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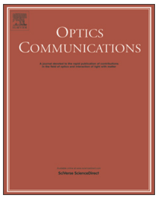

The local field dependent effect of the critical distance of energy transfer between nanoparticles

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ABSTRACT

The fluorescence resonance energy transfer between various types of fluorophore pairs was investigated. Dye molecules, quantum dots, fluorescent nanoparticles (dye molecules encapsulated in polymer matrices) were used as donor D. Dye molecules and gold nanoparticles were used as acceptor A. We found that the experimental Förster critical transfer distance R_0 is 1–10 nm when both D and A are dye molecules, and becomes larger than 10 nm when the donor is fluorescent nanoparticles. When the acceptors A are gold nanoparticles, the case is considered as localized plasmon coupled nanosurface energy transfer (NSET), the experimental critical distance d_0 increases up to few ten nanometers when D are dye molecules or quantum dots. For the first time, un-expected giant resonance energy transfer (G-RET) phenomenon is observed in our experiments with very large critical transfer distance d_0, which increases from few ten nanometers to micrometers when the donors are fluorescent and the acceptors are gold nanoparticles. A model "nanowave emitter station and antenna" is given to explain the local field dependence of the critical distance of energy transfer between those nanoparticles. Moreover, a simple theoretical model with size–number contribution (for fluorescent nanoparticles) and surface plasmon coupled enhancement effect (for gold nanoparticles) is proposed to explain these obtained experimental results.

1. Introduction

Fluorescence or Förster resonance energy transfer (FRET) has been widely used in biology and chemistry for measuring the distance r between two fluorophores to detect molecular interactions in a number of systems, thanks to their distance-dependent dipole–dipole interaction mechanism. FRET can be used as spectroscopic ruler in various areas such as the interaction of biological molecules in vitro and in vivo assays in cellular research, nucleic acid analysis, signal transduction, light harvesting and metallic nanomaterial etc. Based on the mechanism of FRET a variety of novel chemical sensors and biosensors have been developed [1–5]. Conventional FRET exhibits the R^{-6} dependence law of energy transfer rate and characterized by the Förster distance or critical distance R_0, which defined as the distance at which the energy transfer efficiency is 50%. The R_0 is given by

$$R_0 = 0.211\left[\kappa^2 n^{-4} \phi_D J(\lambda)\right]^{1/6} \tag{1}$$

where ϕ_D is the fluorescence quantum yield of the donor (D) in the absence of the acceptor (A), κ^2 is the dipole orientation factor, n is the refractive index of the medium, and $J(\lambda)$ is the spectral overlap integral. $\kappa^2 = 2/3$ for isotropically oriented dipoles [6]. The FRET suffers from a limited length scale of approximately 10 nm. On the other hand, there are many works demonstrated the non-Förster distance dependence of energy transfer. Bagchi et al. showed the R^{-2} dependence rule for electronic excitation transfer (EET) from a segment of polyfluorene to tetraphenylporphyrin. The Förster expression seems to be inappropriate for the condensed-phase systems where donors and acceptors can be closely packed [7]. The Förster energy transfer is also breaking down when the energy transfer occurs from a dye molecule to a nanometal surface, which was attributed to the surface energy transfer (SET) and follows R^{-4} distance dependence. This phenomenon was explained by the surface plasmon coupled nonradiative energy transfer [8,9]. Energy transfer between dye molecules or quantum dots (QDs) – donors and metallic nanoparticles (MNPs) – acceptors demonstrates a longer range energy transfer phenomenon due to the

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localized surface plasmon coupled and described by the nanosurface energy transfer (NSET) mechanism. Due to a large difference in donor and acceptor dimensions, the system is considered as a point dipole interacting with an infinite metal surface for small separation distances and large GNPs. The characteristic distance for which the NSET efficiency is 50%, denoted as d_0 and can be calculated by formula of the Persson–Lang model [7]:

$$d_0 = \left[0.225\frac{c^3\phi_\mathrm{D}}{\omega_{dye}^2 k_\mathrm{f}\omega_\mathrm{f}}\right]^{1/4} \tag{2}$$

where c is the speed of light in vacuum, ϕ_D is the quantum yield of the donor, ω_{Fluo} is the angular frequency for the donor, ω_f and k_f are the Fermi angular frequency and wavevector of metal. It can be seen in formula (2), the distance d_0 do not depends on both donor and GNP size. This model of the energy transfer from point dipoles to MNPs has been used to calculate the characteristic distance for single emitter–metallic nanosphere pairs [10,11] and for planes of QD–gold nanospheres [6,12–14]. These works emphasized the influence of localized plasmon field (concentration or size of gold nanoparticles) effects on FRET energy transfer between quantum dots, also the plasmon coupled frequency dependence of this type of energy transfer. Distance dependence of localized plasmon coupled energy transfer was also investigated for rare earth doped and dye doped plasmonic core–shell NPs [15]. It was found that the interaction distance was observed up to few ten nanometers [10–12,16] and NSET model provides only a good qualitative description of the distance dependence of the quenching efficiencies since the measured values were always larger than the predicted ones [6,11]. It can be said that the difference in the calculated and measured values of plasmon coupled energy transfer distance comes mainly from two reasons: (i) the point dipole condition or the dimension difference in donor and acceptor pairs, (ii) the influence of the size of nanoparticles participated in the transfer process. In the case of emitter–metallic nanosphere pairs where both D–A nanoparticles are comparable in size, the point dipole condition will be not satisfied and a big difference in calculated and measured values of characteristic distance d_0 will be expected.

This work presents our results on studies of the energy transfer between various type of donor and acceptor pairs; dye molecules, quantum dots, fluorescent nanoparticles are used as donors D and dye molecules, gold nanoparticles are used as acceptors A. The critical transfer distances R_0/d_0 was calculated and experimental estimated for all cases of D–A type. It was found that the critical transfer distances R_0/d_0 depend on the local field of both donor and acceptor when they cannot be considered as the point dipoles. A large d_0 distance up to micrometer was experimental observed when donors are fluorescent and acceptors are gold nanoparticles. A model “nano-wave emitter station and antenna” is given to explain this phenomenon. A theoretical formalism was introduced to compute the energy transfer rates for the experimental results.

2. Experimental section

The donor and acceptor used for experiments are fluorophores and gold nanoparticles (GNPs). The fluorophores are dye molecules, fluorescent nanoparticles and quantum dots (QDs) (Fig. 1). The Cyanine dyes Cy5 were purchased from Invitrogen. The fluorescent nanoparticles are 100 nm Cy3 orange beads (OBs) (Invitrogen) and laboratory manufactured Rhodamine B (RB)-doped silica nanoparticles (RBDSNPs). Each OB contains about ~3000 Cy3 dye molecules. There are about ~4000 RB molecules doped in each 100 nm RBDSNP and ~150 RB molecules in 20 nm nanoparticles. The 4 nm CdTe QDs were provided by Institute of Materials Science, VAST. The GNPs were purchased from BB International with 20 nm in size. The energy transfer experiments were carried out for five types of D–A pairs: OBs–Cy5 dyes, Cy5 dyes–GNPs, CdTe QDs–GNPs, RBDSNPs–GNPs and OBs–GNPs (Table 1).

The experiments were realized at room temperature and at 532 nm excitation for mixture of D–A pairs in aqueous solution. The donor concentration was fixed while the acceptor concentration was varied. There was no chemical reaction either aggregation between D–A pairs in solution. Absorption spectra were measured using JASCO-V570–UV–vis–NIR spectrometer. The fluorescence spectra were recorded on a Cary Eclipse spectrofluorometer (Varian). Transmission and scanning electron microscopes (TEM, JEM 1011 and SEM, Hitachi S-480) were used to determine the shape, size of particles. The absorption λ_{Ab} and fluorescence λ_Fluo maximum of donors and acceptors, also the quantum yield of donors are listed in Table 1.

3. Results and discussion

3.1. Experimental

Fig. 2 presents the curves of fluorescence intensity of donor versus acceptor concentration of D–A pairs under investigation, also their absorption and fluorescence spectra for clearing. As can be seen in (Fig. 2a), the addition of Cy5 dye molecules in mixture causes the decrease of OBs fluorescence intensity due to the energy transfer from Cy3 dye molecules (donors) in OBs to Cy5 molecules (acceptors) in solution. Using the FÖrster theory, we can calculate the characteristic critical transfer distance R_0 according to formula (1) using the spectral overlap J, and quantum yield ϕ_D.

For all other cases (Fig. 2b–e), the energy transfer occurs between the fluorophores and GNPs, which are metallic nanoparticles. In theses pairs, the gold nanoparticles can enhance or quench the fluorescence of fluorophores depending upon the relative magnitudes of two energy transfer mechanisms: (i) the plasmonic field enhancement at the fluorophores emission frequencies (plasmon coupled fluorescence enhancement) and (ii) the localized plasmon coupled Förster energy transfer from fluorescent particles to gold particles, which quenches the

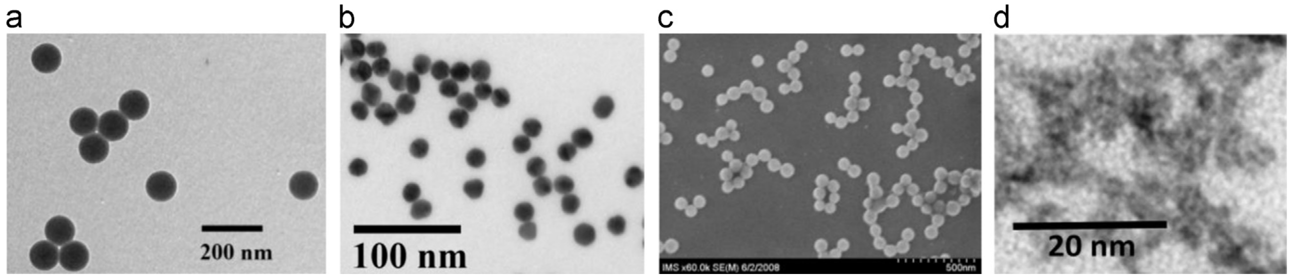

Fig. 1. (a, b and d) Transmission electron microscope (TEM) image of OBs, GNPs and CdTeQDs, respectively; (c) scanning electron microscope (SEM) image of RB DSNPs.