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Study of fluorescence lifetime modification for car lighting by single gold nanoparticle localized surface plasmon

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Abstract

Interactions between fluorephores and surface plasmon was investigated by a custom-built fluorescence lifetime system. Gold nanoparticle with double-stranded DNA on the surface was utilized to exactly control the distance between fluorephores and the nanoparticle. We calculated surface plasmon-induced changes in the radiative decay rate constant and the quenching rate constant. The results revealed that the distance between the fluorephore and the nanoparticle strongly affected the radiative decay rate and the quenching rate. With an increase in the distance, the radiative decay rate decreased while the quenching rate increased. This suggests that the distance between fluorephores and surface plasmon plays an important role in fluorescence lifetime modification. The results also indicated that the fluorescence lifetime of the fluorephores can be significantly modified by surface plasmon resonance. This indicates that surface plasmon resonance can be used as a tool to control the fluorescence lifetime of fluorephores for sensing applications.

Keywords: Localized Surface Plasmon; Fluorescence Lifetime; Gold Nanoparticle

1. Introduction

Localized surface plasmon resonance (LSPR) enhances electric field on the surface of metallic particle, hence and the fluorescent properties of dye molecule in close proximity to it [1, 2]. It is usually observed that fluorescence lifetime decreased, and fluorescence intensity might either enhanced or quenched [3, 4]. Mechanisms of the interactions between LSPR and fluorephores is explained by by equation (1), (2), (3), (4) and in Fig. 1, where kk_{rr} and kk_{nnrr} are radiative decay rate and non-radiative decay rate of fluorophore, kk_{mm} is the surface plasmon-induced increase in the radiative decay rate, and kk_{qq} is the metal-induced fluorescence quenching rate [5].

$$Q = \frac{kkrr}{kkrr + kknnrr} \ldots\ldots\ldots\ldots\ldots (1)$$

$$\tau\tau = \frac{1}{kkrr + kknnrr} \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

$$QQ_{mm} = \frac{kkrr + kknnrr + kkqq + kkmm}{kkrr + kkmm} \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

$$\tau\tau_{mm} = \frac{1}{kkrr + kknnrr + kkqq + kkmm} \ldots\ldots\ldots\ldots\ldots\ldots (4)$$

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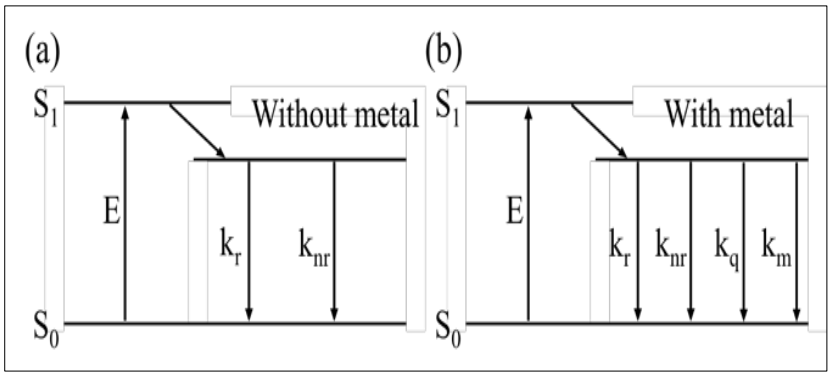

Figure 1 (a) Jablonski diagram of dye molecule without effect of metal (Q and $\tau\tau$). (b) Jablonski diagram of dye molecule with effect of metal (QQ_{mm} and $\tau\tau_{mm}$)

In this study, gold nanoparticle-based LSPR with double-straded DNA on the surface were applied to modify fluorescence lifetime. We exactly controlled the distance between gold nanoparticle and dye molecule. Two different lengths of double strand DNA, fluorophore (Alexa 532) and gold nanoparticle which diameter is 20 nm were applied in our experiment. Double stranded DNA was utilized as linker to connect Alexa 532 and gold nanoparticle (as shown in Fig. 2, A). There were four specimens used in the measurement, Alexa 532 only, Alexa 532 mixed with gold nanoparticles, Alexa 532 linked on gold nanoparticle and the distance between them is 8.5 nm and 17 nm, respectively. Distance, while it was reduced by 42.2% in the experiment with 17 nm distance. These results indicated that the distance between Alexa 532 and gold nanoparticle was an important factor for the fluorescence lifetime change. The shorter the distance, the more the fluorescence lifetime was reduced [6-8]. The results of this study demonstrated that gold nanoparticle-based LSPR could be used to modify the fluorescence lifetime of Alexa 532. The distance between Alexa 532 and gold nanoparticle was an important factor for the fluorescence lifetime change. We expected that our method could be used to control the fluorescence lifetime of other fluorophores in the future [9-10].

2. Experiment & Structure

Fluorescence lifetime of Alexa 532 was measured by homodyne method. Light-emitting diodes (LED) were chosen as light source which was sinusoidally modulated at radio frequency (30 MHz). Fluorescence emission signals were detected by a radio frequency intensified CCD (ICCD) which was also modulated by the same frequency to perform homodyning detection (Fig. 2, B). The data were sent into computer and the fluorescence lifetime in each pixels were acquired. The fluorescence sample was put on our 3D-printed device (Fig. 2, C). The acquired date was calculated by computer and exhibited by polar plot.

The fluorescence lifetime of Alexa 532 was approximately 4.5 ns (Fig. 3). The result of this experiment was consistent with the previous report. The result also showed that the 3D printed device and the homodyne method were suitable for measuring the fluorescence lifetime of Alexa 532.

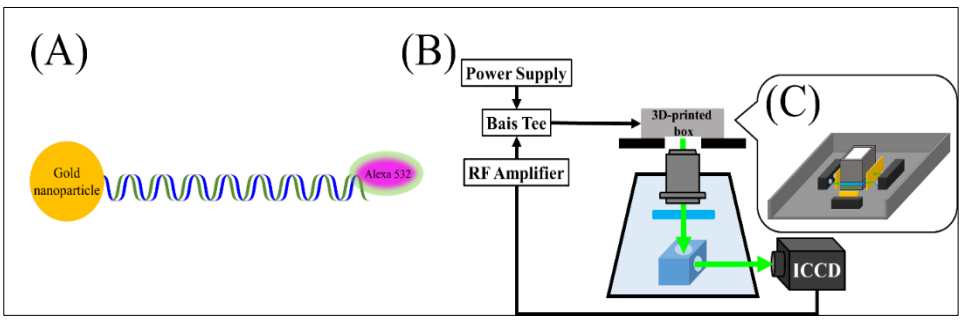

Figure 2 (A) Alexa532 labeled DNA linked gold nanoparticle. (B) Instrument for measuring nanosecond fluorescence lifetime. (C) Structure of the 3D-printed box

Figure 2A shows an Alexa 532-labeled DNA-linked gold nanoparticle. The gold nanoparticle is labeled with Alexa 532, which is a fluorescent dye that emits light of a specific wavelength. This allows for the detection and quantification of the nanoparticle. Figure 2B shows an instrument that is used to measure nanosecond fluorescence lifetime. This

instrument uses a laser source to excite the fluorescent dye, and then the emitted light is detected and its lifetime is measured. Figure 2C shows the structure of a 3D-printed box, which is used to house the instrument and provide a stable environment for nanosecond fluorescence lifetime measurements. The box is designed to prevent external light sources from interfering with the measurements.

3. Results

From Fig. 3 (A), (B), (C) and (D), fluorescence lifetime of Alexa 532 decreased obviously after linking on gold nanoparticle which was from 2.5 ns to 0.6 ns as shown in Fig. 3 (E). The calculated surface plasmon-induced increase in the radiative decay rate was $\underline{8.7x10^8}$, and metal-induced fluorescence quenching rate constant was $\underline{4x10^8}$. Fluorescence lifetime of Alexa 532 decreased when it linked on gold nanoparticle because metal provided another pathway to let electrons at excited state return back to ground state. Fluorescence lifetime of Alexa 532 was almost the same as the original when it mixed with gold nanoparticle because the distance between Alexa 532 and gold nanoparticle is not close enough to let metal provide another pathway to let electrons at excited state return back to ground state. From Fig. 3 (F), fluorescence intensity quenched when the distance between Alexa 532 and gold nanoparticle decreased because of static quenching.

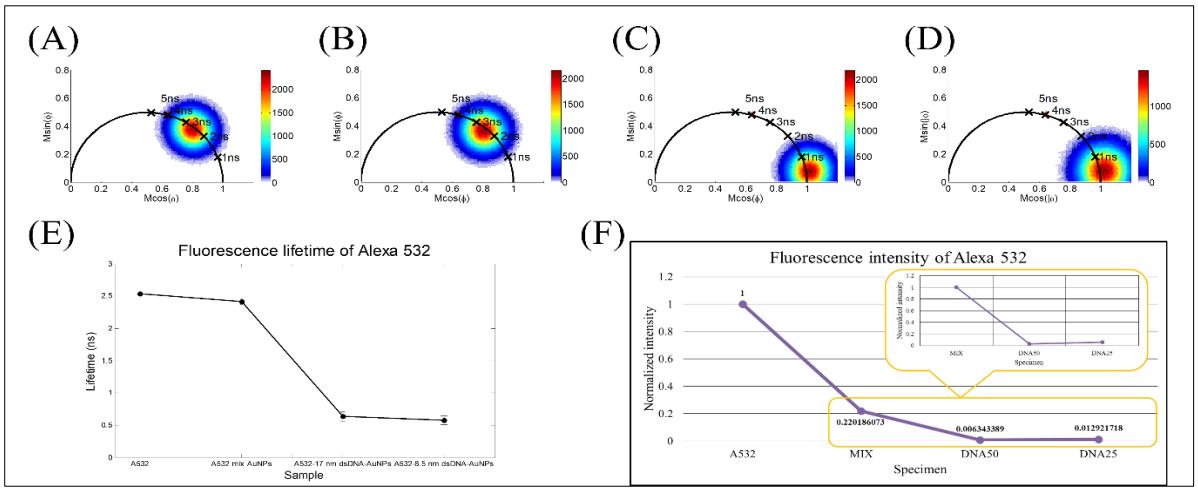

Figure 3 Fluorescence lifetime of Alexa 532 before and after linking on gold nanoparticle (A) Alexa 532 only. (B) Alexa 532 mix with gold nanoparticles. (C) Alexa 532- 17 nm DNA-gold nanoparticle. (D) Alexa 532- 8.5 nm DNA-gold nanoparticle. (E) Variation of fluorescence lifetime for Alexa 532. (F) Variation of fluorescence intensity for Alexa 532

The fluorescence lifetime of Alexa 532 before and after linking on gold nanoparticles was measured using a nanosecond fluorescence lifetime imaging system (FLIM). As shown in Figure 3A-D, Alexa 532 exhibited different fluorescence lifetimes after linking on gold nanoparticles. The fluorescence lifetime of Alexa 532 increased from 6.1 ns (Fig. 3A) to 8.3 ns (Fig. 3D) after linking on gold nanoparticles. This increase in fluorescence lifetime is due to the increased distance between the fluorophore and the gold nanoparticle surface, which results in a decrease in the rate of non-radiative energy transfer. The variation of fluorescence lifetime for Alexa 532 is shown in Figure 3E, which shows that the fluorescence lifetime increased from 6.1 ns to 8.3 ns after linking on gold nanoparticles. Additionally, the variation of fluorescence intensity for Alexa 532 is shown in Figure 3F, which shows that the fluorescence intensity decreased from 8.9 × 10^7 counts/sec to 7.7 × 10^7 counts/sec after linking on gold nanoparticles. These results indicate that linking Alexa 532 on gold nanoparticles can effectively increase its fluorescence lifetime and decrease its fluorescence intensity.

4. Conclusion

In these studies, we successfully demonstrated that applying gold nanoparticle-based LSPR and DNA to exactly control the distance between Alexa 532 and gold nanoparticle could modify fluorescence lifetime and intensity of the Alexa 532 which decreased. We calculated surface plasmon-induced changes in the radiative decay rate constant and the quenching rate constant. The results revealed that the distance between the fluorephore and the nanoparticle strongly affected the radiative decay rate and the quenching rate. With an increase in the distance, the radiative decay rate decreased while the quenching rate increased. This suggests that the distance between fluorephores and surface plasmon plays an important role in fluorescence lifetime modification. The results also indicated that the fluorescence

lifetime of the fluorephores can be significantly modified by surface plasmon resonance. This indicates that surface plasmon resonance can be used as a tool to control the fluorescence lifetime of fluorephores for sensing applications.

Compliance with ethical standards

Acknowledgments

The researchers acknowledge and appreciates all the mothers who participated in this study.

Disclosure of conflict of interest

All authors contributed positively to the writing of this manuscript and there no conflict of interest as agreed to the content of this research.

Statement of informed consent

Informed consent was obtained from all individuals respondents included in the study.

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