Effects of molecular orientation on surface-plasmon-coupled emission patterns

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We observed azimuthal distributions of surface-plasmon-coupled emission from thin layers of randomly oriented and oriented sexithiophene molecules deposited on 50-nm-thick Ag films. For the randomly oriented layer, we observed a uniform and isotropic cone of emission, showing that the surface plasmons are excited isotropically in all directions on the Ag surface. The emission pattern for the oriented layer exhibited a much stronger intensity along the direction of molecular orientation, showing that surface plasmons propagating parallel to the molecular orientation are excited most effectively. These results demonstrate that surface-plasmon-coupled emission provides a new simple approach to the determination of molecular orientation in thin films. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2804563]

It is well known that excited fluorophores placed very close to a metallic surface excite surface plasmon polaritons (SPPs) via near-field interaction.[1,2] The excited SPPs can be converted into light by using an appropriate decoupling device such as a grating or a prism.[3] Recently, the so-called surface-plasmon-coupled emission (SPCE), which arises from the combination of the above two processes, has attracted much interest because it offers a new method of fluorescence detection applicable to a variety of sensing devices, in particular, sensors of biomolecules.[4–6] In SPCE, a thin metal film, usually Ag or Au film, $\sim$50 nm in thickness, deposited on a glass substrate, is used and fluorophores are placed on top of the metal surface. The sample is attached to a base of a glass prism. The fluorophores, excited by light incident either from the air or prism side, excite SPPs and generate highly polarized directional emission at the prism side. The unique properties of the generated emission make SPCE a potentially important tool for many applications.

SPCE depends on a lot of parameters, such as the thickness of the metal film, distance between fluorophores and the metal surface, orientation of fluorophores, refractive index of prism, etc. Winter and Barnes[7] studied the influence of the metal thickness using Ag films and reported that a maximum SPCE intensity is obtained at the thickness of $\sim$50 nm. Very recently, Ray *et al.*[6] studied the effects of fluorophore-metal distance for cyanine dye molecules. They reported a maximum SPCE intensity at the fluorophore-metal distance of $\sim$20 nm. In spite of great experimental efforts made so far, the effects of fluorophore orientation on SPCE properties are not yet well explored. Theoretical analyses performed by Calander[8] predict that the azimuthal intensity variation of SPCE from a dipole oriented parallel to the metal surface is anisotropic and shows a maximum SPCE intensity in the direction of molecular orientation. To our knowledge, such an anisotropic SPCE pattern has not yet been reported. Here, we report on successful observation of anisotropic SPCE azimuthal patterns generated by molecules aligned along a given direction on Ag thin films. Observed patterns are in good agreement with the theoretical prediction.

Thin Ag films 50 nm in thickness were vacuum deposited (10^{-6} Torr) on glass substrates. 20-nm-thick films of sexithiophene (6*T*) were then deposited on the Ag surface with a low deposition rate of 0.5–1.0 nm/min. The 6*T* molecule is known to have the main optical transition dipole parallel to the long molecular axis.[9] According to previous studies of vapor deposited films of thiophene oligomers,[9–11] the films are polycrystalline and show varying degrees of order depending on preparation conditions. When a low deposition rate is used, deposited films consist of grains, in which the long molecular axis is oriented close to normal to the substrate (within $\sim$25°). In the direction parallel to the substrate, the grains are randomly oriented.[10] To our knowledge, no report exists on 6*T* films deposited on vacuum-deposited silver films. However, as confirmed later by polarized photoluminescence (PL) measurements, presently deposited 6*T* films have molecular arrangements similar to those previously reported for the films prepared with a low deposition rate. In order to obtain layers of 6*T* molecules lying horizontally on the Ag surface with their long axis oriented in a preferential direction, we used a rubbing technique similar to that used for octithiophene[11] and *p*-sexiphenyl[12] molecules. A 6*T* prelayer of 10 nm was first deposited on the silver surface. The 6*T* prelayer was then rubbed in a given direction by using a wiping paper. To complete the sample, an additional 6*T* layer 10 nm in thickness was deposited.

The polarized PL spectra of the nonrubbed and rubbed 6*T* samples were examined to confirm the 6*T* molecular orientation. The measurement configuration is shown in Fig. 1(a). Polarized excitation light with wavelength of 408 nm from a laser diode was incident normal to the sample surface. The emitted light was collected at an angle of 45° from the normal by a camera lens and passed through a polarizer. The polarized light was then focused onto the entrance slit of a 25 cm single monochromator equipped with a charge-coupled device. A polarization scrambler was inserted in front of the entrance slit. Polarized emission intensities I_{HH} and I_{VV} are defined as follows: I_{HH} (I_{VV}) is the intensity of the horizontally (vertically) polarized emission produced by a horizontally (vertically) polarized excitation light.
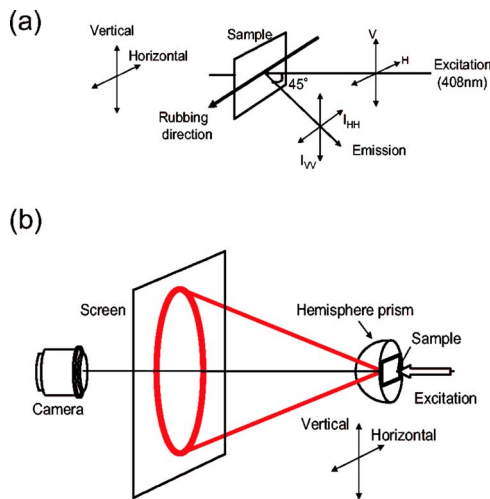
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FIG. 1. (Color online) (a) Polarized PL measurement scheme. (b) Reversed ATR measurement scheme.

Figures 2(a) and 2(b) show PL spectra of the nonrubbed and rubbed 6*T* films, respectively. In Fig. 2(a), we see that both the I_{HH} and I_{VV} spectra exhibit similar profiles with two peaks at ∼550 nm (2.25 eV) and ∼590 nm (2.1 eV), and a shoulder at 645 nm (1.92 eV). The PL band positions are in agreement with those previously reported for 6*T* films deposited by thermal evaporations.[13,14] We see that the PL intensity of the nonrubbed sample is independent of the polarization direction. This suggests that in the nonrubbed sample, the components of 6*T* transition dipole moment parallel to the sample surface are randomly oriented. The PL intensity of the nonrubbed sample is very weak compared to that of the I_{HH} spectrum of rubbed sample shown in Fig. 2(b). This is an indication that the transition dipole of the 6*T* molecule in the nonrubbed sample is oriented almost perpendicularly to the sample surface and, consequently, is not efficiently coupled with the electric field of the exciting laser.

In contrast to the nonrubbed sample, the PL intensity of the rubbed sample shows a strong dependence on the polarization direction, as presented in Fig. 2(b). The results presented in this figure were obtained by setting the rubbing direction to be horizontal. In the figure, I_{VV} spectrum is dis-
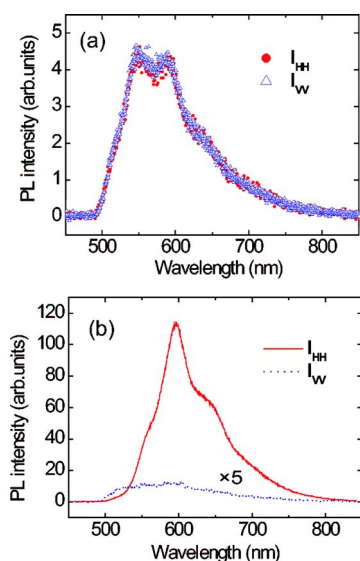

FIG. 2. (Color online) (a) Polarized PL spectra for randomly oriented 6*T* thin film. (b) Polarized PL spectra for oriented 6*T* thin film.
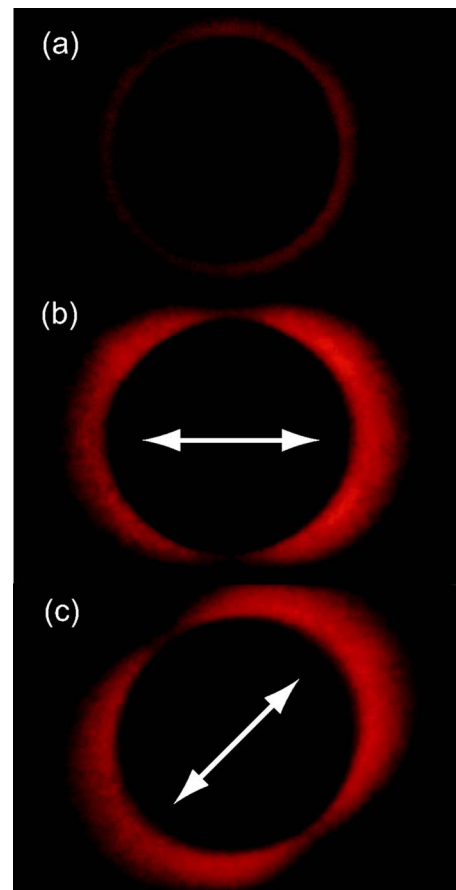

FIG. 3. (Color online) (a) SPCE pattern from randomly oriented 6*T* thin film. (b) SPCE pattern from oriented 6*T* thin film. The rubbing direction was horizontal. (c) Same as (b) but the sample 45° rotated counter clockwise. The arrows in (b) and (c) indicate the rubbing direction.

played after multiplying the raw intensity by a factor of 5. The dichroic ratio I_{HH}/I_{VV} calculated directly from the maximum peak heights is about 45. When the rubbing direction of the sample is rotated around the normal axis from the horizontal direction, the intensity of I_{HH} (I_{VV}) spectrum was found to decrease (increase) and take a minimum (maximum) when the rubbing direction was vertical. As in the cases of analogous molecules,[12,15] these results allow us to conclude that the long axis of 6*T* molecules is preferentially aligned parallel to the rubbing direction on a macroscopic scale. The maximum PL intensity much higher than that of the nonrubbed sample results from much stronger coupling with the incident electric field.

We then observed SPCE patterns from the nonrubbed and rubbed 6*T* films on Ag films to find out the effects of molecular orientation. The samples were attached to a hemisphere prism made of BK7 glass with index-matching fluid. A reversed attenuated total reflection (ATR) configuration was used, as shown in Fig. 1(b). For excitation, we used the 457.9 nm line of an Ar⁺-ion laser. The laser beam with the horizontal polarization was incident normal to the sample surface from the air side. We examined the azimuthal distribution of SPCE produced at the prism side by projecting it onto a screen and taking its photograph. Scattered excitation light at 457.9 nm was eliminated with a long-pass filter with a cutoff wavelength of 530 nm.

Figure 3(a) shows a photograph of a SPCE pattern from the nonrubbed 6*T* film. The pattern observed is the projection of a cone of light emission that is symmetric around the

normal axis. We note here that the emitted light is p polarized and the emission angle agrees well with the angle of ATR dip observed only for p-polarized incident light for the same sample. These facts confirm that the observed emission arises from the excitation and decoupling of SPPs, i.e., SPCE. The symmetric pattern of the emission in Fig. 3(a) implies that SPPs are excited uniformly in all directions on the Ag surface by the nonrubbed $6T$ film. Figures 3(b) and 3(c) show the SPCE patterns of the rubbed $6T$ sample. We observe an anisotropic emission pattern in which the light intensity is the strongest along the molecular orientation and becomes weaker as the azimuthal angle deviates from the molecular orientation. The anisotropic patterns in Figs. 3(b) and 3(c) imply that SPPs propagating along the molecular orientation are excited most efficiently. We note here that in accordance with the results of the polarized PL measurements, the intensity of the SPCE is considerably lower for the nonrubbed sample. This is the consequence of the weak coupling of the molecular dipoles with incident light. The results presented in Fig. 3 demonstrate that the SPCE pattern is directly linked to the orientation of the molecules.

The effects of molecular orientation on the SPCE pattern can be qualitatively explained by considering the efficiency of SPP excitation, which is determined by the magnitude of energy flux associated with transverse magnetic (TM) electromagnetic fields generated by a fluorescent molecule. In theoretical considerations, it is very common to assume an oscillating point dipole embedded in a dielectric layer coating a metallic surface.[1,2,8] To calculate the energy flux, we follow the formulation of Enderlein[16] and use his notations. As given by Eq. (6) of Ref. 16, the dipole field is represented by a sum of plane waves propagating in various directions; each plane wave is characterized by a different in-plane wavevector **q**. When the magnitude of the in-plane wavevector q exceeds that of the wavevector in the dielectric layer k_W, the component of the wavevector normal to the interface l_W becomes imaginary and, consequently, the corresponding dipole fields are evanescent. Although the dipole fields contain p and s waves as explicitly expressed in Eq. (6) of Ref. 16, only the p polarized or TM evanescent waves can excite SPPs at the metal-dielectric interface. It follows that SPPs are excited more efficiently when the intensities of energy flux associated with the TM evanescent waves are higher, resulting in stronger SPCE intensities. The dependence of the energy flux on the direction of **q** determines the azimuthal angular pattern of SPCE.

Using the expression of the electric field of p waves in Eq. (6) of Ref. 16, we can derive an expression for the corresponding magnetic fields and finally obtain the flux intensity (the modulus of the Poynting vector) by a standard manner. The metal-dielectric interface is taken to be the x, y plane, z axis being normal to the interface. A dipole **p** making an angle β with the z axis is located very close to the interface and assumed to lie on the x, z plane. We can write as $\mathbf{p} = (p \sin\beta, 0, p \cos\beta)$, where p is the magnitude. For a TM evanescent wave propagating with an in-plane wavevector **q** specified by an azimuthal angle ϕ relative to the x direction, the flux intensity is given by

$$S_{TM}(\beta, \phi) = S_0 p^2 [u^2 \cos^2\beta \sin^2\phi + (u^2 - \sin^2\beta)\cos^2\phi], \quad (1)$$

where S_0 is a constant and u is the magnitude of in-plane wavevector q normalized to $n(\omega/c)$, with the refractive index

of the dielectric layer n, angular frequency ω, and speed of light in vacuum c.

For a dipole oriented parallel to the surface ($\beta = \pi/2$), Eq. (1) suggests that S_{TM} is proportional to $\cos^2\phi$. This implies that the energy flux takes a maximum value for the evanescent wave propagating along the same direction as the dipole orientation ($\phi = 0$) and decreases as ϕ increases. This behavior of S_{TM} explains fairly well the experimentally observed behavior of the SPCE patterns of the rubbed sample shown in Fig. 3. For a dipole oriented perpendicular to the surface ($\beta = 0$), Eq. (1) becomes independent of ϕ, predicting an isotropic SPCE pattern. By taking into account this fact, an isotropic SPCE pattern obtained for the nonrubbed sample [Fig. 3(a)] can be well explained by the almost perpendicular orientation of the $6T$ molecular axis and the in-plane random orientation of the grains. Although perpendicular dipoles are expected to couple with SPPs more efficiently than parallel dipoles,[1,2] in the present nonrubbed samples, the influence of the small coupling with incident light is much larger, resulting in weak overall SPCE intensities. The above qualitative considerations of SPCE azimuthal patterns are consistent with results of numerical calculation reported by Calander.[8]

In conclusion, we prepared thin films consisting of randomly oriented and oriented $6T$ molecules on top of Ag films and observed SPCE patterns. In contrast to a uniform isotropic cone of emission from the randomly oriented $6T$ layer, the SPCE from oriented $6T$ layer exhibited an isotropic pattern with the strongest intensity at the azimuthal angle at which $6T$ molecules were oriented. This behavior of the SPCE pattern can be well explained by considering the energy flux associated with TM evanescent fields generated by a point dipole. The results presented here demonstrate that the SPCE pattern provides a new versatile analytical tool to determine the molecular orientation with a very simple and low cost instrumentation.

[1] G. W. Ford and W. H. Weber, Phys. Rep. **113**, 195 (1985).
[2] W. L. Barnes, J. Mod. Opt. **45**, 661 (1998).
[3] H. Raether, *Surface Plasmons on Smooth and Rough Surfaces and on Gratings*, Springer Tracts in Modern Physics Vol. 111 (Springer, Berlin, 1988), p. 49.
[4] J. R. Lakowicz, Anal. Biochem. **324**, 153 (2004).
[5] I. Gryczynski, J. Malicka, Z. Gryczynski, and J. R. Lakowicz, Anal. Biochem. **324**, 170 (2004).
[6] K. Ray, H. Szmacinski, J. Enderlein, and J. R. Lakowicz, Appl. Phys. Lett. **90**, 251116 (2007).
[7] G. Winter and W. L. Barnes, Appl. Phys. Lett. **88**, 051109 (2006).
[8] N. Calander, Anal. Chem. **76**, 2168 (2004).
[9] P. Lang, R. Hajlaoui, F. Garnier, B. Desbat, T. Buffeteau, G. Horowitz, and A. Yassar, J. Phys. Chem. **99**, 5492 (1995).
[10] W. Gebauer, M. Skolowski, and E. Umbach, Chem. Phys. **277**, 33 (1998).
[11] C. Videlot, V. Grayer, J. Ackermann, A. E. Kassmi, D. Fichou, and G. Hadziioannou, Synth. Met. **139**, 115 (2003).
[12] N. Aoki, Y. Koshiba, and Y. Ueda, Jpn. J. Appl. Phys., Part 1 **44**, 4088 (2005).
[13] A. Mani, J. Schoonman, and A. Goosseens, J. Phys. Chem. B **109**, 4829 (2005).
[14] D. Como, M. A. Loi, F. Dinelli, M. Murgia, F. Biscarini, R. Zamboni, and M. Muccini, Synth. Met. **155**, 287 (2005).
[15] Y. Yoshida, N. Tanigaki, K. Yase, and S. Hotta, Adv. Mater. (Weinheim, Ger.) **12**, 1587 (2000).
[16] J. Enderlein, Chem. Phys. **247**, 1 (1999).