



Enhanced one- and two-photon excited fluorescence of cationic (phenothiazinyl)vinyl-pyridinium chromophore attached to polyelectrolyte-coated gold nanorods



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ABSTRACT

In this paper we evaluate the effect of plasmonic enhancement on the fluorescence properties of cationic (phenothiazinyl)vinyl-pyridinium (PVP) chromophore attached to polyelectrolyte-coated gold nanorods (PE-AuNRs). We provide reliable evidence for the convenient enhancement of both one- and two-photon excited fluorescence of PVP molecules on PE-AuNRs due to their favorable entrapment away from the metallic surface via multilayer PE coating. While the enhancement under one-photon excitation is mainly ascribed to the amplification of the emission rate due to plasmon effect, the two-photon excited enhancement is believed to arise from a combination of local electric field amplification and competition between increased radiative and non-radiative decay rates. Additionally, we perform numerical simulation using Finite-Difference Time-Domain method to understand better the mechanism of fluorescence enhancement under two-photon excitation.

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1. Introduction

The complex interaction of metallic nano-objects with fluorescent molecules has been intensively addressed over the last few decades as an extremely challenging issue enabling the development of novel functional hybrid nanomaterials [1–4]. Despite the already reported applicability of such nanohybrids, there is still a growing need to develop more efficient and reliable fluorescent labels for bio-imaging applications. Among various types of imaging techniques, nonlinear optical imaging represents nowadays a promising tool in bio-medical applications [5,6]. Its popularity relies on the improved imaging contrast that can be obtained by excitation with intense and extremely short laser pulses. For example, the nonlinear optical effect of two-photon excited (2PE) fluorescence has recently grown in interest in recent years due to

improved 3D spatial resolution and, in the case of near-infrared excitation of living organisms, deep penetrability and less photo-damage [6–8]. Therefore, the design of efficient two-photon active fluorescent nanosystems with applicability in cell imaging represents a worthwhile research field. Moreover, the quadratic dependence of two-photon absorption on the excitation intensity enables the possibility of enhancing the 2PE fluorescence of chromophores by placing them within intense electromagnetic fields. Such a condition can be attained by using plasmonic nanoparticles (NPs), due to the intense electromagnetic fields generated in their close proximity by localized surface plasmons (SPs) excitation [9]. Consequently, the light absorption efficiency and quantum yield of the nearby located chromophores can be significantly enhanced. However, the enhancement factor is dependent on several factors such as chromophore-metal distance, size and shape of NPs, dipole orientation, excitation wavelength, spectral overlap between the fluorescence spectrum and the SP band of metal nanoparticles [9–11]. While metal-enhanced 2PE fluorescence has been demonstrated on solid substrates starting with the 90s [12], the enhancement of 2PE fluorescence in colloidal suspensions was first

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report only few years ago by Li et al. [13]. They account the enhancement of two-photon emission of quantum dots by adjacent silica-coated gold nanorods (AuNRs) in solution as a result of the resonant excitation of localized surface plasmon resonance of AuNRs. Then, Sivapalan et al. reported the enhancement of the two-photon absorption cross section of an organic chromophore coupled with polyelectrolyte-coated AuNRs in both resonant [14] and off-resonant [15] excitation conditions. A most recent study reports for the first time, the metal-enhanced 2PE fluorescence of both 2PE absorption efficiency and emission quantum yield of a porphyrin molecule covalently bound to silica-coated AuNRs [16].

Among various types of metallic nanoparticles, AuNRs are of particular interest in applications exploiting metal-enhanced effects owing to the intense electromagnetic fields concentrated at their ends. The accumulation of charges at the sharp metallic edges and corners of plasmonic NPs is known to give rise to intense and highly localized electromagnetic, phenomenon termed the “lightning rod effect” [17]. This effect contributes to the enhancement of fluorescence signal of molecules located nearby. AuNRs are also appealing due to the longitudinal surface plasmon resonance with large and controllable tunability across the visible and near infrared region, in addition to good chemical stability and biocompatibility under biological conditions which make them extensively exploited in applications such as sensing, cancer therapy, imaging and drug delivery [18,19].

In this paper we investigate the effect of plasmonic enhancement on both one- and two-photon excited (1PE and 2PE) properties of cationic chromophore (*i.e.* (phenothiazinyl)vinylpyridinium (PVP) [20]) attached onto multilayered polyelectrolyte-coated gold nanorods (PE-AuNRs). Specifically, three layers of PE (*i.e.* poly(styrene sulfonate) (PSS) and poly(diallyldimethylammonium chloride) (PDADMAC)) were first deposited onto positively charged cetyltrimethylammonium bromide (CTAB)-coated AuNRs via layer-by-layer (LbL) technique. The overall multilayered coating confers a final 7–8 nm coating around the metallic structure while the negative outer PE layer supports the adhesion of PVP molecule. The PE coating ensures the entrapment of PVP molecules away from metallic surface, at a distance where the fluorescence quenching can be avoided but the electromagnetic enhancement is still operational. The 1PE and 2PE fluorescence of PVP molecules attached to PE-AuNRs is investigated through steady-state and time-resolved fluorescence spectroscopy. We obtain a 6 – fold enhancement of the 1PE fluorescence of PVP molecules on PE-AuNRs compared to free case. More significantly, we provide evidence for the enhancement of 2PE fluorescence of PVP chromophore by 4 orders of magnitude when molecules are attached to PE-AuNRs as a result of local electric field amplification provided by AuNRs. Throughout literature, notable enhancement factors have been reported separately in plasmon-assisted 1PE and 2PE fluorescence enhancement assays, [10,21,22]. However, there are only few reports available on the enhancement of both 1PE and 2PE fluorescence signals with comparable factors onto the same platform, in colloidal suspension [13,16].

2. Experimental methods

2.1. Reagents

Tetrachloroauric acid ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$), cetyltrimethylammonium bromide (CTAB), ascorbic acid and poly(diallyldimethylammonium chloride) solution (PDADMAC, 20 wt% in H_2O) were purchased from Aldrich. Sodium borohydride (NaBH_4 , 99%) and silver nitrate (AgNO_3) were obtained from Merck. Polystyrene sulfonate (PSS, MW 70,000) was purchased from Alfa Aesar. Cationic (phenothiazinyl)vinyl-pyridinium (PVP) chromophore was obtained in

laboratory based on a chemical synthesis detailed elsewhere [20]. All reagents were used as received. Ultrapure water (resistivity 18.2 M Ω) was used as solvent in all the experiments.

2.2. Samples preparation

CTAB-coated AuNRs were synthesized using the seed-mediated growth approach detailed in a previous publication [23]. After synthesis, the CTAB-AuNRs were purified twice through centrifugation and redispersed in ultrapure water before envelopment in polyelectrolyte coating and functionalization with two-photon active PVP molecules. The procedure of coating AuNRs with multilayered polyelectrolyte as well as labeling with PVP molecules is depicted in Scheme 1.

The positively charged CTAB bilayer present at the surface of the as-prepared CTAB-AuNRs served as the basis for the electrostatic deposition of the first layer of negatively charged polyelectrolyte, the PSS. Briefly, CTAB-AuNRs, with a concentration of 0.45×10^{-9} M, were incubated with 0.045 mg/ml PSS in aqueous solution for 2 h at room temperature. The excess of PSS was removed through centrifugation and the pellet was redispersed in ultrapure water. Thereafter, for the deposition of subsequent positively charged layer, the negatively charged AuNRs (10^{-9} M) were incubated with 0.83 mg/ml PDADMAC for another 2 h, washed through centrifugation and redispersed in ultrapure water. Finally, a third layer of polyelectrolyte was obtained by repeating the procedure for PSS coating, previously detailed. The negatively charged AuNRs enveloped in three layers of polyelectrolyte, hereafter PE-AuNRs, were then decorated with positively charged PVP molecules *via* electrostatic interaction by incubating 1 ml aqueous solution of PE-AuNRs (0.4×10^{-9} M) with 20 μl of 2.1 mM methanol solution of PVP chromophore. The obtained sample will be further refer to as PVP@PE-AuNRs. Reference sample of PVP was obtained by redispersing 20 μl of 2.1 mM PVP methanol solution in 1 ml of water.

2.3. Experimental measurements

Absorption spectroscopy was performed on a double-beam V-670 UV–Vis/NIR spectrophotometer (Jasco) with 1 nm spectral resolution, equipped with a deuterium lamp (190–350 nm) and a halogen lamp (330–2700 nm). Transmission electron microscopy (TEM) investigations were performed on a JEOL 100 U type microscope operated at 100 kV accelerating voltage. Colloidal sample were dropped onto carbon-coated copper grids and dried at room temperature. No staining was used. Particle size distribution and zeta potential were measured by a Zetasizer NanoZS90 instrument (Malvern Instruments) equipped with a He-Ne laser (633 nm, 5 mW). All analysis was performed at a scattering angle of 90° and temperature of 25 °C while the numbers of measurements were optimized automatically by the software. The steady-state and time-resolved fluorescence properties of the as-prepared samples were analyzed using: (i) a Jasco LP-6500 spectrofluorimeter (Jasco) - used for recording 1PE fluorescence spectra, bandwidths of 3 nm were used in both excitation and emission and (ii) a MicroTime200 time-resolved confocal fluorescence microscope system (PicoQuant), equipped with an inverted microscope (IX 71, Olympus) and coupled to a SR-163 (Andor Technology) single-molecule sensitive spectrograph equipped with a Newton 970 EMCCD camera, through a 50 μm optical fiber, and a Mira 900 Titanium:Sapphire tunable femtosecond laser (Coherent) - 1PE fluorescence lifetime decays were obtained under excitation with a 5 μW diode laser head (LDH-D-C-405, PicoQuant) operating at 405 nm and 40 MHz; signal was collected through a UPLSAPO 60 \times /NA 1.2 water immersion objective and was spatially and spectrally filtered by a

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