



Enhanced emission of Nile Red on plasmonic platforms

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ABSTRACT

Strongly enhanced fluorescence of Nile Red deposited in the vicinity of silver nanoparticles and gold semitransparent mirror was observed. The properties of three different plasmonic platforms based on TiO₂, TiO₂-GLYMO (1:1) and SiO₂ matrices were studied with spectroscopic and microscopic techniques. Significant differences of Nile Red spectroscopic properties in both matrices were observed. In particular, the sensitivity of Nile Red fluorescence enhancement and its peak location to the polarity of local surrounding was found.

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1. Introduction

Luminescence enhanced due to the interactions between fluorophores and surface plasmons induced on metal surfaces has been a subject of immense interest over last years [1–4]. This is due to many reasons like extremely sensitive detection of weakly fluorescent species, detection and following of some biochemical reactions, biomedical applications, construction of optoelectronic devices or probing excitation energy and proton transfer in nano-materials [4–16].

Nowadays, the emission enhancement is more and more frequently realized due to specifically designed plasmonic platforms. In the case of this study plasmonic platform was formed by silver nanoparticles deposited and arranged on partly transparent gold nanomirrors. Localized plasmons activated by light at the surface of nanoparticles interact with traveling plasmons at a conductive noble metal surface which leads to extremely strong local electric fields.

Due to the exposure to these high local electric fields fluorescent species deposited on the platform surface are excited with higher rate constant. Moreover, their emission intensity and brightness in

microscopic imaging of the probes is also significantly enhanced. These phenomena may be accompanied with the fluorescence lifetime decrease.

Nile Red belongs to those important fluorophores which are used effectively as molecular probes to study interactions between dye molecules and their local environment in numerous media like liquid solutions, Langmuir-Blodgett films, biological systems like DNA, membranes and tissues [17–23]. Luminescent properties of Nile Red have been also recently studied in selected materials like polymers, some sol-gel derived bulk matrices or laponites to name a few [24–28]. Due to its stability and spectroscopic sensitivity towards local polarity it may be considered as a promising base of organic part of various optoelectronic devices and lasers. It seems that selective solubility of Nile Red, high dependence of its quantum yield on the vicinal properties of the medium and solvatochromic spectral shifts may be used to obtain information on local polarity, local accumulation of dye molecules, their local concentration, aggregation or energy transfer processes at nano-scale. However, a lot if not the most information on these subjects for Nile Red is still missing or requires comprehensive collection and better understanding.

In this short paper we would like to report selected spectroscopic properties of Nile Red on sol-gel derived plasmonic platforms. In particular, the enhancement of Nile Red fluorescence due to the interactions with surface plasmons originating from silver

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nanoparticles and gold nanolayers on TiO₂ and SiO₂ based thin films will be presented.

2. Experimental part

2.1. Preparation of silver nanoparticles

All materials used to prepare silver nanoparticles were purchased from commercial sources and used without further treatment. Silver nitrate, AgNO₃ (99.99%); trisodium citrate dihydrate, (OH)C₃H₄(COONa)₃ × 2H₂O (99%) and borohydride NaBH₄ (98%) were bought from Aldrich Company. Deionized (DI) water was obtained from a Hydrolab system.

2.1.1. Preparation of small silver nanoparticles

The silver nanoparticles of 50 nm size were obtained through reduction of silver nitrate in aqueous solution in the presence of sodium borohydride to the developed procedure presented earlier [29]. First, the sodium borohydride was placed in an ice bath for 20 min. In the next step silver nitrate solution was added dropwise to a stirred, cold solution of NaBH₄. During this step, all solutions were mixed vigorously for about 15 min when the color changes evidently from colorless to yellow.

2.1.2. Preparation of large silver nanoparticles

The large silver nanoparticles (about 120 nm size) were obtained by the reduction of silver nitrate in aqueous solution in the presence of trisodium citrate to the procedure outlined earlier [30]. In the first step, the sodium citrate was added dropwise to a stirred solution of AgNO₃. Then, all solutions were mixed vigorously and heated up to 90–95 °C until change of color was evident (yellow). After that the mixture was incubated in ice bath for 15–20 min. Finally, the silver nanoparticles were purified by centrifugation at 3500 rpm for 8 min and the precipitate was suspended in 1 ml of 1 mM trisodium citrate.

2.2. Preparation of sols for thin films

The starting reagents for the preparation of sols to obtain the thin films on the plasmonic platforms were of analytical grade. Nile Red (NR) was spectroscopically pure and it was purchased from Aldrich (Germany). Tetramethyl orthosilicate (TMOS), titanium(IV) izopropoxide, 3-glycidyloxypropyl-trimethoxysilane (GLYMO), polyethylene glycol p-(11,33,-tetramethylbutyl)-phenyl ether (Triton X-100) and acetyloacetone were also purchased from Aldrich Company (Germany). Propan-2-ol, ethanol, methanol sodium hydroxide and hydrochloric acid were purchased from POCH Company (Poland). Deionized (DI) water was obtained from a Hydrolab system.

NR-TiO₂ – the precursor solution was obtained using titanium(IV) izopropoxide, propan-2-ol, acetyloacetone and Triton X-100. All components were mixed vigorously for 60 min. Than water and hydrochloric acid were added and mixed for 90 min. Separately, NR was dissolved in methanol and two solutions were mixed by vigorous stirring when 90 min elapsed.

NR-TiO₂-GLYMO (1:1) – the system was synthesized in a similar manner, as described above. In this case, 1:1 mixture of titanium(IV) izopropoxide and 3-glycidyloxypropyl-trimethoxysilane were mixed together with propan-2-ol, acetyloacetone and Triton X-100 for 5 min. Further activities were the same as during NR/TiO₂ preparation.

NR-SiO₂ – the precursor solution was obtained using TMOS and methanol, which were mixed by vigorous stirring for 15 min (it is very important to reach homogeneity of the solution). After a while Nile Red was dissolved in methanol and added to the precursor

solution. In order to initiate the sol-gel process an appropriate volume of water was added. However, three drops of sodium hydroxide as a catalyst were added to speed up the condensation reaction.

The final concentration of NR in the three sols was 10⁻⁴ M.

2.3. Preparation of plasmonic platforms

The plasmonic platforms were obtained according to the procedure outlined earlier [30]. In the first step, gold mirrors (Thin Metals Films Ltd. (UK)) were cleaned, drop coated with silver nanoparticles and dried in air atmosphere. After several days when a liquid from solution of silver nanoparticles was evaporated, different structures on gold mirrors were formed. In the next step, Nile Red in three different sols was applied on gold mirrors with silver nanoparticles using spin-coating method. The spin coating was done at 150 rpm for 45 s to disperse the sol after 60 min from the moment of mixing all of the components. A detailed procedure on thin films preparation can be found in our earlier work [31]. After that, the plasmonic platforms were allowed to dry in an air atmosphere for 24 h. It is worth to add, that, SiO₂ or TiO₂ layers protected the nanoparticles against the oxidation. The thickness of the layers used with Nile Red was about 150 nm (48 nm of gold layer plus the thickness of the matrix).

The graphical idea of the platform is shown in Scheme 1.

2.4. Apparatus

Fluorescence spectra were measured using a Carry Eclipse spectrofluorometer (Varian Inc., Australia) with the front face geometrical format. The emission was scanned from 550 nm to 800 nm upon excitation at 525 nm and using long pass filter on the emission side. The emission spectra were corrected for spectral sensitivity of the photomultiplier and polarization effects.

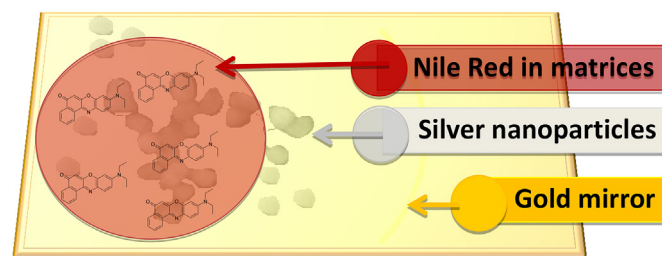
Fluorescence lifetimes of all the samples were obtained using especially designed pulsed spectrofluorometer described previously [6]. In this work as the excitation source we used Picoquant LDH510 laser diode emitting pulses at 510 nm of FWHM = 288 ps. The apparatus was configured in the front face mode.

To minimize polarization effects the fluorescence intensity decays were collected from the front side upon so called magic angle excitation (54.7° between the excitation beam and the normal to the sample surface).

Data analysis was performed with FluoFit 4.0 version software (Picoquant) using multiexponential intensity decay model as follows:

$$I(t) = \sum_{i=1}^n A_i \exp\left(-\frac{t}{\tau_i}\right) \quad (1)$$

where A_i is the amplitude of the fluorescence intensity decay of the i -th lifetime component τ_i .



Scheme 1. Scheme of plasmonic platform.

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