

Core-shell plasmonic nanostructures to fine-tune long “Au nanoparticle-fluorophore” distance and radiative dynamics

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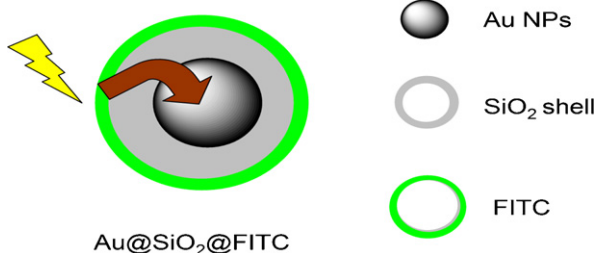
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HIGHLIGHTS

- ▶ Au@SiO₂@FITC core-shell plasmonic nanostructures are designed and constructed.
- ▶ Precise, long separation distance control between Au core and FITC is realized.
- ▶ A long-range fluorescence quenching distance of over 34 nm is observed.

GRAPHICAL ABSTRACT



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ABSTRACT

The accurate description of the energy and/or charge transfer mechanism involving Localized Surface Plasmon Resonance (LSPR) is crucial for the research field of plasmonics. The investigation is however frequently hampered by the inaccurate definition of separation distance between the energy and/or charge donor-acceptor pair. Herein we designed and constructed core-shell plasmonic nanostructures to realize precise, long separation distance control between the gold core (energy acceptor) and fluorophores (energy donor). Both steady-state and time-resolved fluorescence measurements were employed to investigate radiative properties of the as-prepared nanosystem. The observed overall fluorescence quenching of the core-shell plasmonic nanocomposites with the decrease of shell thickness is attributed to a concurrent increase of nonradiative rates and decrease of radiative rates with the separation distance decrease. However, neither fluorescence resonance energy transfer (FRET) nor nanometal surface energy transfer (NSET) model is suitable for describing the fluorescence quenching efficiency as a function of separation distance reported in this article. Remarkably, a long-range fluorescence quenching distance of over 34 nm is observed, possibly arising from the coincidence of fluorophore emission wavelength with the plasmon resonance of the gold nanoparticles. This study not only gains insight for designing novel plasmonic devices, but also provides new thoughts for investigation on molecular ruler on a larger measurement scale, molecular beacons and new generation photovoltaics.

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1. Introduction

Plasmonics, which merges photonics and electronics on nanoscale dimensions, has attracted intensive interest in recent years due to its significance in fundamental research and potential applications in miniaturized optical devices, sensors, medical

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diagnostics and therapeutics, etc. [1–4]. As is well-established, proper electromagnetic radiation at a metal–dielectric interface might induce coherent oscillations of conduction electrons on the metal surface, which is termed as surface plasmons (SPs). If the surface plasmons are localized on the surface of metallic nanoparticles [1], then localized surface plasmon resonance (LSPR) emerges. Plasmonics is the growing branch of research on such light–metal interactions. Currently in this field, one of the most representative and widely studied systems is plasmonic nanostructures composed of noble metal nanoparticles (NPs), such as Au and Ag, and fluorescent dyes, where energy and/or charge transfer processes involving LSPR occur upon proper photo excitation. The accurate description of the mechanism is crucial for research in the context of new generation photovoltaics [5–7], light emitting diodes (LEDs) [8,9] or other optoelectronic switch devices and chemical/biological sensors [10]. For instance, a recent article published in *Nature* demonstrated a spaser-based nanolaser that outcoupled surface plasmon oscillations to photonic modes at 531 nm, employing a plasmonic nanostructure made of a gold core and organic dye-doped silica shell [11].

In the “Au NPs–fluorophores” plasmonic nanostructures, Au NPs as universal energy acceptors can interact with varied fluorescent dyes, leading to energy transfer process in a way similar to that occurs during Förster/fluorescence resonance energy transfer (FRET) [12–14]. Compared to traditional FRET system, Au NPs as energy acceptors however exhibit several advantages such as long energy transfer distance up to several tens of nanometers (potential for “molecular ruler” on a larger measurement scale) [15,16], and immunity from photobleaching problem that frequently plagues organic dyes. In essence, the uniqueness reflects that the energy transfer mechanism of plasmonic nanostructures involving LSPR excitation displays certain difference from one typical FRET process. Hence, many research groups have proposed various theoretical models to simulate the FRET-like process, such as Gersten–Nitzan [17], CPS–Kuhn [18] and the widely investigated nanometal surface energy transfer (NSET) models recently [15,19].

Unfortunately, although numerous studies on interacting moieties within or slightly larger than FRET working distance of ~10 nm have emerged, the reports on plasmonic nanostructures with very long donor–acceptor separation distance of over 30 nm are rather rare [14,20–24]. In addition, the experimental data often show much inconsistency with the theoretical predictions. Among all the possible error sources, the difficulty to accurately control and define distance between the metallic NPs and the fluorophores is expected to be of great prominence. Therefore, currently considerable efforts are focused on the experimental techniques that could control distance between the energy donors and acceptors, which is a prerequisite to correctly account for the energy transfer mechanism in plasmonic nanostructures that involves LSPR excitation. One classical protocol is to link the Au NPs with fluorophores via complementary DNA double strands. Varying the number of DNA base pairs would conveniently control the distance between the Au NPs and the dyes. This method, however, has drawbacks because of the propensity of the phosphate groups on DNA to interact with Au NP surface, and such non-specific interactions would render the experimental distance inaccurate. The situation deteriorates further for larger Au particles and even detectable LSPR band shift caused by molecular-level perturbations could be observed [25–27]. In addition, the tedious DNA synthesis and purification process, together with relatively high cost of organic dye modified DNA strands also add difficulties to this approach. Therefore, it is urgent to develop reliable and facile methodology to control the “Au NPs–fluorophores” distance in order to investigate the radiative and nonradiative processes thereof.

Herein, we managed to construct Au@SiO₂@fluorophore “core@shell@shell” plasmonic nanostructures to realize the

accurate, long distance control up to a separation distance of 60 nm. By varying the reaction conditions, the thickness of SiO₂ shell, *i.e.*, the spacer between the Au NPs core and outermost fluorescein-5'-isothiocyanate (FITC) fluorophores, were fine-tuned to give defined experimental distance and radiative properties of the plasmonic nanostructure were systematically studied. A growing number of reports as to the fabrication of SiO₂ core–shell structures have emerged these days [28–32], employing this method as one substitute for classical distance control strategies such as polyelectrolyte layer-by-layer (LBL) assembly [21,33] and single/double DNA strand linkers, which are convenient for short distance control but intrinsically defective for long distance defining. “Gold or silver core–silica shell” for fluorescence quenching and/or enhancement have attracted more and more interest [24,34–40]. In this article, we prove the potential of utilization of core–shell architecture to realize accurate, long distance tailoring and defining, and thus provide robust experimental data to build theoretical models for LSPR involved energy transfer process in plasmonic nanostructures. The research would not only gain insight for designing novel plasmonic devices, but also provide new thoughts for investigation on molecular ruler on a larger measurement scale, molecular beacons and new generation photovoltaics.

2. Experimental details

2.1. Fabrication of core–shell plasmonic nanostructures

Preparation of Au NPs: Synthesis of the ~14 nm-diameter Au NPs core was through the reduction of an aqueous boiling solution of HAuCl₄ using sodium citrate as reducing agent and stabilizer, in accordance to previous literature [41]. Briefly, 3.2 mL of 25 mM HAuCl₄ aqueous solution was added to 48.0 mL deionized water and heated to reflux under magnetic stirring, then 8.0 mL of 38.8 mM freshly prepared trisodium citrate aqueous solution was swiftly added. The solution was allowed to reflux for 15 min, until the color changes from faint yellow to dark red. The particle concentration was determined by measuring its absorbance at LSPR maximum by using a molar extinction coefficient of $3 \times 10^8 \text{ M}^{-1} \text{ cm}^{-1}$ as reported in literature [42].

Preparation of spacer of silica shell: The process is in accordance to previous literature [43]. An aqueous solution of poly(vinylpyrrolidone) (PVP, 0.5 mL, 12.8 mg/mL) with average molar masses of 10 kg/mol was added to the 59.2 mL aqueous solution of as-prepared Au NPs. Subsequently at room temperature, the mixture stood for 36 h under magnetic stirring, which allowed PVP molecules to attach to the surfaces of Au NPs. The PVP-attached Au NPs were then separated from solution by centrifuging at 11,000 rpm for 30 min and re-dispersed in 30.0 mL deionized water. Thereafter, 5.0 mL PVP-modified Au NPs were added into a flask containing a total volume of 15 mL mixture composed of ammonia (0.6–1.0 mL) and ethanol (14.4–14.0 mL) under magnetic stirring. Then, calculated amount of tetraethoxysilane (TEOS) in 10 mL ethanol kept in a constant pressure funnel was added dropwise into the flask within a period of 6 h. The total volume of the reaction mixture now reached about 30 mL and was stirred for another 12 h to complete the preparation process. To obtain a series of spacer shell thickness ranging from ~10 to 60 nm, simply adjust the concentration of TEOS to be 1.19, 4.77, 25.2, 72.3 and 149 mM, respectively. The silica layer thickness is thus increased in a controlled way.

Formation of dye doped silica shell: The final step to construct Au@SiO₂@FITC core@shell structures is to dope the fluorophores of FITC into the outermost of the SiO₂ shell. In order to prevent dye leakage from the shell and ensure long-term stability of the luminescence of the assembly as well, FITC was initially

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