

Modification of the fluorescence spectra of dye thin film by surface plasmon resonance.

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【序】 Since last decades, localized surface plasmon (LSPR) excited on metal particles have been attracting much attention, because they could confine the incident light into the near field which gives a great enhancement of the electromagnetic field at their surface [1]. Such enhancement induces new optical phenomena such as surface enhanced Raman scattering [2], fluorescence enhancement [3], second harmonic generation [4] and other nonlinear optical process [5]. Many studies deals with the enhancement of a dye fluorescence due to surface plasmon. One theoretical study by Gersten and Nitzan [6] pointed out that the enhancement factor of the dye fluorescence strongly depends on many parameters such as the fluorescence quantum yield, the distance between the dye and the metallic particle and the particle characteristics (size and shape). Since then, many experimental studies confirm these theoretical predictions showing that we can observe high enhancement of the fluorescence although the mechanism is still unknown. In order to understand the fluorescence enhancement mechanism, we present studies of the spectral modifications (intensity and shape) of core-shell structures made by gold nanoparticles of the fluorescence emission of thin layers of rhodamine 6G (R6G).

【実験】 The gold nanoparticles (100 nm diameter) were immobilized on a glass substrate functionalized by a coupling agent (3-aminopropyltrimethoxysilane). Samples were covered with layers of R6G by vapor deposition and three thickness were studied : 8, 15 and 25 nm. For the fluorescence emission we used an inverted microscope Olympus IX70 coupled through an optical fiber to a monochromator equipped with a charge coupled device detector. The use of a pinhole before the optical fiber allows us to select a spatial area of 2 micron diameter and consider each gold nanoparticles individually. Single particle observation was also confirmed by dark field observation. The excitation source was a mercury lamp. The excitation wavelength of 496 nm was selected with band-pass filter and the emission filter (higher than 515 nm) was used to observe the full ranged fluorescence spectra of R6G. We used a microscope objective X60, N.A. 0.7 Olympus. In order to see modifications of the fluorescence emission of the R6G, we compared spectra taken with and without gold nanoparticle (Fig.1).

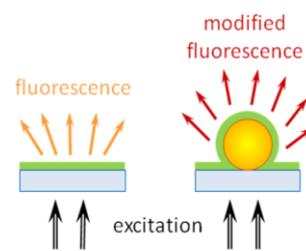


Fig.1 : explanation of the fluorescence study.

【結果と考察】 Many studies deal with the enhancement factor of the dye fluorescence by metallic nanoparticles. Especially they tried to investigate the influence of the distance between the particle and the dye [7] but they only focus on the fluorescence intensity modification. As far as we know, no studies concentrate on the shape's modifications of the fluorescence spectra by LSPR. That's why we use a new experimental approach in order to study these shape's modifications which represent the first step in the understanding of the mechanism of the fluorescence modulation. Our method consists of taking fluorescent emission spectra of R6G deposited on glass

substrate and on a single gold nanoparticle. After, we subtract the fluorescence spectra obtained without gold nanoparticle from the one obtained with gold nanoparticle. In this case we obtained a new spectrum, called the fluorescence modulation spectra, which show the modification not only in fluorescence intensity but also in the spectral shape. Considering the wavelength we can observe which emission band of the dye is modified.

We examined R6G thin layers, with different film thickness (8, 15 and 25 nm). We clearly observe a thickness dependence on the fluorescence modulation spectra (Fig.2). For the 8 nm we observe both quenching (at 555 nm) and enhancement (at 600 nm) of the fluorescence emission. It's the first time these two intensity modifications could be observed at the same time. When we consider

the 15 and 25 nm thickness, the fluorescence modulation spectra are very different. We observe two different enhancement behavior localized around 580 and 660 nm. If we only consider this two thickness the enhancement is less important for the 15 nm whatever the band we consider. These results clearly show different mechanism based on the layer thickness, one with the 8 nm and another with the 15 / 25 nm but the complex fluorescence behavior of the R6G is difficult to understand. As a matter of fact, previous studies [8] has emphasize that R6G could be present as monomer and dimer form considering it's concentration. Each form has different absorption band and also fluorescence emission characteristic (fluorescence quantum yield and quantum rate constant). Such characteristic are very important for the fluorescence modulation like the overlap of the absorption band with the LSPR band. Even if it's very difficult to explain the different mechanism leading to the results we observe, we can easily supposed that the monomer and the dimer form are interacting with the LSPR. In order to understand the mechanism we plan to make further experiment especially with time-resolved fluorescence.

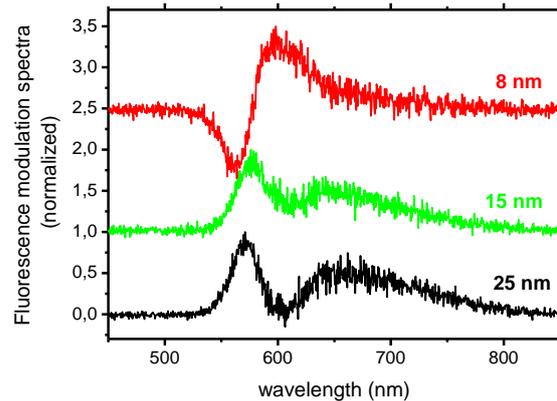


Fig.2 : fluorescence modulation spectra of the three different thickness. They have been vertically shifted for easy comparison.

【まとめ】 Using single particle spectroscopy we have showed that the mechanism of the fluorescence modification due to LSPR can be studied considering a core-shell structure. Especially we have found higher fluorescence enhancement factor than in literature and proved that we could greatly increase the sensitivity of actual fluorescent sensors. Moreover we success to demonstrate that the fluorescence modulation depends on the fluorescence state (monomer and dimer) of the dye.

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