

Spectroscopic investigations on the binding of Methylene Blue and Nile Blue to negatively charged gold nanorods

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ABSTRACT

The effect of longitudinal surface plasmon (l-SP) electric field of gold nanorods (AuNRs) on the optical (absorption and fluorescence) properties of two dyes Methylene Blue (MB) and Nile Blue (NB) has been studied by tuning and detuning the l-SP band with the absorption maxima of the dyes. Binding between dyes and nanorods were established by electrostatic interaction by making the nanorods negatively charged after coating them with polystyrene sulfonate (PSS). The absorption spectra of the dye-nanorod complex showed two prominent absorption bands in the 550–700 nm regions. For the detuned condition these changes are attributed to the nanorod induced aggregation of the dyes. However for the tuned condition, with increasing dye concentration the energy gap between the bands were observed to increase and then saturate. This is attributed to resonance coupling between the l-SP of the nanorod with the dye absorption. Although the fluorescence intensity of the dyes in the presence of increasing amount of AuNRs were observed to be quenched their lifetimes were observed to increase. Both the radiative (k_r) and nonradiative (k_{nr}) rates of the dyes decreases in the presence of AuNRs. The magnitude of decrease for k_r is much higher than k_{nr} , which is attributed to the formation of the non-fluorescent dimeric species. The increase in the fluorescence lifetime is attributed to the suppression of the excited state nonradiative pathways of these dyes adsorbed on the surface of the AuNRs. In addition, the changes of k_r and k_{nr} were observed to be greater for the tuned condition.

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1. Introduction

The surface plasmon (SP) electric field of metallic nanoparticles (NP) can significantly affect the absorption and emission properties of molecular chromophores located nearby. Usually this results in a quenching of their fluorescence [1–10], however a good overlap between the molecular and plasmonic resonance may also result in resonant coupling between them [11–25]. The radiative and nonradiative decay of the excited state of the chromophores is expected to depend critically on size and shape of the nanoparticle, the distance between the chromophore and the nanoparticle, the orientation of the molecular dipole with respect to the dye-nanoparticle axis, and the overlap of the molecule's emission with the nanoparticle's absorption spectrum [26].

In this work we have investigated how the SP field of gold nanorods affects the optical (absorption and emission) properties of two adsorbed dyes when their SP absorption is tuned to the absorption maximum of dye or away from it. For this we have prepared polystyrene sulfonate (PSS) coated gold nanorods (AuNR) of different aspect ratio having their longitudinal surface plasmon band (l-SP) tuned with the absorption maxima of two dyes Nile Blue

(NB) and Methylene Blue (MB) and l-SP band tuned away from the absorption band of the dyes (the detuned condition). Earlier, the SP field of different gold nanostructures have been utilized to enhance the raman scattering from the dyes [27–29].

2. Materials and methods

2.1. Chemicals

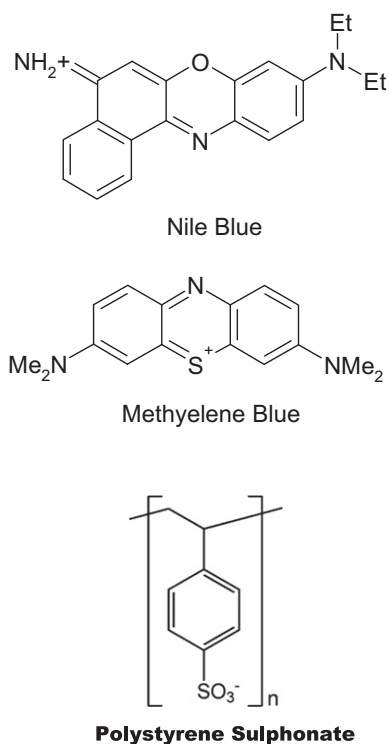
HAuCl₄·3H₂O (99.9%), AgNO₃, and Cetyl tri-methyl ammonium bromide (CTAB) (Sigma), NaBH₄, ascorbic acid, PSS (Alfa Aeser), NB (Exciton) and MB were used as received. The structures of Nile Blue (NB), Methylene Blue (MB) and the repeating unit of PSS are shown in Scheme 1. Deionized (DI) water (Millipore) was used for nanorod preparation and experiments.

2.2. Nanorod preparation

AuNR samples with different l-SP were prepared. The ones, having an ensemble l-SP peak at 730 nm and 700 nm, were grown in aqueous solutions varying the gold to seed ratio, and ascorbic acid to gold ratio, according to a previously reported method [30]. Briefly, the seed solution was made by the addition of HAuCl₄ (0.125 mL of 0.01 M) into a CTAB solution (3.75 mL, 0.1 M) in a glass

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Scheme 1. Chemical structures of the dyes and the polymer PSS used in this study.

test tube. After the solution was mixed by inversion, a freshly prepared, ice-cold NaBH_4 solution (0.3 mL, 0.01 M) was added all at once, followed by rapid inversion mixing for 2 min. The gas produced was allowed to escape. The test tube was kept in a water bath maintained at 27 °C. Seed solution, thus prepared, was used 2 h after the preparation. AuNR with I-SP at 700 nm were prepared similarly by mixing 19 mL CTAB (0.1 M), 1.2 mL HAuCl_4 (0.01 M), 0.12 mL AgNO_3 (0.01 M), 0.2 mL ascorbic acid (0.1 M) and 0.0012 mL seed solution. Shorter rods were prepared by oxidative shortening of an initial rod with I-SP at 700 nm, using H_2O_2 (50%) as the oxidizing agent [25]. The ratio between the H_2O_2 solution and the as-grown nanorod solution was ~1:5. The oxidation reaction was stopped at controlled periods of time by centrifugation at 12,000 rpm for 2–3 min and washing twice with DI water and finally dispersed in DI water. This oxidation process gave the other two AuNR samples with I-SP at 635 nm and 660 nm, matching the molecular absorption of NB ($\lambda_{\text{max}} = 635$ nm) and MB ($\lambda_{\text{max}} = 664$ nm) respectively.

2.3. PSS coating of nanorods

The as prepared rods have a monolayer of CTAB which is positively charged. To make them negatively charged, PSS (75 kDa) was laid on the positively charged rod making the overall surface charge negative for binding of the positively charged dyes. A 0.3% (by weight) PSS solution was made in water containing 6 mM NaCl and to it nanorod solution was added in 1:1 ratio and stirred for a minimum of 4 h. The excess PSS was removed by centrifuging and resuspending the pellet in DI water. The PSS coating of rod did not result in any shift of SPR bands. The PSS coating changed the zeta potential (measured using a 90 Plus size and zeta potential analyzer) of the rods from ~+50 mV to ~-45 mV.

2.4. Absorption and fluorescence spectroscopy

Absorption and fluorescence experiments were carried out in a cuvette of 1 cm path length. The absorption spectra of the

dye-nanorod complex were recorded after addition of a concentrated stock solution (typically few microliters) of dye to a 0.06 nM nanorod solution. The fluorescence spectra of the dye-nanorod complex were recorded after addition of a concentrated stock solution (typically few microliters) of nanorods to a 5 μM dye solution. The changes observed in the spectra after addition of dye was immediate and did not change with time during the experiments. Absorption spectra were monitored using a UV-Visible Spectrophotometer (GBC Cintra) having a resolution of 1 nm. Steady state and time resolved fluorescence measurements of the rod-dye complex was monitored using a Spex Fluorolog 2 Fluorimeter (resolution 4 nm) and time correlated single photon counting module Lifespec-RED from Edinburgh Instrument (response function ~50 ps), respectively. NB and MB were excited at 635 and 665 nm respectively for fluorescence emission measurements. The emission lifetimes of the dyes were obtained by excitation at 635 nm using a picosecond diode laser. The decays are recorded at magic angle. The data obtained is fitted to multi exponential models by FAST 6.0 data analysis software supplied by the manufacturer using an iterative reconvolution technique. The goodness of the fit was judged by the chi-square values and by visual inspection of the residuals. The lifetimes reported here are the average lifetimes (τ_f). The fluorescence quantum yields (Φ_f) of MB and NB in aqueous environment were taken from previous reports [31,32] and the relative quantum yield in the presence of AuNRs were calculated accordingly. The radiative (k_r) and non-radiative (k_{nr}) are calculated according to the relation: $k_r = \Phi_f/\tau_f$ and $k_{nr} = k_r - \Phi_f/k_r$.

3. Results

The normalized absorption spectra of the AuNRs along with the dyes MB and NB are shown in Fig. 1. AuNRs with average aspect ratio of 3.8 ± 0.2 , 3.5 ± 0.2 and 3.0 ± 0.1 had the I-SP peak centered at 730, 660 and 630 nm, respectively. The I-SP of AuNR at 630 nm, matches with the absorption of NB and the I-SP of another set of AuNR at 660 nm, matches with the absorption of MB while AuNRs having I-SP at 730 nm is detuned from the absorption band of both the dyes. The TEM images of the PSS coated AuNRs used in this study are provided in supporting information (Fig. S1).

3.1. Absorption properties of dye-AuNR systems

The changes observed in the absorption spectra of the PSS coated AuNRs upon gradual addition of MB and NB is shown in

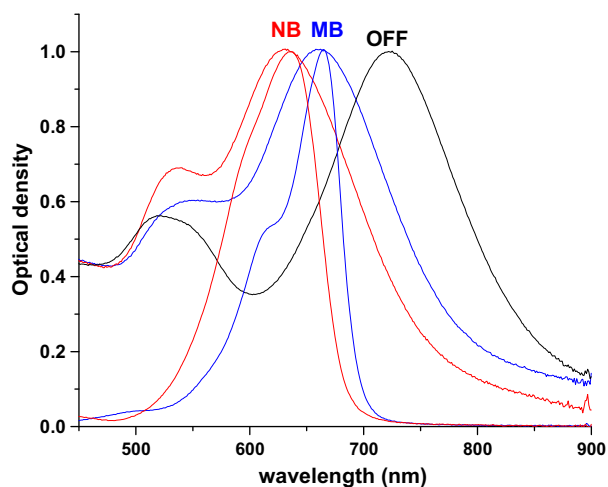


Fig. 1. Normalized absorption spectra of AuNRs used in this study along with the absorption spectra of MB and NB.

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