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Modulation of surface plasmon coupled emission (SPCE) by a pulsed magnetic field

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Kai-Xin Xie[1], Shuo-Hui Cao[1], Qian Liu[1], Wei-Peng Cai[1], Si-Xin Huo[1], Hitoshi Watarai[2*], Yao-Qun Li[1*]

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The unique modulation of surface plasmon coupled emission (SPCE) on Au/Cr/Co/Cr/glass substrate by an external magnetic field has been observed. The most positive regulation was triggered by employing the multilayered substrate with 7.5 nm-thick Co layer. The new magnetoplasmonic strategy provides a simple way to modulate the SPCE signal.

Fluorescence-based detection techniques have been widely used in modern biochemical research and disease diagnosis because of their high sensitivity and versatility. The surface plasmon coupled emission (SPCE) technique, which is based on the near-field interaction between fluorophores and metals,[1, 2] has received considerable attention due to its outstanding characteristics,[3-5] including fluorescence enhancement, polarized and directional emission and distance-determined coupling.[6-9] In SPCE, which can be considered as the reverse process of surface plasmon resonance (SPR), the excited fluorophores couple with the surface plasmons (SPs) near the metal and lead to directional radiation, and the coupling efficiency depends on the distance between the fluorophores and metallic layer.[10, 11] Recently, research in SP-based devices (particularly SPR) has advanced toward adding active functionalities, such as magnetic fields, temperature, electric fields or electromagnetic waves, to explore new phenomena and approaches.[12, 13]

As one of the external forces, magnetic fields have widespread applications. The fluorescence of molecules, such as glyoxal, iodine, and nitrogen dioxide in the gaseous state, can be quenched by a magnetic field.[14] Furthermore, highly sensitive magnetic force-assisted detection using magnetic materials is one of the important applications of an external magnetic field.[15] Moreover, for the past few years, magnetic fields have been successfully applied to various widely used technologies, such as spectroscopy and imaging technology.[16] One of the approaches that simultaneously presents magnetic and plasmonic properties, named magneto-optical (MO) SPR,[17] has become a topic of many studies.[18] When considering the close relationship between SPR and SPCE, the application of a magnetic field to SPCE should reveal new phenomena. In this paper, we present our most recent progress on the combination of a pulsed magnetic field and SPCE. To our knowledge, this is the first observation of the modulation of SPCE fluorescence by a magnetic field.

The experimental substrate was chosen based on the magnetoplasmonic systems produced in multilayers of noble and ferromagnetic metals. Ferromagnetic layers feature a vital drawback in their strong absorption, which leads to the broad associated plasmon resonances and the high propagation losses. A viable way to overcome this drawback is to find a reasonable collocation between noble and ferromagnetic metal layers without losing both magnetic and plasmonic properties.[12] Here, 23 nm Au/3 nm Cr/7.5 nm Co/2 nm Cr multilayer deposited on a quartz glass was chosen as the optimum substrate.[19] The two thin Cr layers were introduced in the multilayer to improve the adhesion and stability of the magnetoplasmonic structure.[19] Then, three different dyes (Rhodamine B, RhB; Rhodamine 6G, R6G; DiI) dissolved in 2% PMMA at the concentration of 1 mM were respectively spin-coated on the substrate. The results of the SPCE modulation by the pulsed magnetic field are shown in Figure 1. The direction of the external

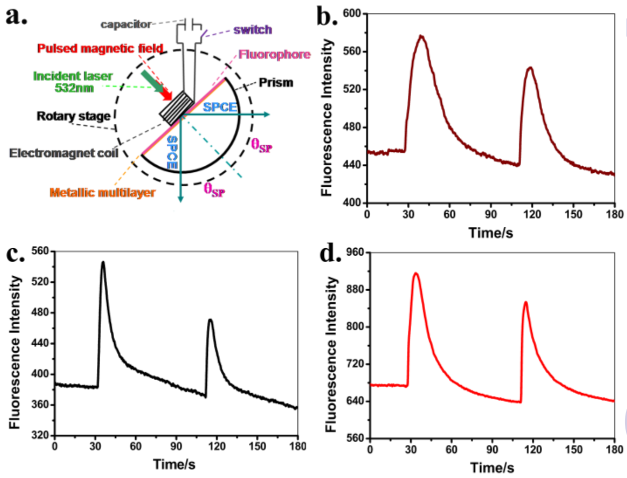

Figure 1. (a) Reverse Kretschmann sample configuration for SPCE observation. The configuration is not drawn to scale. (b-d) SPCE signals of three different dyes ((b) RhB, (c) R6G, and (d) DiI) at the concentration of 1 mM in 2% PMMA responding to the magnetic field separately.

magnetic field was perpendicular to the substrate, the same as the incident 532 nm laser (5 mW), and the SPCE signal was examined in the Reverse Kretschmann configuration (Figure 1a). The magnetic field was generated by an air-core coil with a 4 mm inner diameter connected to a condenser bank of 10,000 μF, which was operated under the charging voltage of 0-400 V. When the capacitor was completely charged in a given voltage, the magnetic field was applied to the substrate by turning on the current flow (Figure 1a). The peak intensity of the pulsed magnetic field can be varied in the range of 0-2.25 T, and the pulse duration time was approximately 4 ms which was sufficiently long to magnetize the metallic multilayer. The SPCE of these dyes exhibited a positive response when the magnetic field of 1.8 T was applied (Figures 1b-d).

RhB was taken as the example for follow-up studies because all three dyes exhibited similar SPCE responses to the magnetic field. The properties of the SPCE of 1 mM RhB-2% PMMA are shown in Figure S1. The typical results of the SPCE modulated by the magnetic field are shown in Figure 2. The positive SPCE response mainly originated from the p-polarized signal (Figure 2a). Moreover, the change in the SPCE intensity increased with the increase in the peak magnetic flux density of the external magnetic field (Figure 2b). The observed result suggested that the impact of the magnetic field on the properties of SPs causes the enhanced SPCE response. In SPCE, the collective charge oscillation propagates along the metal/sample interface when SPs are excited. The direction of the external magnetic field in the present study was perpendicular to the propagation direction of SPs, which might influence the propagation status; the modified SPs will then couple with excited fluorophores to change the SPCE signal.[3, 7, 8] The modulation of SPCE by a pulsed magnetic field on a multilayer with Co layer can be considered as a new magnetoplasmonic system which possesses both magnetic and plasmonic properties. The effect of SPs on the MO activity in magnetoplasmonic systems is caused by the modification of the optical properties as well as of the electromagnetic field in the MO-active layer.[12, 20] In addition, the relationship between the MO activity and SPs is mutual, and the presence of MO activity makes the SPs to be easily altered in magnetoplasmonic systems.[12, 21] Therefore, in the SPCE modulation system, the magnetic field in the MO active layer could enhance the associated electromagnetic field of SPs, which will then strengthen the coupling process with excited fluorophores to increase the SPCE signal. These two considerable factors should be the cause of the positive modulation of the SPCE signal by a pulsed magnetic field. As shown in Figure 2b, even when the peak magnetic flux density of the magnetic field was much higher than the saturated magnetization of the multilayer (~5 mT)[19], the SPCE still linearly increased with the increase in the peak magnetic flux density of the magnetic field. This also implies that the role of the magnetic field utilized to modulate the SPCE is not only to obtain the saturation magnetization of the MO active layer to enhance the associated electromagnetic field of SPs, but also to affect the SPs propagation properties directly.

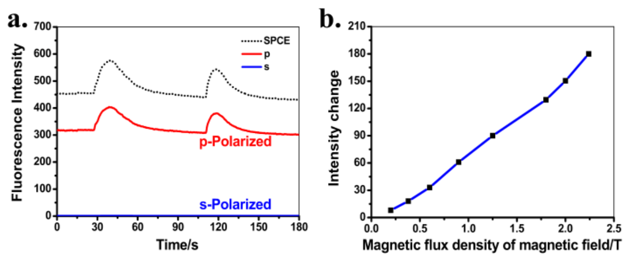

Figure 2. (a) Polarized property of the modulated SPCE by the magnetic field (1.8 T). (b) Dependence of SPCE response on the peak magnetic flux density of the magnetic field.

As shown in Figures 1b-d and 2a, the maximum signal height of the second pulse was lower than that of the first pulse. In our experimental system, the exothermic process of the magnetic coil existed when the pulsed magnetic field was generated, which could increase the temperature of the substrate (Figure S2a). Besides, the time needed to cool the substrate was about 300s (Figure S2a). The SPCE signal could be quenched by the increasing temperature of the substrate (Figure S2b), which means that the temperature increase induced by the magnetic coil would have slightly adverse effect on the performance of the SPCE modulation, and this effect existed in every pulse. In addition, after long contacting period between the magnetic coil and the substrate, the temperature of the substrate became higher, which could lower the peak value of the enhanced SPCE signal. When the time interval between the two pulses was extended to 300 s, the peak value of every pulse remained almost unchanged (Figure S3). Thus, in this case, the effect of the temperature accumulation would be negligible. Moreover, the magnetic flux density of the pulsed magnetic field was first increased rapidly and then decreased back to zero. This process was about 4ms. In the meantime, the SPCE response to the magnetic field also exhibited the "pulse" shape. Along with the interactions affected the SPs properties which were triggered by the magnetic field proceeding over time, the SPCE signal increased to the peak value, and then recovered to the original value. The time required for the recovery process of SPCE (~30 s) was considerably longer than the duration of the external magnetic field. The observed delayed recovery may correspond to a slow annihilation of magnetization of the magnetoplasmonic substrate.

The positive modulation of SPCE by a magnetic field is mainly induced by the enhanced SPCE process due to the change in the SPs relevant properties by an external magnetic field in the magnetoplasmonic system. Considering the properties of SPs and the ferromagnetism of the multilayer (MO activity), which can be seriously affected by the constituent of the multilayer, the SPCE response could be influenced by the composition of the multilayer. The investigation will be beneficial to further confirm the impacts of both the SPs properties and the ferromagnetism of the substrate on the SPCE modulation process.

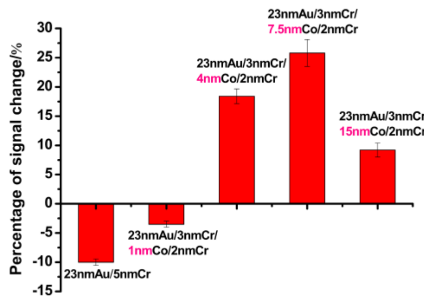

Figure 3. Percentage change in the SPCE signal (1 mM RhB-2% PMMA on 23 nm Au/3 nm Cr/x nm Co/2 nm Cr (x=0, 1, 4, 7. 5, 15)) affected by the magnetic field (1.8 T). The percentage change of the signal is defined as $100(I_{MF}-I_0)/I_0$ (I_{MF} is the maximum intensity of SPCE when the magnetic field is applied, and I_0 is the normal SPCE intensity without the magnetic field).

The magnetic responses of the SPCE signal of 1 mM RhB-2% PMMA deposited on 23 nm Au/3 nm Cr/x nm Co/2 nm Cr (x=0, 1, 4, 7.5, 15) substrates are shown in Figure 3. The calculated SPR reflectivity curves of these substrates (x=0, 1, 4, 7.5, 15) and their SPCE signals (x= 1, 4, 7.5, 15) in the absence of magnetic field are shown in Figure S4.

As shown in Figure 3, the SPCE signal from the multilayer without any Co layer (i.e. Au film) appeared to be negative responses to the magnetic field. Noble metals, such as Au and Ag, require a high magnetic field (tens of tesla) for MO activity.[12] When the substrate was a Au film without Co layer, the SPCE modulation system held no MO activity and Au film has the diamagnetic nature, which could damage the positive modulation of SPCE. Besides, the temperature increase caused by the magnetic coil would also slightly reduce the SPCE signal. Therefore, the SPCE had a negative response to the magnetic field. These negative regulated elements and the positive modulation factors of SPCE noted above are likely mutually competitive processes in the present study. These processes lead to a weak negative SPCE response to the magnetic field in the case of 23 nm Au/3 nm Cr/1 nm Co/2 nm Cr. The composition of the multilayer is essential because of the important roles of the magnetic response of the Co layer (MO activity) and the SPs characteristics. Because the ferromagnetism of the multilayer and the SPs properties had a best compromise for the 7.5 nm-thick Co layer (Figure S4a), the strongest SPCE signal was obtained in this multilayer (Figure S4b) and the positive magnetic response of SPCE of this substrate was strongest (Figure 3). The SPCE signal of the substrate with the 15 nm-thick Co layer expressed a weaker response to the magnetic field (Figure 3) because of the detrimental effect of the broad plasmon resonance on the quality of SPs and the shallow resonance depth of the SPR caused by the thicker Co layer (Figure S4a). Similarly, the change in the thickness of the Au layer could also impact on the SPCE response to the magnetic field. The results are shown in Figure S5, which illustrates that increasing the thickness of the Au layer is detrimental to the SPCE response to the magnetic field. However, the existence of the Au layer is still necessary because of the crucial role of the Au layer in the formation of SPs. The experimental results show that the ferromagnetism of the Co layer, the nature of SPs, and the role of the Au layer work together to adjust the modulation of SPCE by the magnetic field.

In summary, the SPCE signal has been distinctly regulated using an external magnetic field as stimuli. The SPCE intensity was dramatically modulated by applying the external pulsed magnetic field to the noble metal/ferromagnetic metal substrate. This positive modulation is due to the change of the SPs properties by the external magnetic field. The effects of the properties of SPs, Co and Au layer on the SPCE response to the magnetic field have been investigated by adjusting the composition of the substrates. The modulated SPCE by an external magnetic field provides an approach to study the interactions between the magnetic field and plasmons. Furthermore, the SPCE modulation by a magnetic field is a universal approach to adjust and increase SPCE signals as long as a magnetoplasmonic substrate is used. In addition, the regulated results are likely to be optimized by introducing the materials possessing strong magnetic response and active plasmonic properties to the system, such as magnetic nanoparticles and graphene. The combination of SPCE and an external magnetic field have the potential to increase the detection sensitivity, enable the development of a new stimulus response system, and facilitate the construction of active plasmonic fluorescence-based devices.

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Notes and references

1. Department of Chemistry and the MOE Key Laboratory of Spectrochemical Analysis & Instrumentation, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, PR China.
2. Institute for NanoScience Design, Osaka University, Osaka 560-8531, Japan.

Corresponding author:
[1]*E-mail: yaoqunli@xmu.edu.cn;
[2]*E-mail: watarai@chem.sci.osaka-u.ac.jp

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