

Provided for non-commercial research and education use.  
Not for reproduction, distribution or commercial use.



This article appeared in a journal published by Elsevier. The attached copy is furnished to the author for internal non-commercial research and education use, including for instruction at the authors institution and sharing with colleagues.

Other uses, including reproduction and distribution, or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited.

In most cases authors are permitted to post their version of the article (e.g. in Word or Tex form) to their personal website or institutional repository. Authors requiring further information regarding Elsevier's archiving and manuscript policies are encouraged to visit:

<http://www.elsevier.com/copyright>



Contents lists available at ScienceDirect

## Thin Solid Films

journal homepage: [www.elsevier.com/locate/tsf](http://www.elsevier.com/locate/tsf)

# Surface plasmon resonance enhanced photoluminescence from Au coated periodic arrays of CdSe quantum dots and polymer composite thin film

Ming-Chung Wu<sup>a</sup>, Chih-Min Chuang<sup>a</sup>, Hsi-Hsing Lo<sup>a</sup>, Kuo-Chung Cheng<sup>b</sup>,  
Yang-Fang Chen<sup>c,d,\*</sup>, Wei-Fang Su<sup>a,d,\*</sup>

<sup>a</sup> Department of Materials Science and Engineering, National Taiwan University, Taipei 106-17, Taiwan, ROC

<sup>b</sup> Department of Chemical Engineering and Biotechnology, National Taipei University of Technology, Taipei 106-08, Taiwan, ROC

<sup>c</sup> Department of Physics, National Taiwan University, Taipei 106-17, Taiwan, ROC

<sup>d</sup> Center for Condensed Matter Sciences, National Taiwan University, Taipei 106-17, Taiwan, ROC

## ARTICLE INFO

## Article history:

Received 6 December 2006

Received in revised form 15 April 2008

Accepted 16 June 2008

Available online 26 June 2008

## Keywords:

Surface plasmons

Gold period array

Photoluminescence

Cadmium selenide particles

Poly(methyl methacrylate) matrix

## ABSTRACT

We have fabricated an arrayed CdSe quantum dots composite thin film that can enhance the photoluminescence of CdSe under the 488 nm laser irradiation by tuning the gold surface plasmon resonance frequency. This thin film consists of a gold coated periodic array of hybrid material of CdSe and poly(methyl methacrylate) on indium tin oxide coated glass substrate. The main surface plasmon resonance was red shifted as we increased the column diameter of the array. By adjusting the column diameters and lattice constants of the array to coincide with the 488 nm excitation wavelength, an evident increase in luminescence intensity was obtained due to the surface plasmon resonance of gold. As a result of likely efficient energy transfer from gold surface plasmon resonance to CdSe, the photoluminescence intensity of CdSe has been increased to 248% at 570 nm. This composite film has many potential applications in high efficient optoelectronic devices.

© 2008 Elsevier B.V. All rights reserved.

## 1. Introduction

Semiconductor quantum dots (QDs) have attracted great interest in recent years due to their unique photophysical properties, which are attractive to a diverse range of applications. Especially, the composite of inorganic nanoparticles and organic polymers exhibits excellent potential due to low cost, large area, mechanically flexible devices.

Surface plasmon resonance (SPR) is a coupled, localized transverse magnetic electromagnetic field and charge-density oscillation, which may propagate along an interface between two media. If the dielectric response of the media is lumped into corresponding complex dielectric constants, electromagnetic fields associated with the plasmon can be found from Maxwell's equations [1,2].

Excitation of SPR within metal nanoparticles or on roughened surfaces can create strong local optical fields. Surface-enhanced Raman scattering was exploited in the study of molecules adsorbed on metal nanoparticles [3–5] or on rough surface of gold, silver, and copper [6–10]. Gold and silver nanoparticles of different diameters

with numerous surface functionalities can be easily synthesized in liquid media. Surface-enhanced Raman scattering and related optical phenomena observed in these nanoparticles have been considered an enabling technology for highly compacted optoelectronic devices and sensors which take advantage of both quantum confinement effects and nonlinear optical properties [11–19].

Many researchers report that metallic interfaces play complex roles in the basic interactions of an electromagnetic field with optically active materials, and gold and silver are the most widely used metals for the surface plasmon resonance experiments. For example, smooth metallic surfaces reduce the radiation from nearby organic dyes through non-radiative energy transfer, while molecules absorbed onto metallic electrodes show several orders of magnitude increase in surface-enhanced Raman signals [20–22]. Furthermore, quantum dots located within the surface plasmon polariton field of the metal also show a large photoluminescence (PL) enhancement [23–27].

Here, we report an approach to enhance the photoluminescence of CdSe quantum dot by fabricating periodic structured composite thin film. The composite film is made of gold coated hybrid material of CdSe and poly(methyl methacrylate) (PMMA) with array structure on indium tin oxide (ITO) coated glass substrate. The main surface plasmon resonance was red shifted as we increased the column diameter. By adjusting column diameters and lattice constants of the array to coincide with the excitation wavelength, the fluorescence was

\* Corresponding authors. Y.-F. Chen is to be contacted at Department of Physics, National Taiwan University, Taipei 106-17, Taiwan, ROC. Tel./fax: +866 2 33665125. Su, Department of Materials Science and Engineering, National Taiwan University, Taipei 106-17, Taiwan, ROC. Tel./fax: +866 2 33664078.

E-mail addresses: [yfchen@phys.ntu.edu.tw](mailto:yfchen@phys.ntu.edu.tw) (Y.-F. Chen), [suwf@ntu.edu.tw](mailto:suwf@ntu.edu.tw) (W.-F. Su).

remarkably enhanced. The increase is due to the efficient energy transfer from gold surface plasmon to CdSe quantum dots.

## 2. Experimental details

In this experiment, the CdSe nanoparticles were grown by modifying Peng's method [28,29]. CdO 0.06 g, trioctylphosphine oxide 5.00 g, and tetradecylphosphonic acid (TDPA) 0.26 g were loaded in a three neck flask. At about 300 °C, reddish CdO powder was dissolved into a colorless homogeneous solution. By cooling down to 270 °C, then an injection of 0.9 ml Se solution (1.99 g Se dissolved in 50.0 ml tributylphosphine), high-quality CdSe nanoparticles were obtained. The size of the CdSe nanoparticles was evaluated to be  $4.0 \text{ nm} \pm 10\%$ . The UV–vis spectrum of the CdSe nanoparticles shows a sharp absorption peak that indicates the nanoparticles are close to monodisperse.

The nanoparticle solution with CdSe quantum dots having an emission wavelength centered around 570 nm was prepared by dissolving it in chloroform to obtain a 0.5 wt.% target concentration. This solution was mixed with a polymethylmethacrylate (PMMA, Gredmann, M.W. ~996 K) 2.0 wt.% solution in chlorobenzene (1:30 by volume) to make a solution of CdSe/PMMA. After thorough mixing and sonication, the clear CdSe/PMMA chlorobenzene solution (0.016 wt.% CdSe and 1.940 wt.% PMMA in chlorobenzene) was prepared. Fig. 1 illustrates the experimental procedure for the samples preparation and testing. The CdSe/PMMA solution was spin-coated onto an indium tin oxide (ITO) coated glass substrate at 3000 rpm for 90 seconds followed by baking at 180 °C for 5 min (Fig. 1a). Then, the hybrid film was exposed to electron beam (Hitachi, ELS-7500EX) and developed by using mixed solvent of methylisobutylketone and isopropanol (25:75 by volume) for 40 s, then isopropanol for 20 s and finally, de-ionized water for 20 s (Fig. 1b). The resulting hybrid film on ITO was coated with a 300 nm-thick Au film using a thermal evaporator (ULVAC) to make composite film samples (Fig. 1c). The pattern size was typically  $50 \mu\text{m} \times 50 \mu\text{m}$ . The fluorescence of sample was generated by irradiating it from the glass side at 488 nm and detected at normal angle (Fig. 1d). The fluorescence behavior of CdSe in the hybrid thin film was also observed under a confocal microscope (WITec, AlphaSNOM), and the thickness of the film was measured by the spectral microreflectometry (Mission peaks optics, MP100-M).

## 3. Results and discussion

The CdSe/PMMA hybrid thin film thickness was determined to be 250 nm by the spectral microreflectometry measuring the interference

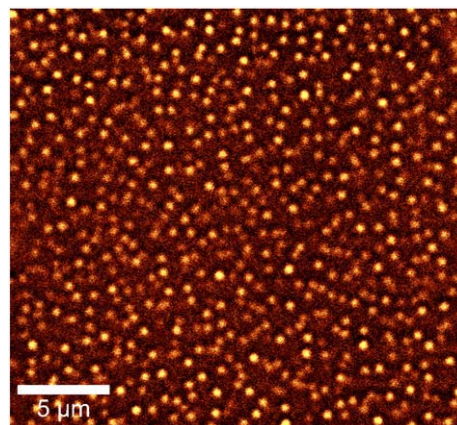


Fig. 2. Confocal fluorescence microscopy images of the CdSe/PMMA hybrid thin film.

between incident and reflected light with wavelengths ranging from UV to visible range (250–1000 nm). From the phase shift, the thin film thickness can be determined. The morphology and roughness of the hybrid thin film was measured by atomic force microscopy (Digital Instruments, Dimension-3100 Multimode), and the film was very smooth with a root-mean-square of 2.45 nm.

The fluorescence distribution of CdSe in the hybrid thin film was measured by confocal fluorescence microscopy. The Ar ion laser (wavelength 488 nm) was used to excite the thin film through a 100× Nikon plan objective (NA 0.9). A single photon counting photo multiplier tube detector was used to detect the fluorescence intensity. For a hybrid film, at a concentration of 0.8 wt.% CdSe in PMMA, no macroscopic fluorescence aggregation of CdSe in the film was observed. The fluorescence domain was about 300 nm (Fig. 2). This is an optimized CdSe concentration in the hybrid film and it is suitable for E-beam process.

Fig. 3(a)–(f) show the field-emission scanning electron microscopy images of triangular arrays seen in a hole in the hybrid thin film with six different column diameters and lattice constants. The respective diameter and lattice constant are as follows: (a) Pattern A-1, 290 and 600 nm; (b) Pattern A-2, 400 and 600 nm; (c) Pattern A-3, 520 and 600 nm; (d) Pattern B-1, 50 and 300 nm; (e) Pattern B-2, 110 and 300 nm; (f) Pattern B-3, 230 and 300 nm. Their optical properties of absorbance and reflectance were studied using a spectral microreflectometer (Mission Peaks Optics, MP100-M). This instrument measures the interference between incident and reflected light with

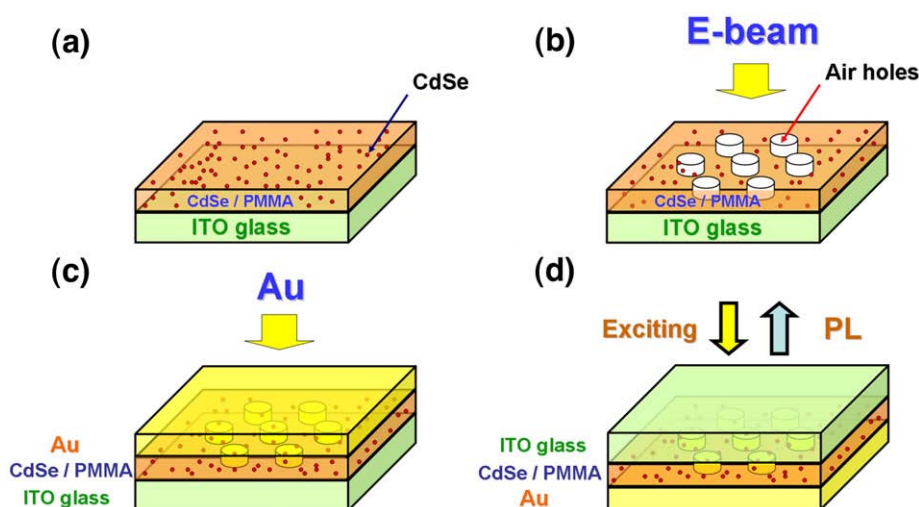
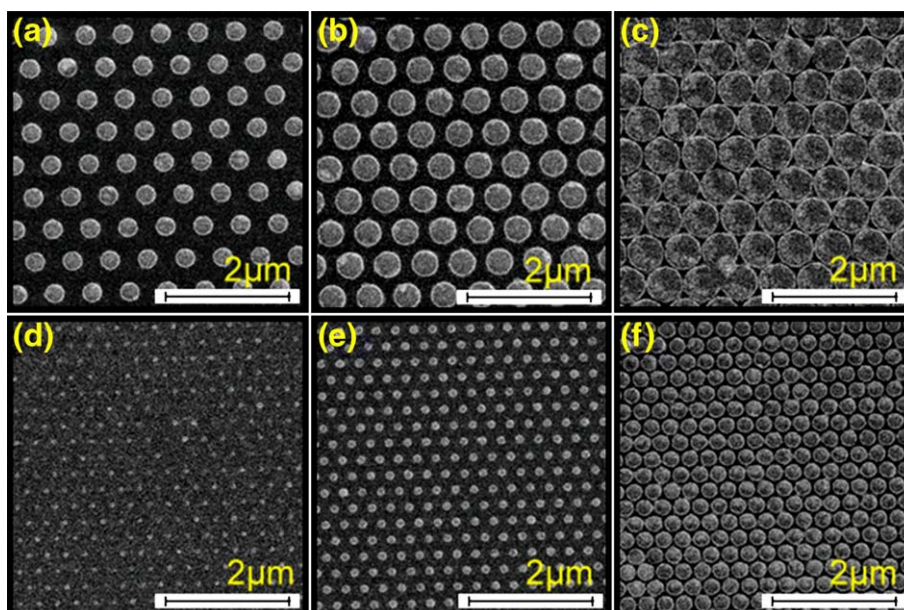


Fig. 1. Schematic illustration of the fabricate process of the Au coated CdSe/PMMA composite thin film on ITO substrate. (a) Spin coat 250 nm-thick CdSe/PMMA hybrid thin film, (b) e-beam lithography, (c) deposit 300 nm-thick Au metal, and (d) Schematic of a typical finished Au coated CdSe/PMMA hybrid composite thin film. Fluorescence is excited by a 488 nm laser on the glass substrate side and detected at parallel to the incident angle.



**Fig. 3.** Field-emission scanning electron microscopy images of triangular array of holes of CdSe/PMMA composite thin film with six different column diameters and lattice constants as: (a) Pattern A-1, 290 and 600 nm; (b) Pattern A-2, 400 and 600 nm; (c) Pattern A-3, 520 and 600 nm; (d) Pattern B-1, 50 and 300 nm; (e) Pattern B-2, 110 and 300 nm; (f) Pattern B-3, 230 and 300 nm.

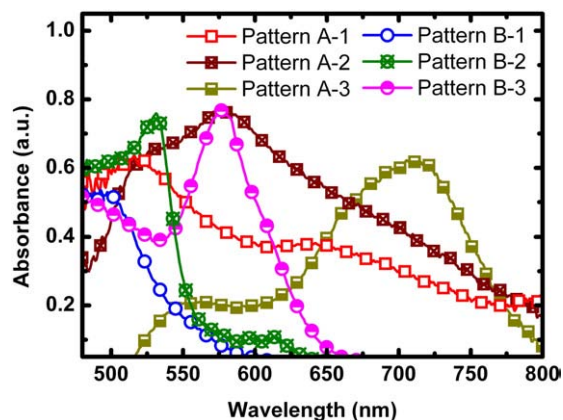
wavelengths ranging from UV to visible range (450–800 nm). Unpolarized light was focused on the composite film to a spot size of  $<30 \mu\text{m}$ . For analysis all six patterns were fabricated on the same substrate. The reflected light at normal incidence from the composite film was analyzed and shown Fig. 4. Our results indicate how the SPR frequencies of the patterns are tunable by varying the geometrical parameters of the array. When we fixed the constant column height at 250 nm and the triangular lattice constant at 300 or 600 nm, the main surface plasmon resonance was red shifted from short wavelength to long wavelength as we increased the column diameter. Therefore, the spectral properties of the surface plasmon resonance are critically dependent on the shape, size, and spatial arrangement of the metal.

The photoluminescence (PL) spectra of the periodic structured composite thin film were characterized by micro-Raman scattering and micro-photoluminescence ( $\mu\text{m-PL}$ , JOBIN YVON-SPEX, T-64000) at room temperature. All the spectra were obtained using an  $\text{Ar}^+$  laser working at a wavelength of 488 nm, which was focused on the periodic structured of composite thin film with different patterns. Both of the incident and detected light beams are parallel to the

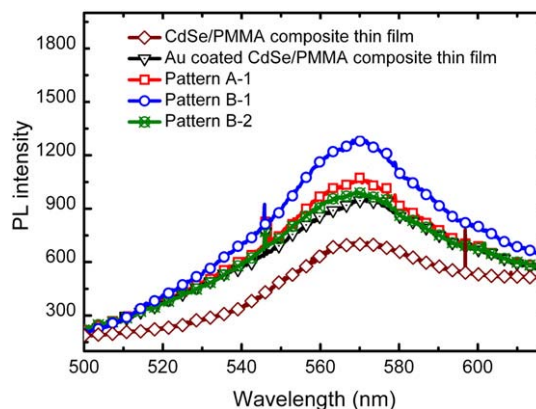
principal axis of the structures. The signal was dispersed by a triple monochromator and collected by a liquid nitrogen cooled CCD. Polarized light was focused on the film to a spot size of  $<10 \mu\text{m}$ . We measured the fluorescence from unpatterned (blank) and patterned composite films. Fig. 5 shows the photoluminescence intensities of the composite films including blank CdSe/PMMA and CdSe/PMMA with Au coating and three patterned samples. After the emission spectra are normalized with respect to the mean area of the films, pattern B-1 (diameter: 50 nm, lattice constant: 300 nm) exhibits the strongest PL intensity. It is because photon energy of the surface plasmon resonance of pattern B-1 was close to that of the excitation and produced the strongest enhancement. As compared to the unpatterned CdSe/PMMA sample with Au coating, the extent of enhancement for pattern B-1 is 248% and pattern A-1 is 188% at 570 nm.

#### 4. Conclusions

In summary, we have fabricated Au coated periodic arrays of CdSe quantum dots and PMMA composite film on ITO substrate. This



**Fig. 4.** Normal incident absorbance spectra of the Au coated CdSe/PMMA composite thin film with six different column diameters and lattice constants as: Pattern A-1, 290 and 600 nm; Pattern A-2, 400 and 600 nm; Pattern A-3, 520 and 600 nm; Pattern B-1, 50 and 300 nm; Pattern B-2, 110 and 300 nm; Pattern B-3, 230 and 300 nm.



**Fig. 5.** Micro-photoluminescence spectra of the Au coated CdSe/PMMA composite thin film with different column diameters and lattice constants as: CdSe/PMMA composite thin film, Au coated CdSe/PMMA composite thin film; Pattern A-1, 290 and 600 nm; Pattern B-1, 50 and 300 nm; Pattern B-2, 110 and 300 nm.

composite film exhibits an enhanced photoluminescence effect of CdSe under the irradiation of 488 nm laser. We can tune the surface plasmon resonance by adjusting the lattice constant and column diameter of the patterned array to coincide with the excitation wavelength. As a result of likely efficient energy transfer from gold surface plasmon to CdSe quantum dots, the composite film exhibited enhanced photoluminescence intensity up to 248% at 570 nm. Therefore, our approach provides excellent opportunities for CdSe quantum dots to be used in high efficient optoelectronic devices.

### Acknowledgement

Financial support obtained from the National Science Council of Taiwan (NSC-96-2628-E-002-017-MY3 and NSC95-3114-P-002-003-MY3) is highly appreciated. The authors also thank Prof. C. H. Kuan, Prof. C. W. Chen, Prof. H. L. Chen, Mr. Y. Y. Lin, Mr. Y. C. Huang and Mr. W. H. Gan of National Taiwan University for helpful discussions and Mr. A. J. Su of University of Pittsburgh for editing the manuscript. The electron beam lithography was carried out using the Elionix's facility located in the National Taiwan University Center for Information and Electronics Technologies.

### References

- [1] C.S. Liu, V.K. Tripathi, *IEEE Trans. Plasma Sci.* 28 (2000) 353.
- [2] M.V. Bashevoy, F. Jonsson, A.V. Krasavin, N.I. Zheludev, Y. Chen, M.I. Stockman, *Nano Lett.* 6 (2006) 1113.
- [3] K. Kneipp, Y. Wang, H. Kneipp, L.T. Perelman, I. Itzkan, R.R. Dasari, M.S. Feld, *Phys. Rev. Lett.* 78 (1997) 1667.
- [4] S. Nie, S.R. Emory, *Science* 275 (1997) 1102.
- [5] Y.C. Cao, R. Jin, C.A. Mirkin, *Science* 297 (2002) 1536.
- [6] K.G. Thomas, P.V. Kamat, *Acc. Chem. Res.* 36 (2003) 888.
- [7] P.T. Miclea, A.S. Susha, Z. Liang, F. Caruso, C.M. Sotomayor Torres, S.G. Romanov, *Appl. Phys. Lett.* 84 (2004) 3960.
- [8] S.G. Romanov, A.S. Susha, C.M. Sotomayor Torres, Z. Liang, F. Caruso, *Appl. Phys. Lett.* 97 (2005) 086103.
- [9] Y. Yang, M. Nogam, J. Shi, H. Chen, G. Ma, S. Tang, *Appl. Phys. Lett.* 88 (2006) 081110.
- [10] C.-M. Chuang, M.-C. Wu, K.-C. Cheng, Y.-F. Chen, W.-F. Su, *Appl. Phys. Lett.* 89 (2006) 061912.
- [11] A.N. Shipway, E. Katz, I. Willner, *Chem. Phys. Chem.* 1 (2000) 18.
- [12] I. Willner, B. Willner, *Pure Appl. Chem.* 74 (2002) 1773.
- [13] M. Brust, C.J. Kiely, *Colloids Surf., A* 202 (2002) 175.
- [14] S. Link, M.A. El-Sayed, *Ann. Rev. Phys. Chem.* 54 (2003) 331.
- [15] M.P. Pileni, Y. Lalatonne, D. Ingert, I. Lisiecki, A. Courty, *Faraday Discuss.* 125 (2003) 251.
- [16] J. Lee, A.O. Govorov, J. Dulka, N.A. Kotov, *Nano Lett.* 4 (2004) 2323.
- [17] M. Mitsushio, K. Miyashita, M. Higo, *Sens. Actuators, A, Phys.* 125 (2006) 296.
- [18] A.K. Sharma, B.D. Gupta, *Nanotechnology* 17 (2006) 124.
- [19] Y. Yang, S. Matsuura, M. Nogami, J. Shi, W. Huang, *Nanotechnology* 17 (2006) 2821.
- [20] A.M. Michaels, M. Nirmal, L.E. Brus, *J. Am. Chem. Soc.* 121 (1999) 9932.
- [21] K. Ishikawa, T. Okubo, *J. Appl. Phys.* 98 (2005) 043502.
- [22] T.D. Neal, K. Okamoto, A. Scherer, *Opt. express* 13 (2005) 5522.
- [23] K.T. Shimizu, W.K. Woo, B.R. Fisher, H.J. Eisler, M.G. Bawendi, *Phys. Rev. Lett.* 89 (2002) 117401.
- [24] Z. Gueroui, A. Libchaber, *Phys. Rev. Lett.* 93 (2004) 166108.
- [25] J.H. Song, T. Atay, S. Shi, H. Urabe, A.V. Nurmikko, *Nano Lett.* 5 (2005) 1557.
- [26] I. Gryczynski, J. Malicka, W. Jiang, H. Fischer, W.C. Chan, Z. Gryczynski, W. Grudzinski, J.R. Lakowicz, *J. Phys. Chem., B* 109 (2005) 1088.
- [27] M.S. Hu, H.L. Chen, C.H. Shen, L.S. Hong, B.R. Huang, K.H. Chen, L.C. Chen, *Nat. Mater.* 5 (2006) 102.
- [28] Z.A. Peng, X. Peng, *J. Am. Chem. Soc.* 123 (2001) 183.
- [29] C.M. Chuang, W.B. Lu, W.F. Su, C.M. Lin, Y.F. Chen, *J. Appl. Phys.* 97 (2005) 096104.