Se injection solution was quickly injected into the hot solution. The reaction mixture was allowed to cool to 290 °C for the growth of the CdSe nanocrystals. CdSe QDs were precipitated out from the growth solution by adding methanol. The CdSe QDs (0.020 g) were loaded into mixture of the TOPO (2.20g) and HDA (1.26 g) in 50 mL three-neck flask, before being heated to 190 °C. Meanwhile, Zn stearate (0.316 g) was dissolved in 2.5 mL of TBP upon gentle heating (ca. 80 °C). After being cooled to room temperature, the resulting 0.2 M Zn/TBP solution was mixed with 2.5 mL of a 0.2 M solution of S/ TBP. Using a syringe pump, this mixture was injected during 1h into the reaction flask containing the core/shell nanocrystals at 190-200 °C. The nanocrystallites were annealed at 190 °C for an additional 1-1.5 h.

In fabricating the gold grating, an overlay of ZEP-520 (the positive electron-beam resists produced by Japan ZEON Co. Ltd.) was spin-coated on a 100 nm gold plated silicon substrate and patterned using electron-beam lithography (ELS-7500EX). The thick gold film of 100 nm was deposited on the patterned electron-beam resists using a thermal evaporating machine (ULVAC). In the lift off process, the gold film on the ZEP-520 layer was removed by rinsing in ZDMAC (the specific remover of ZEP-520) liquid. The resultant gold gratings consist of four different periods, including 450 nm, 500 nm, 550 nm, and 600 nm. The width of the gold lines in all different periods is kept at 200 nm. A typical scanning electron image of the gold grating is shown in Fig. 1. For the study of coupling between QDs and surface plasmons, CdSe/ZnS QDs were spin-coated on the gold grating.

![Image](image_url)

**Fig. 1 The scanning electron microscope image of the gold grating.**

For micro-PL measurements, a pulsed diode laser with a wavelength of 374 nm was used as the excitation source, which is focus on the sample through the microscope, OLYMPUS U-5RE-2 with 50 time objective. The emitted light from the sample collected with the same objective and the spectra were recorded by a 0.5 m Jobin Yvon TRIAX 320 spectrometer and detected by a PMT detector. To study the optical anisotropy of CdSe/ZnS QDs, a polarizer and a depolarizer were placed in front of the spectrometer. The polarizer can distinguish the optical anisotropy of light from the microscope, which is oriented parallel ($I_p$) and perpendicular ($I_v$) to the direction of gold grating axis. The depolarizer eliminates the polarization anisotropy between incident light and spectrometer. The degree of polarization is defined according to $\rho = (I_p - I_v)/(I_p + I_v)$, where $I_p$ and $I_v$ represent the polarization parallel and...
perpendicular to the axis of the gold grating, respectively.

3. Results and discussion

![Photoluminescence spectra of CdSe/ZnS quantum dots deposited on gold film.](image)

Figure 2(a) clearly shows that the photoluminescence signal is unpolarized with CdSe/ZnS QDs deposited on a gold thin film. However, a strong optical anisotropy is obtained as shown in Fig. 2(b) when CdSe/ZnS QDs were deposited on the gold grating with a period of 500 nm, in which the degree of polarization can reach up to 50%. To further confirm the characteristic of the polarization anisotropy of the composite of QDs and gold grating, we have rotated the polarizer from 0 to 360 degree as shown in Fig. 3. The result can be fitted quite well by $I(\theta) = I(0)\cos^2(\theta)$, which is known as Malus’s law.
The observed optical anisotropy can be understood in terms of the coupling between SP and QD emission. The QD emission generates SP of the metal grating through the interaction with the free electrons in the metal. The resultant surface plasmon polaritons are then scattered by the metal grating and emit the polarized radiation. The coupling occurs when the wave vector $\mathbf{k}$ of the scattered wave vector $\mathbf{k}_{sp}$ of the surface plasmon satisfies the equation,

$$ k \sin \theta + n G = k_{sp}, \quad (1) $$

where $G = 2\pi/d$, $d$ is the period of the metal grating, and $n$ is integer. The expression of SP wave vector is $k_{sp} = k \left[ \epsilon / (\epsilon+1) \right]^{0.5}$, where $\epsilon$ is the permittivity of gold [21].

To demonstrate the optical anisotropy indeed arises from the coupling between the SP grating and QD emission, we have performed the dependence of the emission on the period of the gold grating as shown in Fig. 4. It is found that the composite of CdSe/ZnS QDs and the gold grating with 500 nm period has the maximum optical anisotropy when the collection angle of the objective is set at 14°. This fact can be well interpreted by the dispersion relationship between the incident angle and wavelength calculated according to Eq. (1) as shown in Fig. 5. As indicated by the dashed line in Fig. 5, for the peak emission wavelength around 590 nm of the CdSe/ZnS QDs studied here, the diffracted wave due to surface plasmon resonance occurs at an angle of 14° for the metal grating with a period 500 nm. Due
to the resonant effect, the 500 nm gold grating therefore has a maximum degree of optical anisotropy. To further test our interpretation, we have measured the angular distribution of the emission for CdSe/ZnS QDs deposited on 450 nm gold grating as shown in Fig. 6. We can see that the maximum now occurs at around 37°, which is consistent with the calculated value based on Eq. (1). As one should expect, the grating with a smaller period should have a larger diffracted angle.

![Fig. 5. Dispersion relationship of the 500 nm gold grating calculated according to Eq. (1). The occurrence of surface plasmon resonance follows the calculated curves. When the emission wavelength 590 nm, the diffracted wave due to surface plasmon resonance occurs at an angle of 14° for the metal grating with 500 nm period as shown by the dashed line.](image)

![Fig. 6. Angular distribution of the emission for CdSe/ZnS quantum dots deposited on 450 nm gold grating.](image)

Finally, let us examine the optical anisotropy of the Raman scattering arising from the composite of CdSe/ZnS QDs and gold grating. The micro-Raman scattering measurements were performed at room temperature in a backscattering geometry using a Jobin Yvon T64000 system working in the triple-subtractive mode. A polarized continuous wave (cw) Ar laser of 488 nm acted as the excitation source. By rotating the sample, we are able to orient the polarization of the Ar laser parallel (I_||) or perpendicular (I_⊥) to the axis of gold grating. As shown in Fig. 7, two Raman peaks corresponding to one and two longitudinal optical phonon replica of CdSe can be clearly observed [22]. It is interesting that they also show a strong anisotropic effect. Similarly, if the polarization of excitation is fixed and parallel to the axis of
gold grating, the Raman scattering signal of CdSe/ZnS QDs does exhibit anisotropic behavior. All these results can be easily understood in terms of the coupling between light beam and surface plasmon of gold grating as described above.

![Raman scattering spectra](image)

Fig. 7. Anisotropy of Raman scattering spectra arising from CdSe/ZnS quantum dots deposited on 500 nm gold grating. 1LO and 2LO corresponding the Raman signals of one and two longitudinal optical phonon replica of CdSe.

4. Conclusions

In conclusion, we have demonstrated that the composite of QDs and metal grating can be used to manipulate the optical anisotropy of the constituent QDs. The underlying mechanism is attributed to the coupling between the emission arising from QDs and surface plasmon of metal grating. With the polarized light, we could reduce the polarizer film deployed in liquid crystal display, which may reduce the illuminance of light. In addition, polarization dependent emitters and sensors could vastly increase the information bandwidth of optical interconnection and be incorporated into photonic-based circuits [11]. In view of the great potential application of QDs, our study shown here should be very useful and timely.

Acknowledgment

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