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Enhancing effects of gold nanorods on luminescence of dyes

Anni Partanen [a,*], Markus O.A. Erola [b], Jarkko Mutanen [a], Hanna Lajunen [a], Sari Suvanto [b], Markku Kuittinen [a], Tuula T. Pakkanen [b]

[a] *Institute of Photonics, University of Eastern Finland, P.O. Box 111, FI-80101 Joensuu, Finland*
[b] *Department of Chemistry, University of Eastern Finland, P.O. Box 111, FI-80101 Joensuu, Finland*

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ABSTRACT

In this work the effects of gold nanorods (GNRs) on luminescence of two dyes were studied. Pyronin B and Direct Yellow 96 are used as the source of luminescence and the dimensions of the GNRs were varied. The luminescence intensities of aqueous solutions containing only luminescent dye and solutions containing luminescent dye and GNRs were measured. The measured emission spectra were normalized by normalizing the luminescence intensities to the dye concentration and GNR concentration. The luminescence enhancement was examined as a function of GNR's diameter, surface area and volume. Our results indicate that when plasmonic GNRs become larger the luminescence enhancement increases for both PyrB and DY96 dyes.

1. Introduction

Recently, the interest in nanoparticles (NPs) has increased as their synthesis has become more efficient and their properties have been studied more [1,2]. Especially metallic NPs have been under an active study because of their optical properties. Metallic NPs have also been used in applications such as surface enhanced Raman spectroscopy [3–6] and fluorescence enhancement [7,8].

The enhancement of luminescence by plasmon resonances of gold NPs has been widely studied lately [9–13]. There are at least three different mechanisms for the luminescence enhancement to happen near metal surfaces [14]: i) Energy transfer quenching, ii) local incident field enhancement on the fluorophore and iii) increase in intrinsic radiative decay rate of the fluorophore. Firstly, the energy transfer quenching is strongly dependent on the distance between metal and fluorescent material and is valid only in distances less than 50 Å. Secondly, enhancement of local field on the fluorophore increases the rate of excitation but since radiative rate is not changed the fluorescent lifetime remains the same. The size of local field and hence the enhancement factor are highly dependent on the size and geometry of NPs. Additionally, when the distance between NP and luminescent material increases the field enhancement is decaying rapidly [15]. Thirdly, as the intrinsic radiative decay rate of the fluorophore increases, the fluorescence intensity rises (fluorescent lifetime is decreased) that can lead to an enhanced fluorescence. In luminescence enhancement by metal NPs, the enhancement is assumed to decrease as a function of distance in order: quenching, increased local field excitation and increased intrinsic radiative decay rate [14,16].

In this work, a series of positively charged gold nanorods (GNRs) with different sizes is synthesized, and mixed separately with two different luminescent materials, positively charged Pyronin B (PyrB, Sigma-Aldrich) and negatively charged Direct Yellow 96 (DY96, Aldrich) dyes. The effect of GNRs on the luminescence properties of the dyes is measured with a custom made bispectrometer [17–19], and the effects of GNR's dimensions on the luminescence intensity enhancement are studied.

2. Preparation of samples

In this work, the silver(I)-assisted seed mediated synthesis protocol was employed for the synthesis of GNRs [20,21]. Synthesis of spherical GNPs was carried out by a seeding growth approach [20]. $HAuCl_4 \times 3H_2O$ ($\geq 99.5\%$, Oy FF-Chemicals) was used as the gold precursor. $AgNO_3$ ($> 99\%$, Sigma-Aldrich) was used as the assistance of GNRs synthesis. Hexadecyltrimethylammonium bromide (CTAB, $\geq 98\%$, Sigma) was used as the capping agent in a seed solution and in growth solutions of the GNR synthesis. The physical volume of GNRs was varied by controlling the volume of seed solution in use. The relative volumes of seed solution added in the growth solutions of the same concentration and of the same volume from the smallest (Rod8) to the largest GNRs (Rod1) were 24, 10, 6, 5, 4, 3, 2 and 1. The GNRs were washed using centrifugation and re-dispersed in deionized water. The dimensions of GNRs were measured with a STEM mode of a Hitachi SEM S-4800 scanning electron microscope. The operating voltage used was 30 kV and samples were prepared by dipping the carbon

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[*] Corresponding author. Tel.: +358 504423310.
E-mail address: anni.partanen@uef.fi (A. Partanen).

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Table 1
The dimensions, surface areas, volumes and extinction coefficients of the GNRs.

	Length (nm)	Diameter (nm)	Area (nm^2)	Volume (nm^3)	Extinction coefficient[a] ($10^9 \times (M \times cm)^{-1}$)
Rod1	45 ± 6	18 ± 3	2500	10000	3.70
Rod2	39 ± 5	14 ± 2	1700	5400	2.24
Rod3	38 ± 5	13 ± 2	1500	4500	1.98
Rod4	35 ± 4	12 ± 1	1300	3300	1.45
Rod5	35 ± 4	11 ± 1	1200	2900	1.29
Rod6	34 ± 4	10 ± 1	1100	2500	1.08
Rod7	31 ± 4	9 ± 1	870	1700	0.81
Rod8	27 ± 3	7 ± 1	590	930	0.45

[a] Reduction of gold ions is assumed to be 100%.

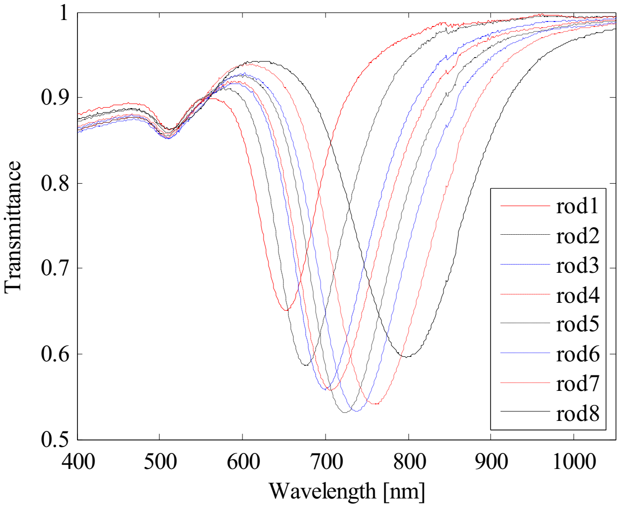

Fig. 1. Measured transmittances of GNRs with different dimensions (series C).

coated Cu grid in GNR solution. The dimensions, surface areas and volumes of GNRs are presented in Table 1 (the shape of gold nanorod was assumed to be cylinder with hemispherical ends).

Three different series of aqueous solutions were prepared (series A, B and C). Two of them were prepared with stock solutions of luminescent materials: 294 µg/L for DY96 (series A) and 44 µg/L for PyrB (series B). The third series was used as a reference and did not contain any added luminescent material (series C). Nine solutions were made for each series: eight with different GNRs added (Table 1) and one without GNRs (reference sample). All solutions were diluted to the volume where the concentrations of DY96 and PyrB were 29.4 µg/L and 4.4 µg/L, respectively. The wavelengths of the maximum absorbance of the DY96 and the PyrB were 396 nm and 555 nm, respectively.

3. Characterization

The transmittances of aqueous GNRs solutions (rods randomly orientated) were measured with unpolarized light using a Perkin-Elmer Lambda 900 UV/vis/NIR spectrometer. The transmittance spectra (vis/NIR) of GNRs presented in Fig. 1 show two plasmon bands for each GNR solution: one at around 510 nm arising from the light absorption in the transverse direction (diameter) of the GNRs and the other at 600–850 nm from the absorption in the longitudinal direction (length).

The molar concentrations of the GNR synthesis solutions were calculated by $C_{GNR}=(n_{Au} \times M_{Au}) / (\rho_{Au} \times N_A \times V_{GNR} \times V)$, were n_{Au} is the total molar amount of gold added in the synthesis (assumed that reduction of gold ions is 100%) and M_{Au} is molar mass of gold (197 g/mol). The ρ_{Au} is the density of gold (gold atoms are assumed to form a uniform fcc structure in with the density of 19.33 g/cm^3) and N_A is Avogadro's constant. V_{GNR} and V are the volumes of the GNR (dimensions are shown in Table 1) and the reaction mixture in liters, respectively. Results of calculations for C_{GNR} are shown in Table S1. A similar procedure has been used for spherical Au particle in Ref. [22]. Even though the yield of GNR synthesis has been reported in some cases to be around 20% [23], the reduction of gold salt was assumed in this work to be 100%. Variation in the GNR yields between separate syntheses may be insignificant [23] since the GNR syntheses were done using the growth solutions with the same concentration and volume and carried out under the same reaction conditions.

The extinction coefficients presented in Table 1 were determined according Beer–Lambert law. Each GNR solution prepared was diluted to five different concentrations and absorption spectra of the solutions were measured. The maximum absorption of the longitudinal signal was recorded and plotted versus the molar concentration of the GNRs in the solution and the extinction coefficient was obtained from slope of the linear region of the curve (Fig. S2). The obtained values of extinction coefficients are supported by the literature results [24]. After solving the extinction coefficients the concentrations of the GNRs in the series A, B and C (Table S2) were calculated.

The excitation–emission matrices (EEMs) of the samples containing luminescent dye were measured with a bispectrometer. The light from a 450 W xenon lamp (Oriel M-66923 housing, Newport corporation, Irvine, California and Osram XBO 450 W bulb, Osram AG, Switzerland) was directed to the sample through a Czerny–Turner monochromator (DTMc300, Bentham Instruments Ltd, United Kingdom). The used peak width and sampling interval of the excitation light were both 5 nm. The emitted light was collected with a lens to an optical fiber attached to a spectrograph detector (PMA-12, Hamamatsu Photonics K.K., Japan). The spectrograph operates at the wavelength range 200–950 nm with 0.72–0.76 nm spectral sampling. In the used measurement geometry the angle of incidence was 0° and the detection angle was 45°. The beam spot size was 5 mm.

4. Results and discussion

In a solution of luminescent molecules, plasmonic metal nanoparticles can increase the luminescence intensity of the molecules due to an intense electromagnetic field located at their surface. Furthermore, other substances in the solution, such as a surfactant and solvent, can have influence on the enhancement by changing the surface charge of the nanoparticles and thus altering the distance between nanoparticles and luminescent molecules. It has been shown that the positive or negative charge produced by surfactant molecules for NPs is an important factor influencing enhancement of the luminescence intensity in the solid state [13]. The charge difference between metallic nanoparticles and luminescent material affects the distance between particle and luminescent dye. The distance together with the shape and dimensions of NPs have been shown to have major influence on the luminescence enhancement [25]. However, in the solution state the charge difference may play a minor role compared to the solid state. In solution nanoparticles and dye molecules are in a continuous Brownian motion which ensures that nanoparticles are colliding all the time with each other [26] and with dye molecules. This thermal motion can reduce the electrostatic interaction between charged metal particles and dye molecules.

The luminescence intensities of Direct Yellow 96 and Pyronin B in the solutions of gold nanorods were measured in the wavelength range from 250 nm to 700 nm for all luminescent samples