

PHOTOLUMINESCENCE OF CDSE/ZNS QUANTUM DOTS ENHANCED BY SILVER COLLOIDS

Bo-Tau Liu^{1*} and Kuan-Han Wu²

ABSTRACT

In this study, we fabricated CdSe/ZnS-SiO₂-Ag colloid three-layer hybrid films by the layer-by-layer coating. The CdSe/ZnS layer and the Ag-nanoparticle layer were separated by a SiO₂ layer fabricated from tetraethyl orthosilicate. The localized surface Plasmon resonance wavelength of Ag colloids has a red shift after the SiO₂ layer is covered on the Ag colloids. Experimental results showed that the optimal photoluminescence (PL) enhancement occurred at an appropriate distance and could reach to 3.1-fold compared to the PL of pristine quantum dots (QDs). The result may arise from the fact that the enhanced electromagnetic field caused from localized surface plasmon resonance is weakened with distance between CdSe/ZnS QDs and Ag colloids much more slowly than the nonradiative energy transfer.

Keywords: CdSe/ZnS; Quantum dot; Ag colloid; Photoluminescence; Localized Surface Plasmon Resonance.

1. INTRODUCTION

Compared to bulk materials, quantum dots (QDs) feature extraordinarily optoelectronic properties due to the charge carriers confined in a restricted space. Over the past decade, QDs have received considerable attention regarding their application on solar cells (Huynh *et al.* 2002; Jung and Kang 2011), sensors (Nazzal *et al.* 2003), light emitters (Coe *et al.* 2002; Kim *et al.* 2008), and bioassays (Gao *et al.* 2004). It was found that the photoluminescence (PL) of QDs can be enhanced by surface plasmons excited in metal nanostructural surfaces, nanoparticles, or nano-holes, whereas planar metal surfaces are known to quench the PL (Aslan *et al.* 2008; Barnes 1998; Lu *et al.* 2010b; Shuford *et al.* 2007; Soganci *et al.* 2007; Wu *et al.* 2011). Many studies have reported that the fluorescence enhancement arises from the excitation of localized surface plasmon resonance (LSPR) of metal nanostructures, which amplifies the local electric field to alter the optical properties of QDs (Biteen *et al.* 2005; Song *et al.* 2005; Sugawa *et al.* 2009). In fact, the PL suppression also occurs simultaneously in the presence of nanostructural metals due to nonradiative energy transfer from QDs to metals. As a result, both the PL quenching and enhancement are observed after the excitons of QDs coupling with LSPR of metal nanostructures. Because the Forster energy transfer exhibits a shorter range effect than the enhanced electromagnetic field, the PL quenching will be weakened with distance and much faster than the LSPR enhancement. At longer distance, the PL enhancement decrease gradually (Aegerter and Al-Dahoudi 2003; Chan *et al.* 2009; Kulakovich *et al.* 2002; 2006). The distance of

the QDs from metal nanostructural surfaces affects the competition between enhancement and quenching. Moreover, the LSPR absorption characteristic depends strongly on the size, shape, and coupling of metal nanoparticles and the dielectric properties of their surrounding medium (Kreibig and Vollmer 1995; Medda *et al.* 2005; Shen *et al.* 2009). Therefore, effect of nano metals on optoelectronic conversion of QDs is complicate and undetermined.

In this paper, we studied plasmon-enhanced fluorescence from CdSe/ZnS-SiO₂-Ag colloid three-layer hybrid films. The CdSe/ZnS layer and the Ag-colloid layer were separated by a SiO₂ layer fabricated from tetraethyl orthosilicate (TEOS). Effects of the thickness of the SiO₂ layer on PL enhancement of the CdSe/ZnS excited by the LSPR of Ag nanoparticles were investigated.

2. EXPERIMENT

2.1 Preparation of Water-Soluble CdSe/ZnS Core-Shell QDs

CdSe/ZnS core-shell QDs dispersed in chloroform were synthesized by the well-established solvothermal methods as reported previously (Liu *et al.* 2014). Briefly, solvent-based CdSe/ZnS QDs dispersed in chloroform (Echo Chemical) were synthesized by the solvothermal methods: CdSe core and ZnS shell were prepared at 290°C for 5 min and at 220°C for 1 min, respectively. Excess 3-mercaptopropionic acid (MPA, Sigma-Aldrich) was added into 10 wt% KOH methanol solution, and the mixture was violently stirred. The as-prepared CdSe/ZnS chloroform solution was added into the MPA solution at the volume ratio of 2:1. After 5-min mixing, the QDs in the suspension was precipitated with the addition of acetone. The QDs was purified through centrifugation (9,000 rpm, 10 min), decanting the supernatant, and redispersing the precipitate with methanol. Finally, the precipitate was redispersed in water, resulting in MPA-capped CdSe/ZnS QD aqueous solution.

Manuscript received June 30, 2018; revised September 3, 2018; accepted October 15, 2018.

^{1*} Professor (corresponding author), Department of Chemical and Materials Engineering National Yunlin University of Science and Technology, Yunlin, Taiwan 64002, R.O.C. (e-mail: liubo@yuntech.edu.tw).

² Formally Master student, Department of Chemical and Materials Engineering National Yunlin University of Science and Technology, Yunlin, Taiwan 64002, R.O.C.

2.2 Preparation of Ag Colloids

Ag colloids were synthesized using the citrate-reduction method. Briefly, 0.085 g AgNO_3 (Showa) was dissolved in water of 500 mL, and then the solution was heated to 100°C . 1 wt% sodium citrate (2 mL, Mallinckrodt) was rapidly injected into the boiling AgNO_3 solution. After 30-min reaction under reflux, the resulting solution was centrifuged at 2,000 rpm to remove the precipitate, resulting in the Ag colloids.

2.3 Preparation of QD-SiO₂-Ag Hybrid Films

Glass substrates were immersed in an 8 wt% NaOH solution at 55°C for 2 min and then washed with DI water. The washed glass substrates were immersed in a 10 wt% 3-aminopropyltrimethoxysilane (APTS, Fluka) solution for 1 h and then washed with DI water to remove excess APTS. The APTS-modified glass substrates were dried at 120°C for 2 h. Then, the glass substrates were dipped into the as-prepared Ag-colloid solution. Because the APTS-modified glass substrates and Ag colloids possess opposite charges on their surfaces, the self-assembling Ag-colloid layer can be prepared through electrostatic interactions. After 6-h soaking, the Ag-colloid-coated glass substrates were washed with DI water and then annealed thermally under a nitrogen atmosphere at 260°C for 1 h. Various TEOS (Acros) ethanol solutions (0.5, 1, 1.5, 2, and 3 solid-content wt%) with a small amount of 0.1 M HCl were heated at 70°C for 1 h. The Ag-colloid-coated glass substrates were dipped into the TEOS solution and then raised from the dipping bath at a rate of 5 mm min^{-1} . The coated substrates were placed in an oven at 260°C for 30 min. A dense SiO_2 layer was formed on the surface of Ag-colloid layer. The coated glass substrates were dipped in aqueous poly(diallyldimethyl ammonium chloride) (PDDA, Aldrich) solution for 20 min, then wash with DI water to remove excess PDDA, and finally dried on an oven at 60°C . CdSe/ZnS QDs were subsequently deposited upon the dielectric layer by dipping in the QD solution through electrostatic adsorption, resulting in the CdSe/ZnS-SiO₂-Ag three-layer hybrid film.

2.4 Measurements

Particle size and morphology of the as-prepared Ag colloids and CdSe/ZnS QDs were examined using a field-emission scanning-electron microscope (JSM-7401F, JEOL) and a high-resolution transmission electron microscope (JEM-2010, JEOL). The absorption spectra of CdSe/ZnS QDs and hybrid films were measured using a UV-Vis spectrophotometer (Lambda 850, PerkinElmer). PL spectra of CdSe/ZnS and their hybrid films were measured using fluorescence spectrophotometer (LS-55/45, PerkinElmer).

3. RESULTS AND DISCUSSION

The Ag colloids synthesized by the citrate reduction method feature the particles with the diameter of 40-100 nm. Most of the colloids are granular, but some display rod-like (Fig. 1a). The Ag colloids show two corresponding LSPR wavelength maximum (λ_{LSPR}) at near 400 and 700 nm (Fig. 2), indicating radial and axial absorption with respect to the nanorods, respectively. After the thermal annealing at 260°C under nitrogen atmosphere condi-

tion, the particle size of Ag colloids increases and the long Ag nanorods disappear (Fig. 1b), being more effective to enhance PL of QDs by surface plasmons (Liu *et al.* 2011; Lu *et al.* 2010a). The result is consistent with the observation in the LSPR absorption; the shorter λ_{LSPR} is shifted from 400 to 422 nm and the longer λ_{LSPR} disappears. The as-prepared CdSe/ZnS QDs feature a diameter of near 5 nm (Fig. 3), an absorption peak at 573 nm and a PL emission wavelength near 600 nm (Fig. 4). CdSe/ZnS QDs can be excited anywhere above bandgap energy and widely applied in diverse researches. The QDs feature well luminescence as shown in the insert of Fig. 4.

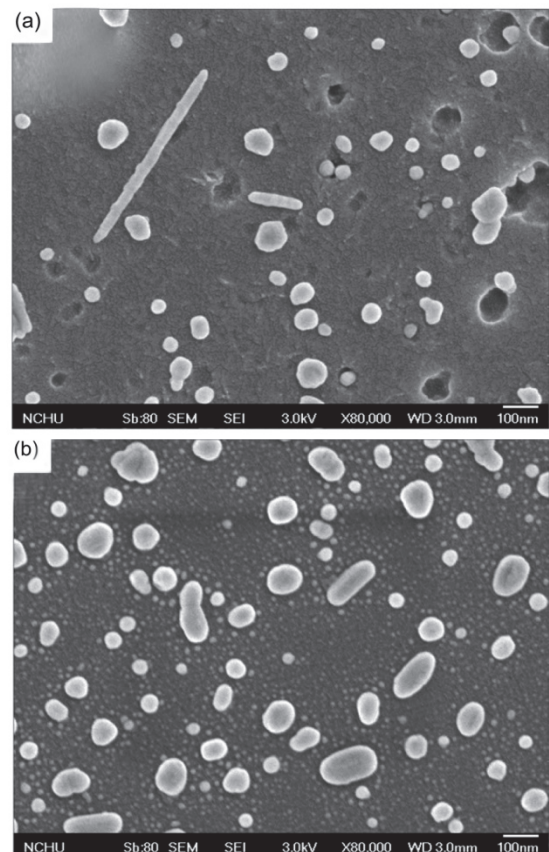


Fig. 1 SEM images of Ag-colloids (a) before and (b) after an annealing at 260°C

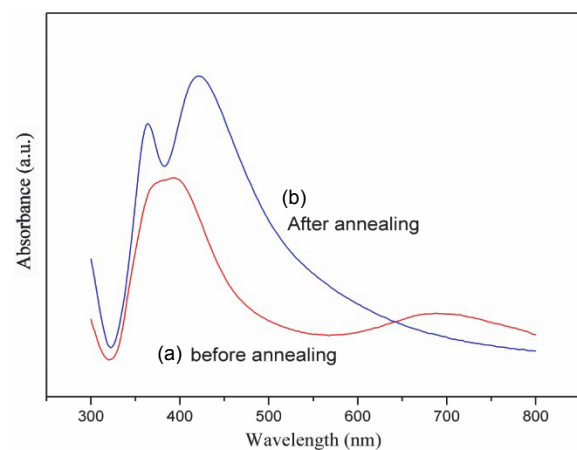


Fig. 2 Absorption spectra of Ag-colloids (a) before and (b) after annealing at 260°C

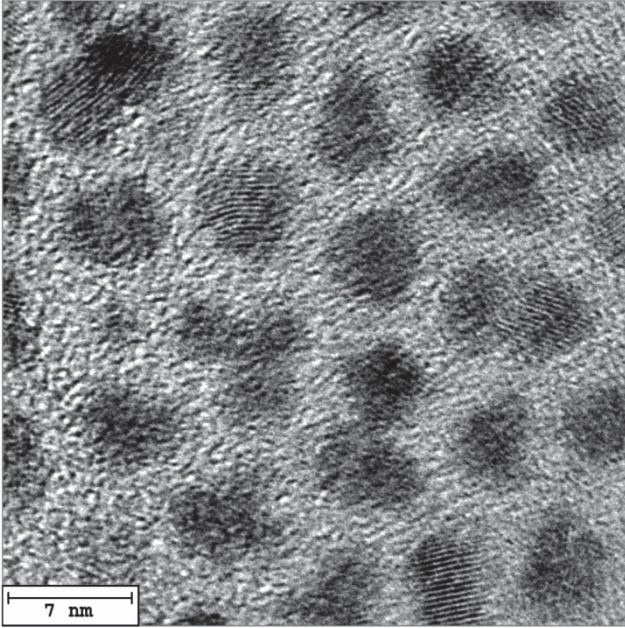


Fig. 3 HRTEM image of the as-prepared CdSe/ZnS QDs

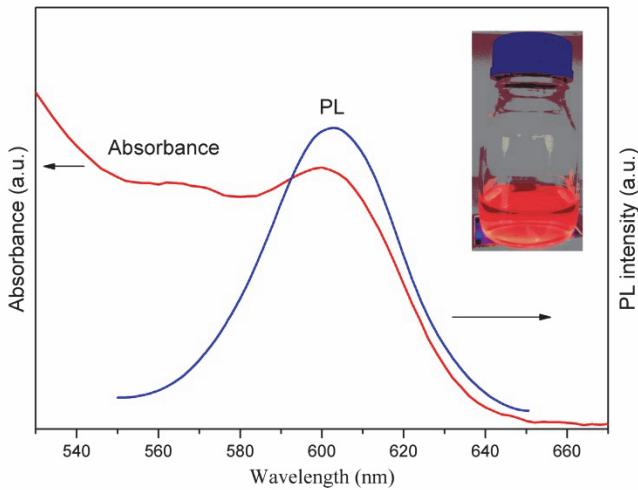


Fig. 4 PL and absorption spectra of the as-prepared CdSe/ZnS QDs. The insert is the image of the photo-excited QDs

While the bulk electron collision frequency is low, we can find the relationship for the λ_{LSPR} from the Plasmon coupling between two proximal metal nanoparticles (Jain and El-Sayed, 2008): $\lambda_{LSPR} \propto \sqrt{\epsilon_{\infty} + \kappa\epsilon_m}$. In the expression, ϵ_{∞} is the high-frequency contribution to the dielectric function of metal nanoparticles, ϵ_m is the dielectric constant of the surrounding medium, and κ is the geometry factor. Therefore, the LSPR band depends on the dielectric constant of the surrounding medium. Fig. 5 shows a red shift of LSPR bands from 422 to 442 nm when the Ag-colloid layer is covered by the SiO₂ layer. It is easily understood that the red shift is caused by the increase of dielectric constant of the surrounding medium due to the fact that the surrounding air of Ag colloids is replaced by SiO₂, where the dielectric constant of SiO₂ is larger than that of air. In order to further realize the effect of the SiO₂ layer on the PL enhancement,

we analyzed the PL spectra of CdSe/ZnS-SiO₂-Ag colloid hybrid films with various thicknesses of the SiO₂ layer. Fig. 6 shows the variation of PL intensity with various SiO₂ contents (proportional to the thickness). The corresponding variation of PL intensity at λ_{LSPR} with various SiO₂ contents is shown in Fig. 7. The PL intensity at λ_{LSPR} increases with the increase of the thickness of the SiO₂ layer, reaches a maximum (at 1 wt% SiO₂), and decrease with the further increase in the thickness of the SiO₂ layer. The result confirms with the postulation that the enhanced electromagnetic field from LSPR is weakened with distance between CdSe/ZnS QDs and Ag colloids much more slowly than the non-radiative energy transfer and the optimal PL enhancement occurs at an appropriate distance. Compared to the pristine QDs, the PL intensity of the CdSe/ZnS-SiO₂-Ag colloid hybrid films increases from 52.0 to 158.7 a.u., reaching a near 3.1-fold enhancement.

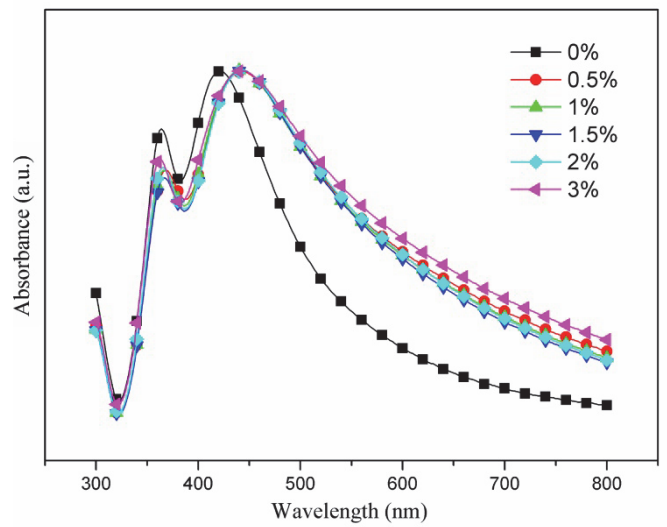


Fig. 5 Absorption spectra of the SiO₂-Ag colloid hybrid films with the SiO₂ layer made from various solid-content solutions

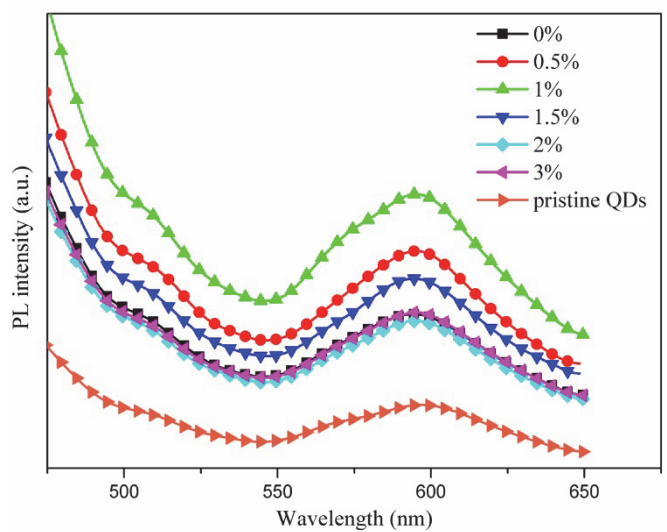


Fig. 6 PL spectra of the (CdSe/ZnS)-(TiO₂/SiO₂)-(Ag colloid) three-layer hybrid films with the SiO₂ layer made from various solid-content solutions. Excitation wavelength = 442 nm.

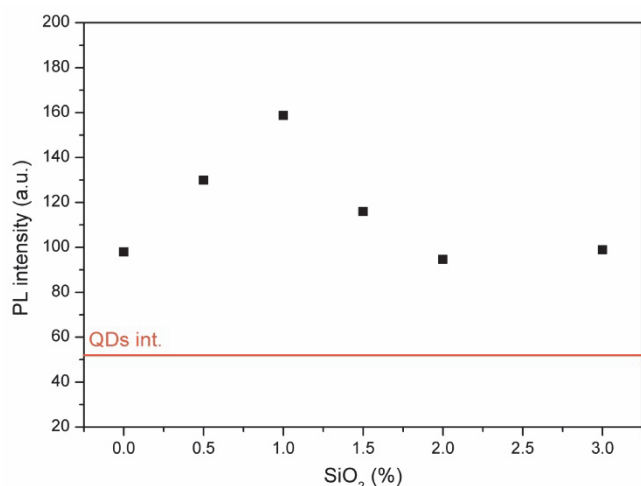


Fig. 7 Variations of the maximum PL intensity of the CdSe/ZnS-SiO₂-Ag colloid three-layer hybrid films with the SiO₂ layer made from various solid-content solutions

4. CONCLUSIONS

The CdSe/ZnS-SiO₂-Ag colloid three-layer structure has been fabricated to evaluate the effect of the distance between QDs and metal nanoparticles on PL intensity of QDs enhanced by surface plasmons. The SiO₂ layer covering Ag colloids leads to a red shift of the localized surface Plasmon resonance wavelength. The SiO₂ layer made from the solution with 0.1 wt% solid content displays the optimal enhancement (3.1 folds) on PL. Because LSPR is weakened with distance between CdSe/ZnS QDs and Ag colloids much more slowly than the nonradiative energy transfer, the optimal PL enhancement occurs at an appropriate distance.

ACKNOWLEDGMENTS

This work was financially supported by the Minister of Science and Technology, the Republic of China (MOST 105-2221-E-224-059-MY3).

REFERENCES

Aegerter, M.A. and Al-Dahoudi, N. (2003). "Wet-chemical processing of transparent and antiglare conducting ITO coating on plastic substrates." *Journal of Sol-Gel Science and Technology*, **27**, 81-89.

Aslan, K., Malyn, S.N., and Geddes, C.D. (2008). "Angular-dependent metal-enhanced fluorescence from silver island films." *Chemical Physics Letters*, **453**, 222-228.

Barnes, W.L. (1998). "Fluorescence near interfaces: the role of photonic mode density." *Journal of Modern Optics*, **45**, 661-699.

Biteen, J.S., Pacifici, D., Lewis, N.S., and Atwater, H.A. (2005). "Enhanced radiative emission rate and quantum efficiency in coupled silicon nanocrystal-nanostructured gold emitters." *Nano Letters*, **5**, 1768-1773.

Chan, Y.H., Chen, J.X., Wark, S.E., Skiles, S.L., Son, D.H., and Batteas, J.D. (2009). "Using patterned arrays of metal nanoparticles to probe plasmon enhanced luminescence of CdSe Quantum Dots." *ACS Nano*, **3**, 1735-1744.

Coe, S., Woo, W.K., Bawendi, M., and Bulovic, V. (2002). "Electroluminescence from single monolayers of nanocrystals in molecular organic devices." *Nature*, **420**, 800-803.

Gao, X.H., Cui, Y.Y., Levenson, R.M., Chung, L.W.K., and Nie, S.M. (2004). "In vivo cancer targeting and imaging with semiconductor quantum dots." *Nature Biotechnology*, **22**, 969-976.

Huynh, W.U., Dittmer, J.J., and Alivisatos, A.P. (2002). "Hybrid nanorod-polymer solar cells." *Science*, **295**, 2425-2427.

Jain, P.K. and El-Sayed, M.A. (2008). "Noble metal nanoparticle pairs: effect of medium for enhanced nanosensing." *Nano Letters*, **8**, 4347-4352.

Jung, M.H. and Kang, M.G. (2011). "Enhanced photo-conversion efficiency of CdSe-ZnS core-shell quantum dots with Au nanoparticles on TiO₂ electrodes." *Journal of Materials Chemistry*, **21**, 2694-2700.

Kim, B.H., Cho, C.H., Mun, J.S., Kwon, M.K., Park, T.Y., Kim, J.S., Byeon, C.C., Lee, J., and Park, S.J. (2008). "Enhancement of the external quantum efficiency of a silicon quantum dot light-emitting diode by localized surface plasmons." *Advanced Materials*, **20**, 3100-3104.

Kreibig, U. and Vollmer, M. (1995). *Optical Properties of Metal Clusters*. Berlin: Springer.

Kulakovich, O., Strekal, N., Artemyev, M., Stupak, A., Maskevich, S., and Gaponenko, S. (2006). "Improved method for fluorophore deposition atop a polyelectrolyte spacer for quantitative study of distance-dependent plasmon-assisted luminescence." *Nanotechnology*, **17**, 5201-5206.

Kulakovich, O., Strekal, N., Yaroshevich, A., Maskevich, S., Gaponenko, S., Nabiev, I., Woggon, U., and Artemyev, M. (2002). "Enhanced luminescence of CdSe quantum dots on gold colloids." *Nano Letters*, **2**, 1449-1452.

Liu, B.T., Liao, T.H., Tseng, S.J., and Lee, M.H. (2014). "Enhanced luminescence of quantum dot/dielectric layer/metal colloid multilayer thin films." *Applied Surface Science*, **292**, 615-619.

Liu, L., Xu, X.L., Lei, J.M., Liu, Y.S., and Yang, Z. 2011. "An-nealing structured Au nanoparticles enhanced light emission from CdSe quantum dots." *Thin Solid Films*, **519**, 5582-5587.

Lu, L., Chen, D.F., Sun, F.W., Ren, X.F., Han, Z.F., and Guo, G.C. (2010a). "Photoluminescence quenching and enhancement of CdSe/PMMA composite on Au colloids." *Chemical Physics Letters*, **492**, 71-76.

Lu, L., Xu, X.L., Shi, C.S., and Ming, H. (2010b). "Localized surface plasmon resonance enhanced photoluminescence of CdSe QDs in PMMA matrix on silver colloids with different shapes." *Thin Solid Films*, **518**, 3250-3254.

Medda, S.K., De, S., and De, G. (2005). "Synthesis of Au nanoparticle doped SiO₂-TiO₂ films: tuning of Au surface plasmon band position through controlling the refractive index." *Journal of Materials Chemistry*, **15**, 3278-3284.

Nazzal, A.Y., Qu, L.H., Peng, X.G., and Xiao, M. (2003). "Photoactivated CdSe nanocrystals as nanosensors for gases." *Nano Letters*, **3**, 819-822.

Shen, W.Q., Liu, F., Qiu, J., and Yao, B.D. (2009). "The photoinduced formation of gold nanoparticles in a mesoporous titania gel monolith." *Nanotechnology*, **20**, 105605.

Shuford, K.L., Ratner, M.A., Gray, S.K., and Schatz, G.C. (2007). "Electric field enhancement and light transmission in cylindrical nanoholes." *Journal of Computational and Theoretical Nanoscience*, **4**, 239-246.

Soganci, I.M., Nizamoglu, S., Mutlugun, E., Akin, O., and Demir, H.V. (2007). "Localized plasmon-engineered spontaneous emission of CdSe/ZnS nanocrystals closely-packed in the proximity of Ag nanoisland films for controlling emission linewidth, peak, and intensity." *Optics Express*, **15**, 14289-14298.

Song, J.H., Atay, T., Shi, S.F., Urabe, H., and Nurmikko, A.V. (2005). "Large enhancement of fluorescence efficiency from CdSe/ZnS quantum dots induced by resonant coupling to spatially con-

- controlled surface plasmons." *Nano Letters*, **5**, 1557-1561.
- Sugawa, K., Kawahara, T., Akiyama, T., Kobayashi, M., Takahara, A., and Yamada, S. (2009). "Enhanced absorption and emission in a copper phthalocyanine-gold nanoparticle system assisted by localized surface plasmon." *Chemistry Letters*, **38**, 326-327.
- Wu, J., S. Lee, Reddy, V.R., Manasreh, M.O., Weaver, B.D., Yakes, M.K., Furrow, C.S., Kunets, V.P., Benamara, M., and Salamo, G.J. (2011). "Photoluminescence plasmonic enhancement in InAs quantum dots coupled to gold nanoparticles." *Materials Letters*, **65**, 3605-3608.