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Review

Emerging non-traditional Förster resonance energy transfer configurations with semiconductor quantum dots: Investigations and applications

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ABSTRACT

Förster resonance energy transfer (FRET) configurations incorporating colloidal semiconductor quantum dots (QDs) have proven to be a valuable tool for bioanalysis and bioimaging. Mirroring well established techniques with only fluorescent dyes, "traditional" FRET configurations with QDs have involved single-step energy transfer to organic dye acceptors mediated by biomolecular interactions. Here, we review recent progress in characterizing non-traditional FRET configurations incorporating QDs and their application to challenges in biosensing, energy conversion, and fabrication of optoelectronic devices.

Abbreviations: η, power conversion efficiency; 0D, zero-dimensional; 1D, one-dimensional; 2D, two-dimensional; 2PE, two-photon excitation; AFP, alpha-fetoprotein; APC, allophycocyanin; AOT, dioctyl sulfosuccinate; Au NP, gold nanoparticle; BIPS, 1′-3-dihydro-1′-(2-carboxyethyl)-3,3-dimethyl-6-nitrospiro-[2H-1-benzopyran-2,2′-(2H)-indoline]; BRET, bioluminescence resonance energy transfer; CNT, carbon nanotube; CRET, chemiluminescence resonance energy transfer; CrONO, *trans*-Cr(cyclam)$(ONO)_2^+$; CT, charge transfer; DMPET, dipole-to-metal particle energy transfer; dsDNA, double-stranded DNA; DSSC, dye sensitized solar cell; EYFP, enhanced yellow fluorescent protein; FLIM, fluorescence lifetime imaging microscopy; FRET, Förster resonance energy transfer; FWHM, full-width-at-half-maximum; GO, graphene oxide; IPCE, incident-photon-to-current conversion efficiency; ITO, indium-doped tin oxide; LbL, layer-by-layer; LDH, layered double hydroxide; LED, light emitting diode; LLnC, luminescent lanthanide complex; LSPR, localized surface plasmon resonance; LTbC, luminescent Tb^{3+} complex; MAA, mercaptoacetic acid; MBP, maltose binding protein; MOF, metal organic framework; MPA, 3-mercaptopropionic acid; M-PC, metallophthalocyanines; NO, nitric oxide; NSET, nanosurface energy transfer; PALM, photoactivation localization microscopy; PC, phthalocyanine; pcFRET, pohotochromic FRET; PDDA, poly(diallyldimethylammonium chloride); PDT, photodynamic therapy; PL, photoluminescence; PP, polypyridine; PSS, poly(sodium-4-styrene sulfonate); QD, quantum dot; QDSSC, quantum dot sensitized solar cell; SOFI, super-resolution optical fluctuation imaging; SPR, surface plasmon resonance; ssDNA, single-stranded DNA; STORM, stochastic optical reconstruction microscopy; TA, transient absorption; WSPO, spironaphthoxazine dye.

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Such non-traditional FRET configurations with QDs include substitution of organic dyes with lanthanide complexes, polypyridyl transition metal complexes, azamacrocyclic metal complexes, graphene (oxide), carbon nanotubes, gold nanoparticles, and dyes exhibiting photochromism. Other non-traditional configurations of interest include FRET relays (with or without organic dyes) that feature multiple sequential energy transfer steps, and thin films of QDs where discrete FRET pairs cannot be defined, including those where QDs are layered in a size-sequential or "rainbow" structure. The calculation of FRET efficiencies and donor–acceptor distances in the above configurations are reviewed, as are distance scaling relationships for non-zero dimensional acceptors, and the related dipolar energy transfer mechanism, nanosurface energy transfer (NSET). To illustrate the utility of non-traditional QD-FRET configurations, we highlight examples of optically switchable probes, photonic wires, time-gated and multiplexed probes for biosensing, enhanced light harvesting in QD and dye sensitized solar cells (DSSC), and colour conversion in light emitting diodes (LEDs). We close by providing a perspective on how the combined utility of these non-traditional QD-FRET configurations may be useful for engineering complex nanoscale devices in the future.

1. Introduction

Colloidal semiconductor nanocrystals, better known as *quantum dots* (QDs), are prospective materials for a wide variety of applications. QDs are characterized by a unique set of optical properties that primarily arise from quantum confinement effects [1–4]. Foremost among these properties is their bright photoluminescence (PL), the colour of which can be tuned on the basis of nanocrystal size and composition. Other favourable optical properties include broad absorption spectra with large one-photon ($\varepsilon = 10^4$–$10^7\ M^{-1}\ cm^{-1}$) and two-photon ($\sigma_{2PE} = 10^3$–10^4 GM) absorption cross-sections, large *effective* Stokes shifts (up to hundreds of nanometers), spectrally narrow and symmetric PL emission (full-width-at-half-maximum, FWHM = 25–35 nm), and good resistance to photobleaching [1]. These properties have made QDs very attractive probes for bioimaging and bioanalysis, where they are often touted for their multiplexing capability and suitability for single particle visualization and tracking [1,5–10]. Equally important in such applications is the interface of the QD, which represents a nanoscale scaffold for chemistry and functionalization. The physical properties of the QD can be tailored through application of ligand or polymer coatings [11], and biological activity can be obtained through bioconjugation [12]. The latter can include binding or other reactions with biomarkers, targeting of cells and tissues, and delivery of therapeutics. In abiotic roles, QDs also represent building blocks for optically active thin films, superlattice structures [13], and various composite materials [14] for optoelectronic applications such as light emitting diodes (LEDs) and displays, lasers, photodetectors, and solar cells [15].

QDs become even more powerful tools when their above-mentioned attributes are combined with electron transfer or Förster resonance energy transfer (FRET) processes that can, for example, modulate QD PL to generate active signaling or sensitize a secondary process. FRET is perhaps best known as a spectroscopic tool for biophysical studies, including vesicle fusion and membrane dynamics [16], protein folding [17], DNA detection [18], enzyme assays [19], ligand–receptor and protein–protein interactions [20], both in the ensemble and at the single molecule level [21–23]. In typical FRET experiments, a biomolecule is co-labeled with a donor fluorophore and an acceptor chromophore, or, alternatively, two interacting biomolecules are individually labeled with donor and acceptor. In the former case, conformational changes affect the fluorescence from the donor (and acceptor) due to the nanometric distance-dependence of FRET; in the latter case, changes in fluorescence are due to association or dissociation. To a large extent, these highly successful biological applications of FRET have inspired similar developments that incorporate QDs and their unique optical properties as participants in FRET, typically as donors. There is now a myriad of studies where QDs are used in either of the two general FRET configurations noted above, and several comprehensive reviews have been written on the utility of these configurations in bioimaging and bioanalysis [24–26].

This review examines some of the recent work in the literature involving *non-traditional* FRET configurations based on QDs. We use the term "traditional" to refer to energy transfer in a single step between a QD and an organic dye molecule, usually as a discrete pairing of a QD donor with one or more equivalent organic dye acceptors in bulk solution. Here, we discuss QD-FRET configurations that depart from this norm in one or more important ways. Deviations may include the substitution of conventional organic dyes with other chromophores; for example, lanthanide and other metal complexes, gold nanoparticles, carbon allotropes, or even organic dyes with unusual properties such as photochromism. Special attention is paid to the characterization of energy transfer in these systems, including other mechanisms that may supersede or compete with FRET. Moreover, by our definition, a departure from traditional QD-FRET configurations is not limited to the choice of acceptor. Non-traditional configurations may also include architectures where multiple energy transfer pathways are incorporated; for example, as in the case of multistep sequential energy transfer, otherwise known as a FRET "relay" or "cascade." Configurations of this nature have been realized with QD-bioconjugates in solution and with thin films of QDs at an interface. The latter are also non-traditional FRET configurations in that discrete donor–acceptor pairs cannot be defined. While the success of traditional QD-FRET methods has been impressive, even greater capability and innovations are expected from non-traditional QD-FRET configurations. As will be discussed, new capabilities in bioanalysis and therapeutics, enhancements in solar energy conversion, and fabrication of improved optoelectronic devices have already been demonstrated.

2. Quantum dots and FRET

Prior to discussing non-traditional QD-FRET configurations, it is worthwhile to review the fundamentals of FRET theory, including its "traditional" application with QDs. FRET is a resonant dipole–dipole coupling interaction that occurs through-space to transfer excitation energy from a donor fluorophore to an acceptor chromophore. The energy transfer is radiationless, occurring without the involvement of photons. Theodor Förster, after whom the process is named, first elucidated the mechanism between 1946 and 1948 [27–30]. The genius of Förster was that he was able to describe this process in terms of spectroscopic donor and acceptor properties that could be measured through relatively simple experiments.

The rate of energy transfer in FRET is given by Eq. (1), where $\tau_D^{-1} = k_0 = k_r + k_{nr}$ is the inverse native lifetime of the donor