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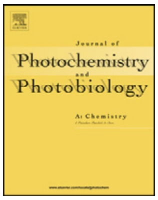

Superquenching of coumarin 153 by gold nanoparticles

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ABSTRACT

Superquenching of the laser dye, coumarin 153 (C153), by 16–59 nm gold nanoparticles (AuNPs) is reported from the steady state and time-resolved fluorometric investigations. Quenching of the steady state fluorescence of C153 and its fluorescence lifetime reveals energy transfer from the probe to AuNP in the photoexcited state. The Stern–Volmer constants (K_{SV}, 10^7–10^9 mol^{-1} dm^3) determined from the quenching of the donor lifetime in the presence of AuNPs of varying sizes are orders of magnitude higher than those for the normal photochemical quenching processes. The quenching efficiency increases with an increase in the size of the nanoparticles. The importance of the work lies in providing a new and simple system to be exploited for developing biosensor with high degree of sensitivity.

1. Introduction

While bridging the gap between the atomic/molecular state and the bulk phases, nanoscale materials reveal novel physical and chemical properties which are often different from those of either of the phases. Potential applications of the nanostructured materials recognized in recent years have triggered a massive research in the area [1–4]. In this respect, gold and silver nanoparticles draw special attention because of their widespread applications [5–9]. Nanoparticles of noble metals possess unique optical attributes due to their surface plasmon resonance (SPR) which is the collective coherent oscillation of the free electrons in resonance with an electromagnetic wave. The plasmon oscillation is considered essentially as a photon strongly confined to the nanoscale size of the metal particle. The plasmon resonance results in a strong light absorption and scattering by the nanoparticles at the resonance frequency, which has found uses in photonics and biomedicine including highly sensitive diagnostic assays, thermal ablation, radiotherapy enhancement, drug delivery, etc. [10–12]. Because of the massive demand, novel methods of synthesis of metal nanoparticles have found prominence in the contemporary research.

Besides applications in optoelectronics and biomedicine, AuNP is known to have a superior quenching efficiency in a wider range of wavelengths compared to the organic quenchers [13–25]. The high quenching efficiency of gold nanoparticles has found potential applications as immunosensors [26] and in the development of fluorescence-based assays for DNA, RNA and protein markers [27]. Gold and silver nanoparticles are also observed to quench the conjugated polymers super-efficiently which has its applications in the polymer-based biosensing at the subpicomolar analyte concentration [15–17].

The efficiency of quenching of fluorescence and fluorescence lifetime of the donor in the presence of AuNPs depends very much on the size of the nanoparticles as well as the distance of separation of the fluorophore from it. To have a control on the latter, people have adopted techniques like tagging DNA type spacers of definite lengths (tunable spacers) [19,20,22,28,29], sheathing the AuNPs by variable number of monomolecular films [30], etc. Single-molecule spectroscopy has also been exploited to explore and understand the mechanism of AuNP induced quenching [31–33]. Although increase in the fluorescence is observed with smaller AuNPs (≤10 nm) which is rationalized from an enhanced local field induced by the nanoparticle [32], for larger nanoparticles (≥10 nm) quenching always dominates. The general observations imply that larger AuNPs quench the donor fluorescence more efficiently. The quenching is mostly explained from a dipole-induced non-radiative energy transfer from the fluorophore to the nanoparticles although sometimes stress is put on a reduction in the radiative rate constant [30,32].

The high extinction coefficient near the plasmon resonance frequency enhances the efficiency of the gold nanoparticles towards quenching of the fluorescence of the matched fluorophores [34]. Energy transfer (ET) from fluorescent donors to the nanoscale acceptors is one of the prime topics of current research. The excited state non-radiative energy transfer is typically a distance dependent, through-space process in which an electronically excited

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'donor' molecule transfers its excitation energy to an 'acceptor' leading to a reduction in the fluorescence intensity as well as lifetime of the donor [35]. Two mechanistic propositions are put forward to explain the energy transfer process: nanoparticle surface energy transfer (NSET) and Förster resonance energy transfer (FRET). In NSET the dipolar interactions occur due to the presence of free conduction band electrons in the metal nanoparticle that provides dipole vectors on the surface of the metal ready to accept energy from the donor, while in FRET the excitation energy is transferred to the acceptor dipole [21–23,28,35–40]. Apart from the conceptual difference, the major difference between FRET and NSET from the applicational point of view remains in the fact that while the efficiency of the former process depends on the inverse sixth power of the donor–acceptor distance ($1/r^6$), for the latter the dependence lies on the fourth power ($1/r^4$). Anyway, the high sensitivity of the energy transfer process on the donor–acceptor distance makes both FRET and NSET '*spectroscopic rulers*' for measurement of intramolecular/intermolecular distances and has provided physicists, chemists and biologists a powerful and versatile tool for studying the structure and dynamics of small or large molecules in condensed phases [21–23,28,35–40].

Particularly because of providing a simple strategy for sensor-based applications, continuous efforts are on for studying the energy transfer process using gold nanoparticles. Several works on the quenching by AuNPs report the non-radiative energy transfer from the donors to the nanoparticle acceptor to follow long range probe–AuNP interaction following either FRET or NSET depending on the specific case [19–25,41]. Driven by the need and the widespread applications, in the present work we have explored the quenching of the fluorescence of a well-known laser dye from the coumarin family, namely coumarin 153 (C153), by gold nanoparticles (AuNPs) of four different particle diameters (d) in the range of 15–60 nm. Apart from being a laser dye, because of its solvent sensitive spectral behavior the dye is exploited for deciphering various aspects including exploration of the properties of the different domains of microheterogeneous environments and solvation dynamics [42–45]. Considering a good overlap between the fluorescence spectrum of C153 emitting at ~550 nm in water [42] and the absorption spectra of AuNPs (λ_{abs}^{max} in the range of 520–535 nm), the C153–AuNP pair has been chosen for a plausible energy transfer from the donor (C153) to the acceptor (AuNPs). The objective of the work is to demonstrate an energy transfer system revealing super-efficient fluorescence quenching as well as to decipher the impact of the dimension of the gold nanoparticles on the efficiency of quenching. The impetus of the work lies in providing a newer and simple system to be exploited for developing biosensor with high degree of sensitivity.

2. Materials and methods

Coumarin 153 and hydrogen tetrachloroaurate trihydrate ($HAuCl_4$) purchased from Sigma–Aldrich (U.S.A.) and trisodium citrate dihydrate from Merck (India) are used without further purification. Triply distilled water has been used to prepare the aqueous solutions wherever required.

Gold nanoparticles of different sizes have been synthesized following the citrate reduction of $HAuCl_4$ as introduced by Frens [46,47]. Standardization of the particle diameter has been done by controlling the fractional concentration of the reducing agent in the reaction mixture [47].

Room temperature absorption and steady state fluorescence measurements are performed using a Shimadzu UV-2450 spectrophotometer and a Spex fluorolog-2 spectrofluorometer equipped with DM3000F software respectively. Fluorescence lifetimes are determined from time-resolved intensity decays by the method of time-correlated single-photon counting (TCSPC) using a nanosecond diode excitation source at 403 nm (IBH, UK, nanoLED-07) and TBX-04 as the detector. The instrument response time is ~1 ns. The decays are deconvoluted using IBH DAS-6 decay analysis software. Quality of the fits is judged by the reduced χ^2 criterion and the randomness of the fitted function to the raw data. Bi-exponential decay profiles are described by $I(t) = a_1 \exp(-t/\tau_1) + a_2 \exp(-t/\tau_2)$, where τ_1 and τ_2 are the decay times and a_1 and a_2 are their relative amplitudes. The amplitude averaged fluorescence lifetime (τ) has been defined as

$$\tau = \frac{a_1\tau_1 + a_2\tau_2}{a_1 + a_2} \qquad (1)$$

All the experiments are performed at ambient temperature (27 °C) with air-equilibrated solutions.

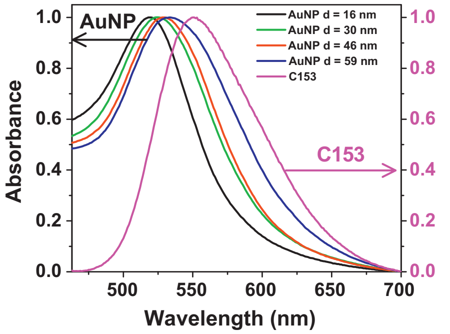

Fig. 1. Overlap between the fluorescence spectrum of C153 (donor) and the absorption spectra of AuNPs (acceptor).

Table 1
Spectral characteristics of the synthesized AuNPs.

Particle diameter (nm)	Absorption maximum (nm)	Extinction coefficient, ε ($mol^{-1}\,dm^3\,cm^{-1}$)
16	520	2.7×10^8
30	525	7.0×10^8
46	530	3.0×10^9
59	534.5	1.5×10^{10}

3. Results and discussion

3.1. Steady state studies

In aqueous medium photoexcitation of C153 at its lowest energy absorption band (430 nm) yields a broad and unstructured fluorescence peaking at around 550 nm [42]. The synthesized gold nanoparticles of varying particle diameters reveal characteristic plasmon bands in their respective absorption spectra. With an increase in the particle size the absorption maximum reveals a gradual bathochromic shift (Fig. 1). The high extinction coefficients (10^8–10^{10} $mol^{-1}\,dm^3\,cm^{-1}$) are manifested in the intense absorption bands. The extinction coefficients of the particles at the respective absorption maxima increase remarkably with an increase in the particle diameter [19]. The spectral characteristics of the synthesized AuNPs of different dimensions are given in Table 1. Consistent with literature the AuNPs are non-emissive.

In aqueous solution of C153 (~1×10^{-5} mol dm^{-3}) successive addition of picomolar concentrations of AuNPs leads to a remarkable quenching of the emission of the fluorophore. Repetition of the steady state quenching using gold nanoparticles of four different dimensions reflects that the degree of fluorescence quenching increases radically with an increase in the size of the gold nanoparticle.