Two-photon excited fluorescence enhancement using nano-engineered gold particles

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Abstract
Two-photon excited fluorescence of organic dye by embedding them with gold nanostructures fabricated on a glass substrate was enhanced on the basis of increasing electromagnetic field induced by nanogap configuration.

Quantum lithography, which exploit non-classical correlations between entangled photon states, requires high-yield entangled photon sources and photosensitive materials with efficient two- or multi-photon absorption. To realize such system, it is important to fabricate efficient multi-photon reaction field. Metal nanoparticles and/or nanorods are promising as the multi-photon reaction field because of high plasmonic electromagnetic (EM) field. Nanoparticle colloidal solutions of the noble metals such as copper, silver, and gold show a very intense color, which is derived from localized surface plasmon (LSP) resonance.1-3 Plasmon resonances which are collective oscillations of the conduction electrons, give rise to EM fields whose near-field part has locally enhanced field strength may result in the enhancement of several optical phenomena such as fluorescence,4,5 Raman scattering,6-8 second harmonic generation,9,10 etc. To increase EM field using LSP, it is necessary to couple the surface plasmon with the electric field of laser light. Therefore, it is most important to control the field enhancement and the spectral properties of the nanoparticle LSP states. This requires to control the size, density and other parameters of the nanoparticles. It is predicted that EM field enhancement may be very large when two resonant particles are brought close to each other and that most of the energy is located between the particles. We have fabricated gold nanoparticles with various sizes and shapes having nano gaps separated them, and investigated the possibility to enhance the two-photon absorption rate in organic dyes by embedding them with gold nanostructures.

The gold nano-blocks were fabricated on glass substrates using a high resolution electron beam lithography on a scanning electron microscope (SEM, ELS-7700, Elionix Co. Ltd., Tokyo, Japan) at 100 kV accelerating voltage and lift-off of a 2 nm Cr/40 nm Au bilayer deposited by sputtering.

Scanning electron microscope (SEM) image of the glass substrate containing checker-board arrays of cubic (100 × 100 × 40 nm size) gold nanostructures is shown in Fig. 1. In each square field, the gap between the corners of the neighboring cubes is different. For transmission measurements in the visible region (400-800 nm), a halogen light beam was passed through a pinhole (φ200 µm) and introduced to an optical microscope where it was focused on the sample by a (x20, NA = 0.4) microscope objective. The paraxial focusing ensured a quasi-parallel probe beam, with waist of about 8 µm. The transmitted beam was collected by a multichannel photodetector (Hamamatsu Photonics, PMA-11) which recorded its spectrum normalized to the spectrum of the incident beam. Infrared absorption spectra (800-3000 nm) were measured by a Fourier-Transform Infrared Spectrometer with microscope attachment. The structures were spin-coated by 1,4-Bis(bis(dibutylamino)styryl)-

Figure 1 Scanning microscope image of gold nanoblock arrays with different gap sizes.
2,5-dimethoxybenzene (MBAPB, 1 mM) chloroform solution, and their fluorescence intensity maps recorded by a scanning two-photon microscope which used a Ti:Sapphire laser (wavelength 800 nm, pulse length 100 fs) as an excitation source.

The absorption spectra of Au nano-blocks with various gap sizes (x) are shown in Figure 2. As shown in Figure 2(a), the base peaks extend over wide wavelength ranges in structures with small gaps because of interactions between the adjacent nano-structures. Note, that the absorbance in the near infrared region decreases with increasing gap size. Furthermore, when the gap size changed from 10 nm to 30 nm, the bandwidth decreased and the $\lambda_{\text{max}}$ of the spectra were red-shifted as shown in Figure 2(b). In the case of gap size of 40 nm, the spectra were identical to the LSP spectra of individual structures with same geometry (not shown here).

Fluorescence intensity maps shown in Fig. 3 indicate stronger fluorescence in structures with smaller gaps. This result indicates that size of the gap controls the parameters of the multipole plasmonic resonance, which can be thereby tuned to maximize the extinction of the incident radiation. We estimate that for gap narrower than ten nanometers, local enhancement of the electric field of the order of 100 was achieved.

Figure 2 Absorption spectra of Au nano-block arrays with gap dimensions of 0, 4, 8 nm (a) and 10, 20, 30 nm (b).

Figure 3 Two-photon excited fluorescence map of the same structure as SEM image in Figure 1.

References