Scientific Research

Near Infrared Fluorescence Enhancement by Local Surface Plasmon Resonance from Arrayed Gold Nanoblocks

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ABSTRACT

The near infrared (NIR) fluorescence enhancement by local surface plasmon resonanoce from arrayed gold (Au) nanoblocks was investigated by NIR fluorescent dyes, IR780, immobilized in hydrophobic DNA thin film on glass substrates, to clarify the gap mode effect on the fluorescence enhancement. In the substrate with Dimer type Au nanoblock arrangement, average total fluorescence intensity was larger by 10.0, 2.4, and 12.4 times for non-polarized, P- and S-polarization as compared with that on a glass substrate alone, respectively. These findings suggested that enhancement of excitation light intensity at nanogap in the Dimer type Au nanoblock arrangement affected the fluorescence intensity. Average total fluorescence intensity, on the other hand, was smaller by 0.63 times as compared with that on a glass substrate alone in the checkerboard type Au array. It is suggested that the fluorescence quenching was caused by the energy transfer from the excited state of IR780 to Au nanoblocks or by the increased deactivation of excited dye molecules induced by resonance with Au nanoblocks at the checkerboard arrangement. We have firstly achieved the NIR fluorescence enhancement by LSPR due to the gap mode.

1. Introduction

Local surface plasmon from metal nano structures provides strong photon-molecule coupling fields [1], which markedly assist photochemical reaction such as photocatalysis [2], photovoltaic cell [3], photochromic reaction [4,5], and optical excitation process [6]. One of the applications of the liner excitation process is the fluorescence enhancement of the dye by surface plasmon resonance [7]. The near-infrared (NIR) fluorescent dyes have several disadvantages such as low fluorescence quantum yield, low stability, and low durability compared with visible fluorescent dyes in aqueous solutions and solid films, although the NIR fluorescent dyes have been widely used in biochemical and medical fields for in vivo imaging [8]. The molecular structure of NIR dyes with extended π-conjugation is mostly responsible for these properties. The low fluorescence quantum yield is essentially governed by the Strickler-Berg relation [9]. The

energy transfer from porphyrin to NIR fluorescent dyes along the DNA double helix was investigated upon excitation at the visible region in order to overcome these disadvantages [10]. The NIR fluorescence was enhanced up to 86 times due to the efficient energy transfer from the excited porphyrin in the presence of DNA. The DNA matrix contributes not only to make efficient energy transfer, but also to improve stability and durability of NIR dye by immobilization between base pairs or in the groove. We also reported the application of confined and electric field enhanced light at surface plasmon resonance (SPR) condition to highly sensitive fluorescence detection of dyes in DNA ultrathin films deposited on a metal film and to high performance nitrogen oxides gas sensing [11]. These results demonstrated that DNA chain is one of the most powerful tools for nanoassemblies and will give novel concepts of materials design.

Fluorescence enhancement by LSPR was reported by several groups [12-15]. We have also been making efforts to enhance NIR fluorescence by LSPR from metal nanostructures using the regularly arranged Au nanoblocks
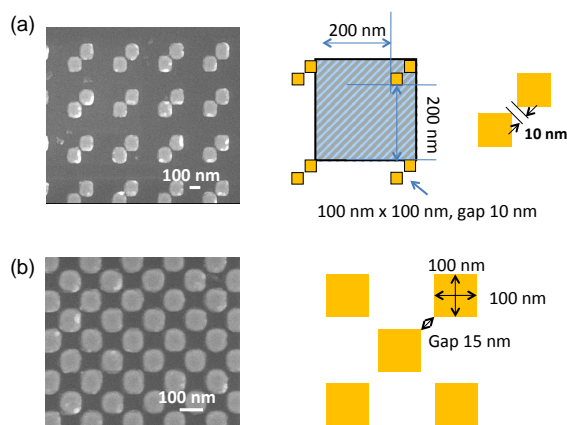

(Au arrays) without interaction between nanostructures which show specific absorption in the NIR region [16, 17]. Average total fluorescence intensity was larger by about 1.1 to 2.5 times depending on the Array structure. The fluorescence enhancement depends on the location of LSPR absorption. We also investigated polarization dependence of excitation light for fluorescence enhancement of the NIR dye in the same systems [17]. The enhancement factor for S-polarized excitation was about 1.2 to 1.5 times as large as that for P-polarized light. The calculated enhancement factor due to the projection of horizontal direction values was identical to that due to the excitation by S-polarization, suggesting that the observed fluorescence enhancement by the Au arrays originated from the resonance of photo-electric field along the plasmon band of transverse and longitudinal mode.

In this paper, we report the enhancement of NIR fluorescence intensity using the regularly arranged Au nanostructures with interaction between nanostructures, which show specific absorption in the NIR region to clarify the gap mode effect on the fluorescence enhancement.

2. Experimental

Regularly arranged Au nanoblocks were fabricated by the electron beam lithography on glass plates [18,19]. **Figure 1** shows SEM images of Au nanoblock array. The Dimer type of Au arrays (Dimer) with designed dimensions of $100 \times 100 \times 40$ nm were prepared as shown in **Figure 1(a)**. The gap distance of Dimer Au blocks, which is defined as the shortest distance between the nearest corners of the blocks, were 10 nm. Checker board type of Au arrays (Checker) with designed dimensions of $100 \times 100 \times 40$ nm, whose gap is 15 nm as shown in **Figure 1(b)**. As a NIR fluorescent dye, 2-[2-[2-Chloro-3-[(1,3-di-hydro-3,3-dimethyl-1-propyl-2H-indol-2-ylidene)ethyli-

dene]-1-cyclohexen-1-yl]ethenyl]-3,3-dimethyl-1-pro-pyl indolium iodide (IR780; Aldrich Co. Ltd., **Figure 2**) was selected. Hydrohobic DNA (H-DNA) was prepared by exchanging sodium ions with hexadecyltrimethylammonium ions according to the reported methods [20,21]. H-DNA thin films with immobilized dyes were prepared by spin coating on glass plates with Au arrays. The film thickness was 40 nm. UV-Vis absorption (extinction) spectra were measured by Hitachi U-4100 spectrometer. Fluorescence spectra were measured by Hitachi F-4500 fluorescence spectrophotometer. The CW laser at 675 nm was used as excitation light. The polarization of excitation light was controlled by a film polarizer. The incident angle for the sample was set at 40°.

3. Results and Discussion

The absorption spectrum of IR780 in H-DNA thin film shows a peak around 800 nm with a shoulder around 730 nm. The fluorescence peak located at 817 nm. The absorption (extinction) spectra of Dimer and Checker exhibit two peaks as shown in **Figure 3** [18]. The extinction spectra of longitudinal (L)- and transverse (T)-modes of Au nanoblocks in Dimer, corresponding to the polarization of parallel and perpendicular to the block pairs, were located around 670 and 760 nm, respectively as shown in **Figure 3(a)**. In Checker, the extinction peak was observed around 700 nm. The L- and T-mode is indistinguishable in Checker due to symmetric arrangement of Au nanoblocks [22].

It is difficult to make selective excitation of L- and T-mode in our measurement system. We attempted the P- and S-polarization dependence for the fluorescence enhancements to discuss semi-quantitatively. **Figure 4(a)** shows the extinction spectra of Dimer under the non-polarized, P- and S-polarization. The extinction peaks both L- and T-mode were observed. **Figures 4(b)-(d)** show fluorescence spectra of IR 780 on Dimer excited at 675 nm with non-polarized, P- and S-polarization light, respectively. Average total fluorescence intensity was larger by 10.0, 2.4, and 12.4 times for non-polarized, P- and S-polarization as compared with that on glass substrate alone, respectively. P- and S-polarization are the vector of electric field defined as parallel and perpendicular to the plane of incidence, respectively. The schematic representation has been reported previously [17]. If the incident angle θ is not equal to zero, the P-polarization can
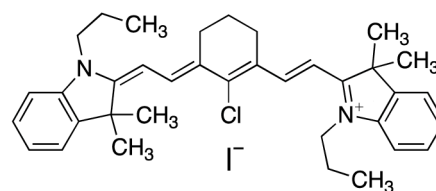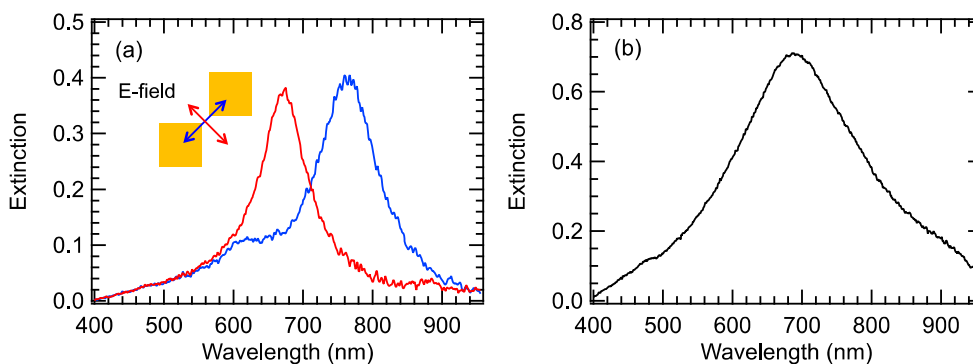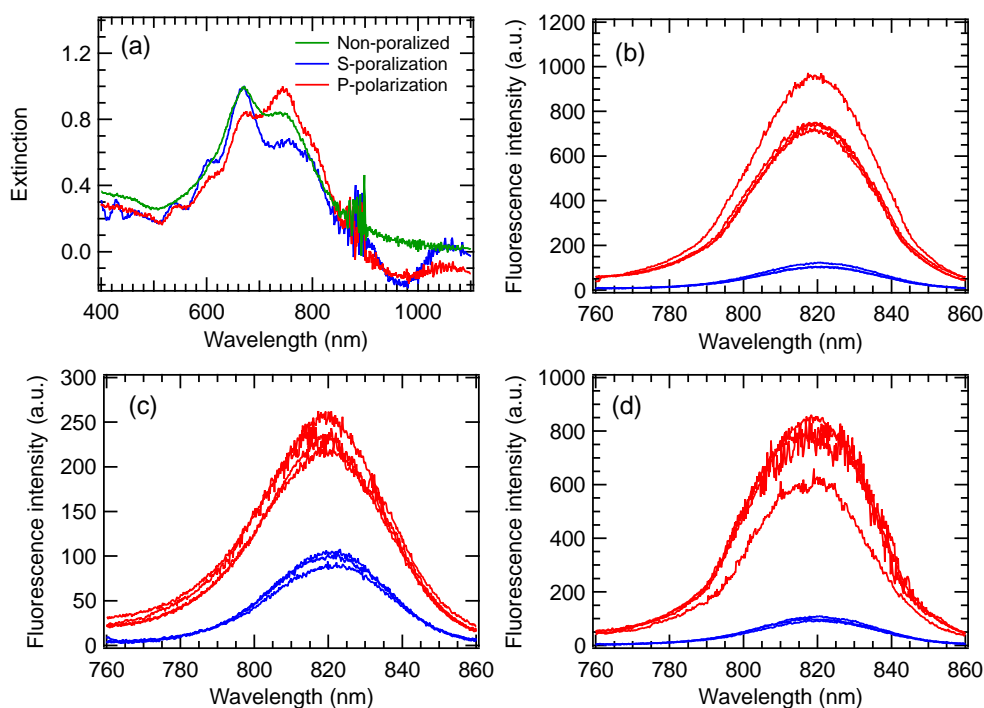

Figure 1. SEM images and schematic representation of a gold nanoblock array. (a) Dimer structure (Dimer; $100 \times 100 \times 40$ nm, gap: 10 nm); (b) Checker board structure (Checker; $100 \times 100 \times 40$ nm, gap: 15 nm).

Figure 2. The molecular structure of IR 780.

Figure 3. Extinction spectra of Dimer (a) and Checker (b); red, blue and black line indicates L-mode, T-mode and non-polarized light excitation.
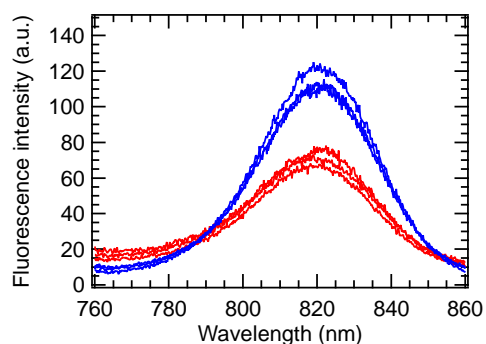

Figure 4. Extinction spectra of IR 780 in H-DNA thin film on Dimer substrate. Fluorescence spectra of IR 780 in H-DNA on Dimer substrate excited at 675 nm with (b) non-, (c) P-, and (c) S-polarization in the presence (red line) and the absence (blue line) of Au blocks.

excite the plasmon band of Au nanoblocks for both vertical and horizontal direction. We have estimated the ratio of P-polarized light for horizontal and vertical direction of Au nanoblocks is estimated to be 1:0.839 from the ratio of sine to cosine in the $\theta = 40°$. S-polarization, on the other hand, can only excite for the horizontal direction. These findings indicated that the electric field intensity of S-polarized excitation light is larger than that of P-polarized one. P-polarized light contributed to the excitation of plasmon band both of horizontal and vertical direction of Au nanoblocks. The vertical direction corresponds to the short axis for height direction which has the absorption in visible region did not contribute to the excitation of the gap mode. The photoelectric field

with parallel component along the substrate contributes to the enhancement of excitation light intensity, that is both L- and T-modes are enhanced [22]. Bek *et al*. were observed an enhancement of fluorescence from a fluorescent molecule, which is sandwiched between two individual gold nanoparticles, forming a hot spot of strong field enhancement [23]. These findings suggested that enhancement of excitation light intensity at nano gap in Dimer affected the fluorescence intensity.

Figure 5 shows fluorescence spectra of IR 780 on Checker excited at 675 nm with non-polarized light. Average total fluorescence intensity was smaller by 0.63 times as compared with that on glass substrate alone. Checker board structure caused the fluorescence quench-

Figure 5. Fluorescence spectra of IR 780 in H-DNA on Checker substrate excited at 675 nm in the presence (red line) and the absence (blue line) of Au blocks.

ing rather than fluorescence enhancement, which means the fluorescence quenching originates from the energy transfer from the excited state of IR780 to Au nanoblocks or the increased deactivation of excited dye molecules induced by resonance with Au nanoblocks.

4. Conclusion

We investigated NIR fluorescence intensity using regularly arranged Au nanostructures with interaction between nanostructures in order to clarify the gap mode effect on the fluorescence enhancement. In Dimer substrate, average total fluorescence intensity was larger by for 10.0, 2.4, and 12.4 times for non-polarized, P- and S-polarization as compared with that on glass substrate alone, respectively. It is suggested that the observed fluorescence enhancement by the Au arrays most probably originated from the resonance of photo-electric field along the plasmon band in nano gap between Au nanoblocks of T- and L-mode. We have firstly achieved the NIR fluorescence enhancement by LSPR due to the gap mode. The fluorescence quenching, on the other hand, was observed at Checker substrate. The fluorescence quenching originates from the energy transfer from the excited state of IR780 to Au nanoblocks or the increased deactivation of excited dye molecules induced by resonance with Au nanoblocks rather than the fluorescence enhancement.

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