

Enhancement and tunability of active plasmonic by multilayer grating coupled emission

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Abstract: The effect of coupled mode surface plasmon polaritons (SPPs) on the active emission of a nanostructure grating with organic semiconductor material, Alq₃, on the surface was investigated in this study. We report surface plasmon grating coupled emission (SPGCE) from excited organic layer on metal grating in both organic/metal (2-Layer) and organic/metal/organic/metal (4-Layer) structures. The dispersion relation was obtained from angle-resolved photoluminescence measurement. The resultant emission intensity can have up to 6 times enhancement on the 4-Layer device and the Full-Width Half-Maximum (FWHM) is less than 50 nm. The combination of SPPs on organic/metal interface allows specific directional emission and color appearance of Alq₃ fluorophores. Potential applications of such an active plasmonics with enhanced resonant energy emission due to interactions on the organic/metal nano-grating as biosensor were presented and discussed.

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References and links

1. H. Raether, *Surface Plasmons on Smooth and Rough Surface and on Gratings* (Springer-Verlag, Berlin, 1988).
2. R. W. Wood, "On a remarkable case of uneven distribution of light in a diffraction grating spectrum," *Phil. Mag.* **4**, 396-408 (1902).
3. A. Otto, "Excitation of nonradiative surface plasma waves in silver by the method of frustrated total reflection," *Z. Phys.* **216**, 398-410 (1968).
4. E. Kretschmann, "The determination of the Optical Constants of Metals by Excitation of Surface Plasmons," *Z. Phys.* **241**, 313-324 (1971).
5. N. Fang, Z. Liu, T.-J. Yen, and X. Zhang, "Regenerating evanescent waves from a silver superlens," *Opt. Exp.* **11**, 682-687 (2003).
6. R. W. Gruhlke, W. R. Holland, and D. G. Hall, "Surface-plasmon cross coupling in molecular fluorescence near a corrugated thin metal film." *Phys. Rev. Lett.* **30**, 2838-2841 (1986).
7. D. K. Gifford and D. G. Hall, "Emission through one of two metal electrodes of an organic light-emitting diode via surface-plasmon cross coupling," *Appl. Phys. Lett.* **81**, 4315-4317 (2002).
8. S. Wedge and W. L. Barnes, "Surface plasmon-polariton mediated light emission through thin metal films," *Opt. Exp.* **12**, 3673-3685 (2004).
9. J. Feng, T. Okamoto, J. Simonen, and S. Kawata, "Color-tunable electroluminescence from white organic light-emitting devices through coupled surface plasmons," *Appl. Phys. Lett.* **90**, 081106 (2007).
10. J. R. Lakowicz, J. Malicka, I. Gryczynski, and Z. Gryczynski, "Directional surface Plasmon-coupled emission: a new method for high sensitivity detection." *Biochem. Biophys. Res. Commun.* **307**, 435-439 (2003).
11. I. Gryczynski, J. Malicka, Z. Grycznski, and J. R. Lakowicz, "Radiative decay engineering 4. Experimental studies of surface Plasmon-coupled directional emission." *Anal. Biochem.* **324**, 170-182 (2004).
12. T. Nakano, H. Kobayashi, K. Shinbo, K. Kato, F. Kaneko, T. Kawakami, and T. akamatsu, "Emission light

- properties from Adrhodamine-B LB films due to surface plasmon excitations in the Kretschmann and reverse configurations,” *Mater. Res. Soc. Symp.* **660**, 1-6 (2001).
13. K. Shinbo, S. Toyoshima, Y. Ohdaira, K. Kato, and F. Kaneko, “Surface plasmon emission light property due to molecular luminescence and molecular interaction,” *J. J. Appl. Phys.* **44**, 599-603 (2005).
 14. G. Winter and W. L. Barnes, “Emission of light through thin silver films via near-field coupling to surface plasmon polaritons,” *Appl. Phys. Lett.* **88**, 051109 (2006).
 15. J. Enderlein and T. Ruckstuhl, “The efficiency of surface-plasmon coupled emission for sensitive fluorescence detection,” *Opt. Exp.* **13**, 8855-8865 (2005).
 16. S. C. Kitson, W. L. Barnes, J. R. Sambles, “Photoluminescence from dye molecules on silver gratings,” *Opt. Commun.* **122**, 147-154 (1996).
 17. J. Kalkman, C. Strohhofer, B. Gralak, A. Polman, “Surface plasmon polariton modified emission of erbium in a metalodielectric grating,” *Appl. Phys. Lett.* **83**, 30-32 (2003).
 18. Y.-J. Hung, I. I. Smolyaninov, C. C. Davis, and H.-C. Wu, “Fluorescence enhancement by surface gratings,” *Opt. Exp.* **14**, 10825-10830 (2006).
 19. S. A. Maier, P. G. Kik, H. A. Atwater, S. Meltzer, E. Harel, B. E. Koel, and A. A. G. Requicha, “Local detection of electromagnetic energy transport below the diffraction limit in metal nanoparticle plasmon waveguides,” *Nat. Mater.* **2**, 229-232 (2003).
 20. I. Pockrand and A. Brillante, “Nonradiative decay of excited molecules near a metal surface,” *Chem. Phys. Lett.* **69**, 499-504 (1980).
 21. J. R. Lakowicz, Y. Shen, S. D’Auria, J. Malicka, J. Fang, Z. Gryczynski, and I. Gryczynski, “Radiative decay Engineering 2: effects of Silver Island films on fluorescence intensity, lifetimes, and resonance energy transfer,” *Anal. Biochem.* **301**, 261-277 (2002).
 22. C.-W. Lin, K.-P. Chen, S.-M. Lin, C.-K. Lee, “Design and fabrication of an alternating dielectric multilayer device for surface plasmon resonance sensor,” *Sens. Actuators B* **113**, 169-176 (2006).
 23. C.-W. Lin, K.-P. Chen, M.-C. Su, T.-C. Hsiao, S.-S. Lee, S.-M. Lin, X.-J. Shi, C.-K. Lee, “Admittance loci design method for multilayer surface plasmon resonance devices,” *Sens. Actuators B* **117**, 219-229 (2006).
 24. C.-W. Lin, K.-P. Chen, M.-C. Su, C.-K. Lee, C.-C. Yang, “Bio-plasmonics: Nano/micro structure of surface plasmon resonance devices for biomedicine,” *Opt. Quantum Electron* **37**, 1423-1437 (2005).
 25. J. Homola, I. Koudela, S. S. Yee, “Surface plasmon resonance sensors based on diffraction gratings and prism couplers: sensitivity comparison,” *Sens. Actuators B* **54**, 16-24 (1999).
 26. D. Sarid, “Long-range Surface-Plasma Waves on very Thin Metal Films,” *Phys. Rev. Lett.* **47**, 1927-1930 (1981).
 27. P. Andrew and W. L. Barnes, “Energy transfer across a metal film mediated by surface plasmon polaritons,” *Science* **306**, 1002-1005 (2004).

1. Introduction

Surface plasmon resonance (SPR) is whereby the free charge oscillation on a metal-dielectric interface due to the coupling of incident light energy via matching momentants of free space and on the interface [1-4]. This phenomenon was first observed by R. W. Woods from metal grating in the early 1900s [2]. Recently, enhanced transmission and emission of organic semiconductor on metallic thin film mediated by energy transfer of coupled SPPs has been used for various design of opto-electronics. Initially, coupled SPPs transmission through a thin metal film was investigated on surface with few hundred nanometer roughness [5] or corrugated microstructure [6-9]. Others have made SPPs coupled emissions from excited fluorescent molecules by evanescent field near the metallic surface [10, 11]. The coupled emission around SPR angle has been observed by using attenuated total reflection (ATR) prism in the Kretschmann and reverse Kretschmann configuration [12-15], grating coupler [16-18] and nanoparticles [19]. The existance of nonradiative decay near metallic surface can have effects on fluorescence intensity and lifetimes. The further interactions of coupled resonance energy by so called surface plasmon coupled emission (SPCE) can have interesting optical properties for many applications [20, 21]. Such a SPCE technique has performed on many structures but not on multilayer grating structure.

In this paper, we prepared the nanostructure with 1-D grating patterns by electron-beam lithography (EBL). We fabricated two devices, 2-layer (Alq_3/Au) and 4-layer symmetrical organic dielectric films ($\text{Alq}_3/\text{Au}/\text{Alq}_3/\text{Au}$), with grating line width and pitch size of 400 nm and 800 nm, respectively. We used the emission of Alq_3 organic molecules to excite SPPs on multilayer grating coupled emission. The emissions correspond to the resonant condition of SP modes on the Alq_3/Au interface and grating couple to the Au/air interface for the emission of light. This technique has surface plasmon grating coupled emission (SPGCE) of light

passing through metal and is a multilayer grating approach for the excitation of SPPs. Our experimental results show that these devices can have specific directional emission, enhanced emission intensity, and reduced Full-Width Half-Maximum (FWHM). We also best fit the measurement results to a revised theoretical model of grating coupler on a thin layer of metal which confirms the existence of SPP mode with the momentum-matching condition of a surface plasmon resonance in our experimental configuration. Further investigations will facilitate the development of novel bio-sensing device having multilayer organic/metal nanostructure for grating coupler active plasmonic biosensor and the use of admittance loci design method for such a purpose [22-24].

2. Experimental setup

In order to use SPPs for SPGCE, we have designed, fabricated, and characterized two SPR configurations, a 4-layer device of [Si / grating (PR) / Alq₃(50 nm) / Au(20 nm) / Alq₃(50 nm) / Au(20 nm)] and a 2-layer one of [Si / grating (PR) / Alq₃(50 nm) / Au(20 nm)]. Cross sections of the 2-layer and 4-layer devices are shown in Figs. 1(a) and 1(b), respectively. Our samples were prepared by an Electron Beam Lithography system (ELS-7500EX, Maker Co. JAPAN). The high-resolution positive electron-beam photoresist (PR), ZEP520A (Zeon Co. JAPAN), was first spin coated on the silicon substrate to form a resist layer having thickness of 100 nm, and then pre-baked at 180 °C for 2 minutes. After exposing to the electron beam of 50 KV, nonstructural gratings having elongated one-dimensional line pattern with size of 400 nm, and pitch of 800 nm were formed. The exposure was carried out for 2 μsec by a pixel map of 60000×60000 dots to give a total exposure area of 1.2×1.2 mm². Next, 50 nm of organic Alq₃ and subsequent 20 nm of gold were deposited on the grating by a thermal evaporator with vacuum level and evaporation rate of approximately 2×10⁻⁶ Torr and 0.2 Å/s, respectively.

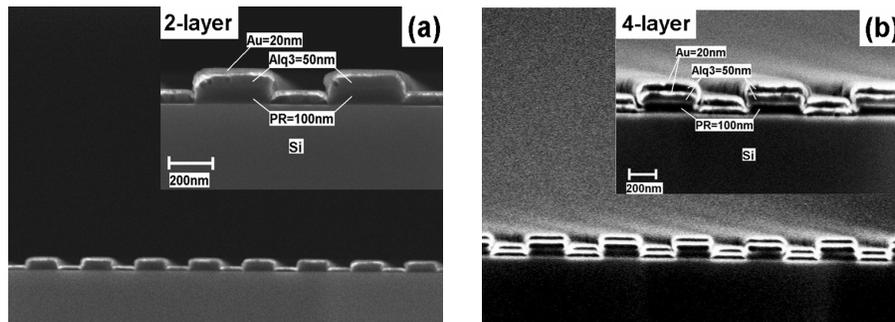


Fig. 1. SEM images of the gratings cross section, which show the arrangement of a periodically lamellar layer a) 2-layer structure of Alq₃/Au and b) 4-layer structure of (Alq₃/Au/Alq₃/Au) on top of a 100 nm PR structure.

We have set up a photoluminescence (PL) measurement system for the angular emission spectra produced by the designated SPGCE from grating structure as shown in Fig. 2. In brief, a 405 nm light source (Spectral Luminator 69050, Newport Oriel Inc., USA) is used to excite Alq₃ molecules on the nano-grating device. The device was placed at the center of a high-resolution rotary stage with computer controllable incident angle, θ_i , emission angle, θ_e , and azimuthal angle, φ . The SPGCE output light was collected and measured by a 2-inch lens with focal distance of 5 cm and a 12-bit spectrometer (USB2000, Ocean Optics Co., USA). Two motorized rotary stages (SGSP-120YAW-W, Sigma Koki, Japan) and its controller (SHOT-204MS, Sigma Koki, Japan) are used to control θ_i and θ_e , between sample and detector stages. The nominal angular resolution is 0.0025 degree. The system uses temperature and humidity sensor (Galltec TFG80J) and data acquisition card (PCI-6070E, National Instrument Inc,

USA) to monitor the environmental operating condition for higher accuracy and reproducibility.

The phenomena of plasmon enhancement effects on the fabricated devices are mainly from the top side of the device through ultra-thin Au film. The spectrometer moved at θ_e angle to measure the PL intensity at each specific emission angle to study the changes of emitted light due to interactions of SPPs. The emission spectra from both 2-layer and 4-layer devices are obtained by optical pumping Alq₃ layer with a 405 nm light source at fixed incident angle of $\theta_i = 45^\circ$. At this angle, it is not corresponding to SPR resonance angle, which is greater than 65° in grating pitch [25], and thus would not be able to excite Alq₃ molecules through evanescent field. The emission of organic Alq₃ layer will be the source to excite the SPPs from thin grating metal film and cross couple for far-field measurement.

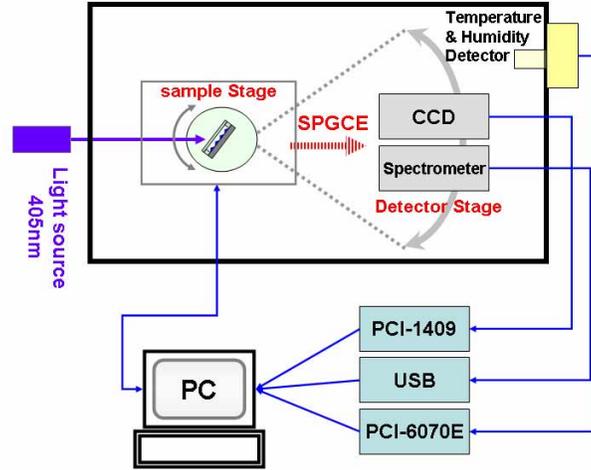


Fig. 2. Schematic diagram shows the experimental setup for our computer controlled PL spectra measurement system. A spectrometer is used to measure the emission from the top side of the multilayer grating coupler device through an ultra-thin Au film for the investigation of possible enhancement effects.

3. Model of active plasmonic via SPGCE

The SPGCE is based on the fluorescent emission from the organic Alq₃ molecules in the active layer and its diffraction in a periodically modulated surface with possible SPPs enhancement due to multilayer structure of metallic thin film. Using 2-layer device as a simplified model, the possible interaction mechanisms are shown in Fig. 3. The Alq₃ molecules in the active layer can be electrical- or photo-pumping to provide non-oriented internal light source to generate SPPs on the metal/dielectric interfaces and de-couple through grating structure for detectable radiative emission or non-radiative waveguide mode. Therefore, there are four possible wave vectors, i.e., k_{rad} (k_r), k_{rad} (k_w), $k_{SP(Au/air)}$, and $k_{SP(Au/Alq_3)}$, that can exist between different interfaces of lamellar grating nanostructure, i.e. air, organic-layer, and two metal-dielectric interfaces. The two SP modes are associated with metal/organic and metal/air interfaces and their corresponding wave vectors are $k_{SP(Au/air)}$ and $k_{SP(Au/Alq_3)}$. Through these possible mechanisms, the emitted light from Alq₃ could couple with surface plasmons under matching conditions while propagating along the grating surface. It can become radiative light again through the decoupling nanostructure for specific directional emission and enhancement in its optical properties.

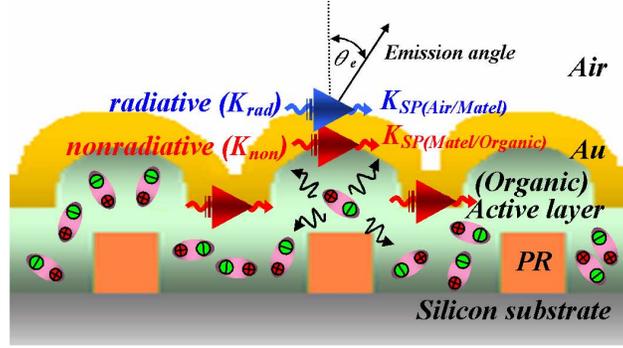


Fig. 3. Cross section view of a simplified 2-layer active plasmonic model device. The Alq₃ molecules in the active layer can provide non-oriented internal light source to generate SPPs on the metal/dielectric interfaces and de-couple through grating structure for detectable radiative emission or non-radiative internal propagation.

The SP grating coupled emission, $k_{//}$, at certain wavelength of λ can result from the matching momentums of the internal Alq₃ emission (θ_e) through grating coupler condition (dielectric constant of Alq₃ and pitch size of Λ) to the metal/air ($K_{sp(Au/air)}$) dispersion curve as shown in the Eq. (1). The SP modes for Au/air interface on the grating layer can be de-coupled into air if its wave vector is smaller than that of the air. Equation (2) gives such a matching condition for the guided mode of the organic layer and the de-coupling of light emission. According to Fresnel's transmission of optics, the guided mode in the Alq₃ layer propagates inside the organic film. The wave vectors for the organic layer mode are represented by Eqs. (2) and (3) shown below.

$$k_{//} = \sqrt{\epsilon_d} \left(k_0 \sin(\theta_{emission}) \pm m \frac{2\pi}{\Lambda} \right) = k_0 \sqrt{\frac{\epsilon_{Au} \cdot \epsilon_{air}}{\epsilon_{Au} + \epsilon_{air}}} = k_{SP(Au/air)}, \quad (1)$$

$$k_w = k_{SP(Au/Alq_3)} \pm m \frac{2\pi}{\Lambda}, \quad (2)$$

$$k_{SP(Au/Alq_3)} = k_0 \sqrt{\frac{\epsilon_{Au} \cdot \epsilon_{Alq_3}}{\epsilon_{Au} + \epsilon_{Alq_3}}}, \quad (3)$$

where $k_{//}$ and k_w are the wave vectors parallel to the surface of the emitted light and the guided mode, respectively. K_{sp} is the SP wave vector parallel to the surface of the interfaces between metal and dielectric, such as the organic/metal and metal/air interface. The emission photon with wave-vector component $k_0 \sqrt{\epsilon_d} \sin(\theta)$ at an azimuthal angle (φ) may now couple directly with SPPs. It is also clear that θ must vary as φ changes in order to maintain coupling. If $\varphi \neq 0$, by simple geometry, we found that the scalar equivalent of Eq. (4) is [16],

$$k_{SPP}^2 = n_d^2 k_0^2 \sin^2 \theta + \left(m \frac{2\pi}{\Lambda} \right)^2 \pm 2n_d m \frac{2\pi}{\Lambda} k_0 \sin \theta \cos \varphi \quad (4)$$

4. Results and discussion

We have measured SPGCE spectra for each of our fabricated samples, as shown in Fig. 1, by using PL measurement system to collect the emitted light intensity from -10 to 15 degree with 1 degree per step. We can then also examine the effect of SPPs excited SPGCE on the angular dispersion of emission spectra. The resultant angular emission spectra of enhanced luminescence from metal/organic grating from multiple emission angles are composed into color coded three dimensional spectrogram as shown in Figs. 4(a) and 4(b) for 2-layer and 4-

layer device, respectively. It is quite obvious from these two figures that 4-layer one does have higher intensity and smaller FWHM. The average shift in peak wavelength is 14 nm/degree for the grating with pitch size of 800 nm. The emission spectra can shift from 750 nm to 480 nm by changing the emission angle for measurement. It results in an angular dependent tunable color device with specific structural parameters, e.g., pitch constant (Λ), the thickness of each layer of the grating and the optical indices of used materials, to satisfy the SPP resonant conditions.

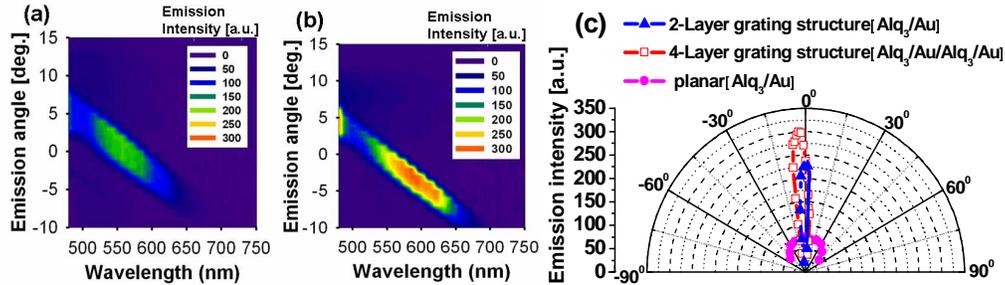


Fig. 4. The PL emission obtained from a grating sample having 2-layer and 4-layer structure (grating size: line 400 nm, pitch 800 nm, area size $1.2 \times 1.2 \text{ mm}^2$). The 4(a) and 4(b) are shows PL 3-D emission image obtained from a grating sample. The dependence of the emission spectra on observation angle (θ) is shown in 4(a) and 4(b) for 2-layer and 4-layer structure, respectively. The 4(c) shows the planar, 2-layer and 4-layer. The emission maximum was about 0° and -3° for 2-layer, 4-layer devices, respectively.

The enhanced emission spectra measured with the coupling at different angles are shown in the characteristic diagram of PL emission in polar coordinates [Fig. 4(c)] for planar devices, 2-layer, and 4-layer, respectively. The ratio of the maximal intensity of these three devices is 1:4:6. The intensity from the 4-layer structure can be strongly enhanced by recovering from three possible mechanisms, i.e., coupled SPP from Alq_3 scattering emission, non-radiative mode, and the long-range surface plasmon polaritons (LR-SPPs) with symmetrical dielectric structure. The LR-SPPs are associated with the interactions of symmetric or antisymmetric magnetic fields on both sides of metal interface [26, 27]. The fields can constructively interact inside the thin metal film (20 nm) and then result in the LR-SPPs, which can extend into both Alq_3 layer for excitation.

Figure 5 shows the effect of pitch size on the directional emission spectra of SPGCE for three different grating structures. The resultant angular dispersion is about $-35^\circ \sim -5^\circ$ for device with pitch size of 500 nm while for pitch size of 800 nm is limited to $-10^\circ \sim 10^\circ$.

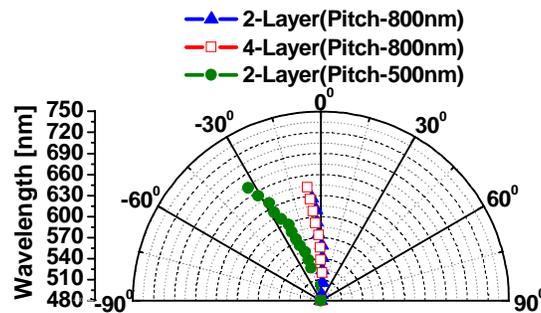


Fig. 5. This shows experimental PL SPGCE diagram in directional emission spectra of pitch 500 nm and 800 nm structures.

It can be concluded that by using 4-layer structure, the SPGCE efficiency was improved greatly. Figure 6(a) shows the CIE-1931 chromaticity coordinates of the coupled emission in the emission angle and color changes from both 2-layer (blue line) and 4-layer (red line)

devices. The colors of SP coupled emission are calculated and plotted on a CIE-1931 diagram, which shows angular dependent spectral changes from red to blue. We also measured the FWHM from the coupled emission spectra at different angles as shown in the Fig. 6(b). For the 4-layer structure, the FWHM is in the range of 40 to 50 nm, whereas for the 2-layer structure is from 57 to 70 nm, which may come from the stronger intensity of the 4-layer devices.

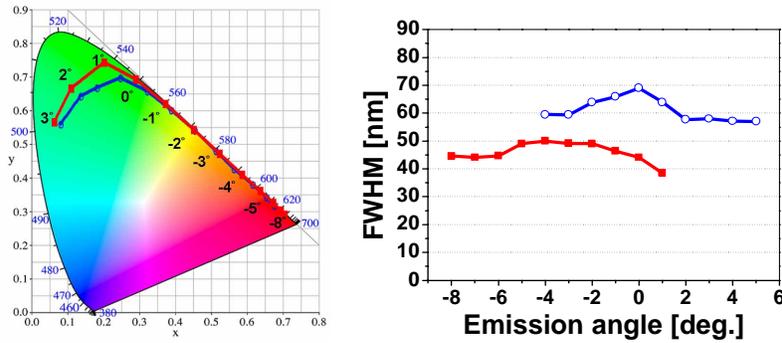


Fig. 6. The SP-coupled emission is via a grating mediated by energy transfer of SP tunable-color and FWHM at 2-layer (—○—) and 4-layer (—■—) grating structure. The 6(a) shows the coupled emission spectrum to 1931 CIE chromaticity diagram, with the coordinates of the spectra and angle. The 6(b) shows the FWHM shifts at different angle.

From the 4-layer measurement data, we can use peak emission wavelength at each emission angle to calculate its dispersion curve with $m=-1$ and $\Lambda=800$ nm by Eq. (1) and show as blue circle in Fig. 7(a). This result is related to the theoretical dispersion relation of SP-grating coupled emission at Au/air interface ($K_{SP(Au/air)}$) with $m=1$, dielectric constants of Alq₃ ($\epsilon_r = 2.973$, $\epsilon_i = 0.012$) and Au ($\epsilon_r = 7.393$, $\epsilon_i = 1.918$) and wavelength at 550 nm by a matching momentum, ΔK of $24.55 \mu\text{m}^{-1}$. It can be explained by using grating coupler dispersion relation as shown in Fig. 7(b), which shows the SPPs propagating along a grating surface has to reduce its wave vector by ΔK in order to have SPGCE. This light emission is a consequence of decoupling via grating structure from the photoluminance of Alq₃ molecules. Such scheme allows a momentum-match between Alq₃ emission photons and SPPs; consequently, tunable SPP mediated light emission was achieved.

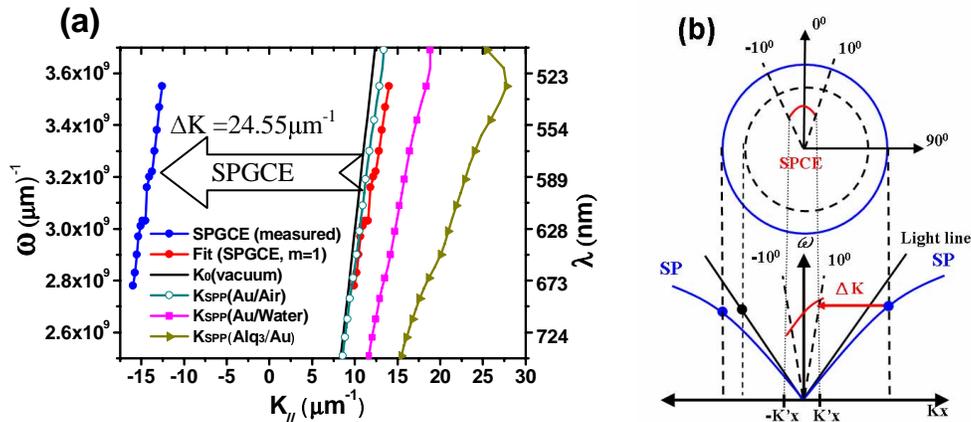


Fig. 7. The figure give fitting results and theoretical interpretation. 7(a) is Frequency vs. wave vector for the measured data (—○—) and fitting data (—■—), the theoretical dispersion relation on interface surface Plasmon dispersion relation Au/air (—○—), Alq₃/Au (—■—), Au/water (—■—), and the light in vacuum (—). The data were taken from the sample with 800 nm pitch. The explained that intrinsic Alq₃ emission and excitation into the Au/air coupler SP emission angle as shown in 7(b).

5. Conclusions

We have demonstrated the phenomenon of 2-layer and 4-layer grating structure for active surface plasmon polaritons propagating along 1-D rectangular lamellar grating in an organic/metal interface via SPGCE for enhancing and tuning far-field light emission. Our results showed that strong coupling resonances in SP-coupled emission from the interactions of Alq₃/Au and Au/air symmetric mode leads to the enhanced optical properties of directional emission, intensity and FWHM for active plasmon devices. The resultant emission intensity can have up to 6 times enhancement on the 4-layer device and the spectral bandwidth (FWHM) is less than 50 nm. The combination of SPPs on organic/metal interface allows specific directional emission and color appearance of Alq₃ fluorophores. Such scattering taking place through a metal film has an important bearing on the generation of useful light. Further investigations will be performed on SPPs with the integration of optimized organic electroluminescent plasmonic for active biosensor devices in biochemical analysis and immunoassay.

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