Suface Plasmon Induced Optical Anisotropy of CdSe Quantum Dots on Well-Aligned Gold Nanorods Grating

Chih-Wei Chen, Chun-Hsiung Wang, Ching-Cheng Cheng, Chih-Ming Wei, and Yang-Fang Chen*

Department of Physics, National Taiwan University, No. 1, Section 4, Roosevelt Road, Da-an District, Taipei 106, Taiwan

ABSTRACT: A simple approach that can be used to create the optical anisotropy of CdSe quantum dots by coupling to the surface plasmon resonance of gold nanorods grating has been demonstrated. The well-aligned gold nanorods grating was fabricated by micropatterning technique. It is found that the dominant factor for the occurrence of optical anisotropy can be attributed to well-aligned gold nanorods, anisotropic properties of gold nanorods, and the resonant coupling between exciton and surface plasmon eigenmode. Our approach opens up a new possibility for the creation of polarization-dependent optoelectronic devices based on semiconductor quantum dots.
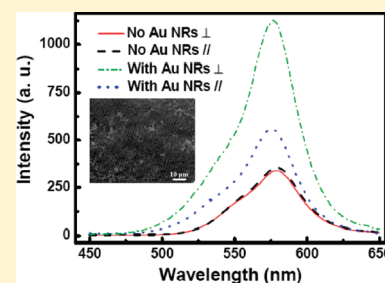
INTRODUCTION

Semiconductor quantum dots (QDs) have been studied extensively both theoretically and experimentally based on their tunable optical properties over the past two decades. The potential applications have been proposed, including light emitting diodes,[1-3] lasers,[4,5] and solar cells.[6] For instance, recently it was reported that the mixing of quantum dots and light emitting diodes offers a great prospect for developing low-cost, efficient, bright, color-saturated, and large-area color displays compatible with flexible substrates.[7] It will be valuable if QDs can exhibit optical anisotropic behavior, which will be able to open up a new dimension for their applicability.

It has been well-established that rough metal surfaces can strongly enhance the optical properties of nearby substrates. One can envisage many stimulating phenomena if semiconductor QDs and metal nanostructures are integrated together. Indeed, the interaction between semiconductor QDs and metal surface plasmons (SPs) has attracted a great deal of attention from the viewpoints of academic as well as industrial interests.[8] There exist several attempts to enhance the emission of semiconductor QDs with the assistance of the coupling of SPs. However, both results of enhancement and quenching effects have been observed.[9,10] It has been suggested that the enhancement and quenching of semiconductor QDs emission are results of the interplay between the local field excitation due to SP and electrons transfer from semiconductor QDs to metal nanostructures.[11] A spacer of dielectric material is therefore needed to effectively employ the advantage of surface plasmon resonance enhancement and to distinguish the quenching by the surface energy transfer.[12] Another interesting behavior of metal nanostructures is that metal nanorods exhibit transverse and longitudinal surface plasmon resonances that respectively correspond to electron oscillations perpendicular and parallel to the rod length direction. Quite interestingly, the longitudinal surface plasmon wavelength of gold nanorod is tunable from visible to infrared regions by adapting their aspect ratio.[13] Besides, the untoxic

property of gold nanorods is a good candidate of conjugation with a variety of biomolecular ligands and other targeting moieties.[14,15]

In this report, by combining both the exciting research fields of quantum dots and SPs of gold nanorods, we demonstrate an interesting phenomenon for the creation of optical anisotropy and emission enhancement arising from the coupling between semiconductor QDs and SPs of gold nanorods. This finding opens up a new possible opportunity for the invention of polarization-dependent optoelectronic devices based on semiconductor QDs.

EXPERIMENTAL SECTION

According to our previous synthetic protocol,[16] CdSe QDs with 1 nm thickness of tri-*n*-octylphosphine oxide (TOPO) were prepared. In order to have the required SPs to enhance the emission of two sizes of CdSe QDs, we have prepared gold nanorods with length around 100 nm encapsulated by silica. There are two steps for the preparation. For the seed solution, 7.5 mL of 0.1 M cetyltrimethyl ammonium bromide (CTAB) solution was mixed with 0.25 mL of 0.01 M HAuCl$_4$. Into the above solution was added 0.6 mL of 0.01 M NaBH$_4$, and this was stirred for 2 min. The growth solution contains 141 mL of 0.1 M CTAB, 1.5 mL of 0.01 M AgNO$_3$, and 7.5 mL of 0.01 M HAuCl$_4$. The 0.75 mL of 0.16 M ascorbic acid was added drop by drop. Then, 4.8 mL of seed solution was added into the growth solution. After mixing, the solution was aged at room temperature for at least 24 h. For the synthesis of porous silica coating on gold nanorods, 15 mL of gold nanorod solution was centrifuged at 15 000 rpm for 15 min and redispersed in 15 mL of 0.01 M CTAB solution. The pH value of the solution was tuned to ~10 by 0.01 M NaOH. Then, 900 μL of 5% tetraethyl orthosilicate/ethyl alcohol (TEOS/EtOH) solution was

added under stirring at 30 °C for 24 h. The product was centrifuged and purified by water.[17]

To assist alignment of gold nanorods for the generation of optical anisotropy, substrates with well-defined grating have been fabricated by micropatterning technique.[18] The basic principle of the micropatterning technique is to create a stamp having the patterns demanded. The structure of the stamp is derived as the "master". In this article, we used poly(dimethylsiloxane) (PDMS) as a stamp and a compact disk (CD) as the master.[18] We applied flexible PDMS on the periodic side of CD and kept the temperature at 50 °C all night. Then we slowly peeled off the PDMS film from the CD, and the straight channeled structure formed on the PDMS film. The fabricated PDMS stamp was placed on the commercial silicon substrate, and then the gold nanorods solution was dropped on the front side of the channels. By taking advantage of capillarity, the gold nanorods solution would slowly flow along the channels. The flow of the solution would create a driving force to make the gold nanorods arrange along the channels. Again by carefully peeling off the PDMS from the silicon substrate, the assembled gold nanorods patterns were left on the silicon substrate and formed a well-defined grating structure. The gold nanorods patterns on the silicon and quartz substrates were used in the experiments of photoluminescence (PL) and absorption measurement, respectively.

For the PL measurement, a SPEX Fluorolog-2 instrument equipped with a double-emission monochromator and a R928 photomultiplier tube were used. Excitation was provided by a 450 W Xe lamp, the output of which was focused into a 0.22 m monochromator to provide wavelength selection. The time-resolved PL (TRPL) was carried out using the technique of time-correlated single-photon counting (TCSPC) and a pulsed diode laser operating at a wavelength of 374 nm as the excitation source. The diode laser produces light pulses with a repetition rate of 5 MHz. The collected luminescence was directly projected into a grating spectrometer and detected with a high-speed photomultiplier tube. The PL signal is fed into a Time Harp counting card, which was triggered with a signal from the diode laser.

■ RESULTS AND DISCUSSION

To study the optical anisotropy of CdSe QDs, a polarizer and a depolarizer were placed in front of the spectrometer. The polarizer can distinguish the optical anisotropy of light from the lens, which is oriented parallel and perpendicular to the direction of the gold grating axis. The depolarizer eliminates the polarization anisotropy between incident light and spectrometer. For the different polarization of incident laser excitation measurement, the sample was rotated in several angles while the polarization of the laser beam was fixed.

Figure 1 shows the scanning electron microscopy (SEM) image of assembled gold nanorods grating structure with CdSe QDs on the top of the grating. The average pitch of the grating was about 2.5 μm, and the width of the grating was about 1.2 μm. To demonstrate the well-aligned gold nanorods assisted by the grating structure, we measure the polarization dependence of the absorption spectrum. As shown in Figure 2, we can clearly see that the transverse and longitudinal modes of surface plasmon resonance do strongly depend on the polarization of incident light beam. It implies that the gold nanorods were well aligned along the channel of grating. Due to the random arrangement of gold nanorods, it should exhibit an isotropic behavior.
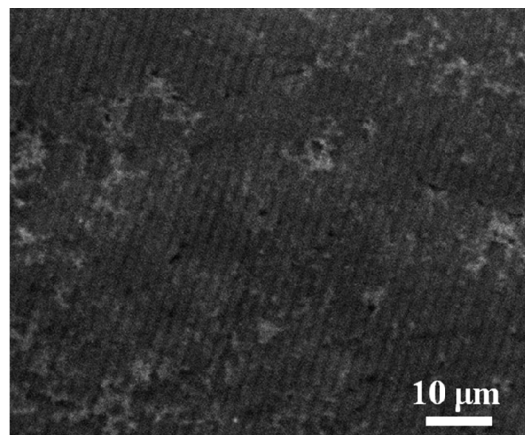

Figure 1. Scanning electron microscopy image of assembled gold nanorods grating structure with CdSe quantum dots on the top.
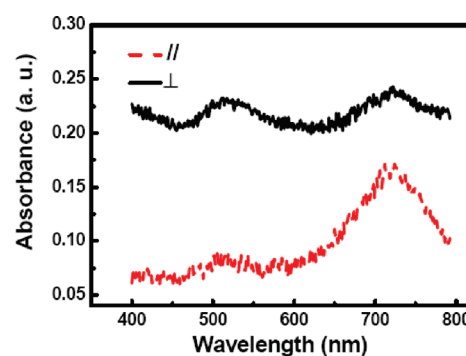

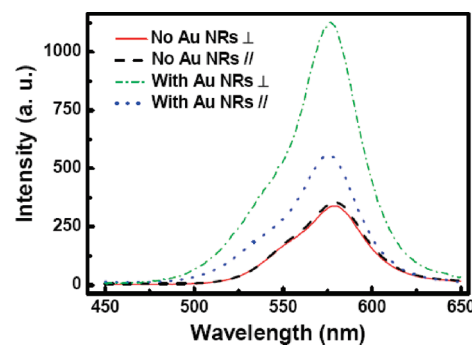**Figure 2.** Polarization-dependent absorption spectra of gold nanorods grating structure.

Figure 3. Photoluminescence spectra of CdSe quantum dots with and without assembled gold nanorods grating structure.

Figure 3 shows the PL measurement of CdSe QDs (emission peak at 575 nm) with and without gold nanorods grating. It is worth noting that the PL intensity of CdSe QDs with gold nanorods grating is much larger than that without the grating. Furthermore, the PL emission exhibits an anisotropy effect that does not appear in the case without the grating. The degree of polarization can be calculated by $\rho = (I_{max} - I_{mini})/(I_{max} + I_{mini})$, where I_{mini} and I_{max} represent the polarization parallel and perpendicular to the grating direction, respectively. The calculated degree of polarization is about 34%.

Let us try to understand the observed anisotropic effect. The composite of metal nanostructures and semiconductor QDs has
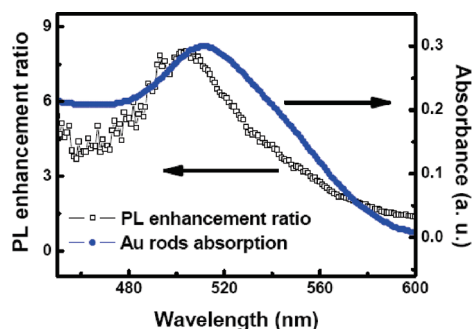
Figure 4. Absorption spectra of gold nanorods and CdSe quantum dots and photoluminescence enhancement ratio of the signal with and without gold nanorods.

two dominant effects causing the quenched and enhanced emission of QDs. The quenching effect is due to energy transfer from QDs to metal nanostructures, and the enhancement effect results from local field excitation caused by surface plasmon resonance.[19,20] In our system, the gold nanorods (with aspect ratio 3.7) have a SiO_2 shell with a thickness of about 10 nm as a spacer to prevent the process of energy transfer from QDs, which dominates the quenching effect. The emission enhancement of CdSe QDs on gold nanorods grating can therefore be attributed to the effect of local field excitation due to surface plasmon resonance.[12] As shown in Figure 2, the absorption of surface plasmon reveals two resonance modes with longitudinal mode at 730 nm and transverse mode at 510 nm.[13−15] To confirm our proposed mechanism, Figure 4 shows the PL intensity ratio with and without gold nanorods and the absorption spectrum of gold nanorods. We can see that the peak of PL enhancement ratio at around 505 nm matches well with the transverse surface plasmon mode of gold nanorods at around 510 nm. When the polarization of QDs emission is turned by 90°, the longitudinal mode of surface plasmon at 730 nm is far away from the emission wavelength of QDs, which greatly reduces the enhancement factor of QDs emission. Therefore, the anisotropic property of QDs emission can be realized.

To further confirm the above mechanism, Figure 5a shows the PL spectra of CdSe QDs (with emission of 550 nm) when the polarization of incident laser is changed with respect to the grating axis. As we can see, the PL intensity increases when the laser polarization changes from parallel to perpendicular. It implies that when the polarization of incident laser is perpendicular to the grating axis, a much stronger transverse SP mode can be excited, which leads to the enhancement of QDs emission. The slight PL peak blue-shifts (closed to the position of the SP mode) in Figure 5a were due to the PL emission enhancement increased with increasing the polarizer angle. This is consistent with the mechanism stated above.

Besides, we have examined our proposed mechanism by performing TRPL with monitoring at a peak of 550 nm as shown in Figure 5b. The TRPL spectra show that the decay time drops as the polarization of laser changes from parallel to perpendicular with respect to the grating axis. This result can be understood quite well according to previous investigations,[21,22] which reported that the local electric field induced by surface plasmon resonance can enhance the radiative recombination rate and reduce the recombination lifetime.

Finally, let us consider the anisotropic effect caused by the interaction between incident light and oriented gold nanorods. From previous research,[23,24] the emission wavelength is much
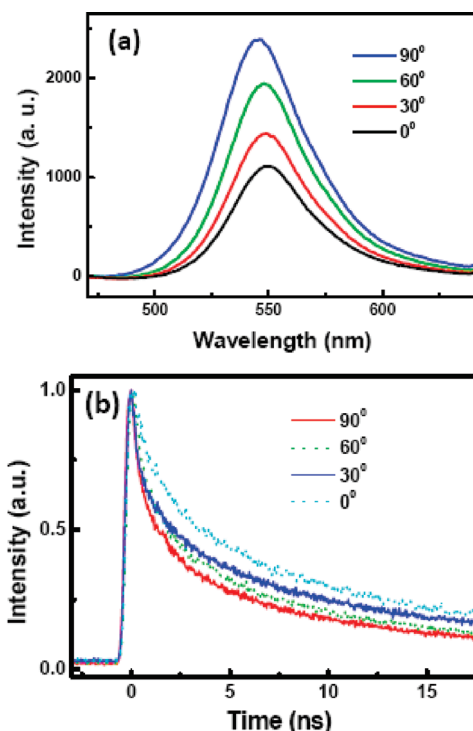

Figure 5. (a) Photoluminescence spectra of CdSe quantum dots on the assembled gold nanorods grating structure with varying the polarization of excitation laser light. (b) Time-resolved photoluminescence spectra for different excitation polarization of incident laser light.
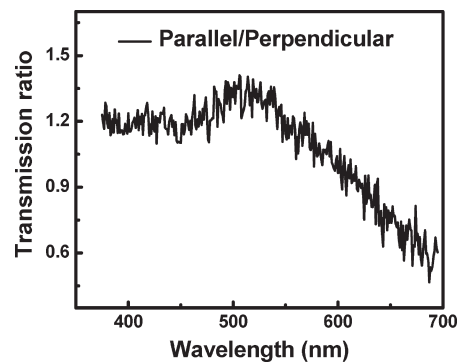

Figure 6. Transmission spectrum ratio between electric fields of light beam parallel and perpendicular to the gold nanorods.

larger than the nanorods diameter, and the electric field passing through the nanorods can be treated as a plane wave with amplitude modulated on the scale of the nanorod's diameter, due to the usual boundary conditions. When the electric field of the incident light is parallel to the nanorods, the electric field is not reduced, while for the perpendicular case, the electric field will be reduced. Hence, it is necessary to correct the anisotropy caused by the interaction of the light fields with the oriented gold nanorods for the real enhancement of the emission arising from QDs. Figure 6 shows the transmission spectrum ratio between the electric fields of light beam parallel and perpendicular to the gold nanorods. We can clearly see that the light fields were modified by the gold nanorods under different orientation. Therefore, after this effect is taken into account, the PL enhancement factor will be further increased.

CONCLUSION

In conclusion, using a simple approach, we have demonstrated optical anisotropy of CdSe QDs arising from the coupling between exciton and transverse SP resonant mode of well-aligned gold nanorods. We believe that our finding can greatly extend the application of semiconductor QDs. For instance, polarization-dependent emitters and sensors could vastly increase the information bandwidth of optical interconnection and be incorporated into photonic-based circuits. In view of the great academic as well as industrial interests in semiconductor QDs, our study shown here should be very useful and timely.

AUTHOR INFORMATION

Corresponding Author

*Tel. +886-2-33665125; fax +886-2-23639984; e-mail yfchen@phys.ntu.edu.tw.

ACKNOWLEDGMENT

REFERENCES

(1) Murray, C. B.; Kagan, C. R.; Bawendi, M. G. *Annu. Rev. Mater. Sci.* **2000**, *30*, 545.

(2) Tsutsui, T. *Nature (London)* **2002**, *420*, 752.

(3) Colvin, V. L.; Schlamp, M. C.; Alivisatos, A. P. *Nature (London)* **1994**, *370*, 354.

(4) Bruchez, M. G.; Weiss, S. P.; Alivisatos, A. P. *Science* **1998**, *281*, 2013.

(5) Chan, W. C.; Nie, S. *Science* **1998**, *281*, 2016.

(6) Nozik, A. J. *Physica E (Amsterdam)* **2002**, *14*, 115.

(7) Xu, J.; Liu, J.; Cui, D.; Gerhold, M.; Wang, A. Y.; Nagel, M.; Lippert, T. K. *Nanotechnology* **2007**, *18*, 025403.

(8) Maier, S. A.; Atwater, H. A. *J. Appl. Phys.* **2005**, *98*, 011101.

(9) Shimizu, K. T.; Woo, W. K.; Fisher, B. R.; Eisler, H. J.; Bawendi, M. G. *Phys. Rev. Lett.* **2002**, *89*, 117401.

(10) Hosoki, K.; Tayagaki, T.; Yamamoto, S.; Matsuda, K.; Kanemitsu, Y. *Phys. Rev. Lett.* **2008**, *100*, 207404.

(11) Hsieh, Y. P.; Liang, C. T.; Chen, Y. F.; Lai, C. W.; Chou, P. T. *Nanotechnology* **2007**, *18*, 415707.

(12) Kulakovich, O.; Strekal, N.; Yaroshevich, A.; Maskevich, S.; Gaponenko, S.; Nabiev, I.; Woggon, U.; Artemyev, M. *Nano Lett.* **2002**, *2*, 1449.

(13) Murphy, C. J.; Sau, T. K.; Gole, A. M.; Orendorff, C. J.; Gao, J.; Gou, L.; Hunyadi, S. E.; Li, T. *J. Phys. Chem. B* **2005**, *109*, 13857.

(14) Katz, E.; Willner, I. *Angew. Chem., Int. Ed.* **2004**, *43*, 6042.

(15) Ni, W. H.; Kou, X. S.; Yang, Z.; Wang, J. F. *ACS Nano* **2008**, *2*, 677.

(16) Chen, C. Y.; Cheng, C. T.; Yu, J. K.; Pu, S. C.; Cheng, Y. M.; Chou, P. T.; Chou, Y. H.; Chiu, H. T. *J. Phys. Chem. B* **2004**, *108*, 10687.

(17) Gorelikov, I.; Matsuura, N. *Nano Lett.* **2008**, *8*, 369.

(18) Shibu, E. S.; Radha, B.; Verma, P. K.; Bhyrappa, P.; Kulkarni, G. U.; Pal, S. K.; Pradeep, T. *ACS Appl. Mater. Interfaces* **2009**, *1*, 2199.

(19) Yun, C. S.; Javier, A.; Jennings, T.; Fisher, M.; Hira, S.; Peterson, S.; Hopkins, B.; Reich, N. O.; Strouse, G. F. *J. Am. Chem. Soc.* **2005**, *127*, 3115.

(20) Chen, C. W.; Wang, C. H.; Wei, C. M.; Hsieh, C. Y.; Chen, Y. T.; Chen, Y. F.; Lai, C. W.; Liu, C. L.; Hsieh, C. C.; Chou, P. T. *J. Phys. Chem. C* **2010**, *114*, 799.

(21) Ito, Y.; Matsuda, K.; Kanemitsu, Y. *Phys. Rev. B* **2007**, *75*, 033309.

(22) Chen, C. W.; Wang, C. H.; Wei, C. M.; Chen, Y. F. *Appl. Phys. Lett.* **2009**, *94*, 71906.

(23) Wang, J. F.; Gudiksen, M. S.; Duan, X. F.; Cui, Y.; Lieber, C. M. *Science* **2001**, *293*, 1455.

(24) Qi, J. F.; Belcher, A. M.; White, J. M. *Appl. Phys. Lett.* **2003**, *82*, 2616.