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Dual electrochemical modulation of reflectivity and luminescence on plasmonic gratings investigated by fluorescence microscopy coupled to electrochemistry

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ABSTRACT

By coupling fluorescence microscopy and electrochemistry at plasmonic electrodes, a first example of simultaneous dual electrochemical modulation of reflected light and luminescence is demonstrated through two examples of fluorophores: one switching by electrochemical reduction (tetrazine derivative) and the other switching by electrochemical oxidation (iridium complex). Opposite behaviors are observed: in the first case, reflected light interacting with plasmons is electrochemically tuned in the reverse way compared to luminescence, while in the latter case, both modulations go in the same direction. Discrimination between reflected light and fluorescence is obtained using an adequate set of excitation filters and backside optical detection. This dual modulation is observed either in direct (epifluorescence) or in total internal reflection (TIRF) excitation configurations.

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1. Introduction

Electrochemistry is a very convenient technique to monitor other phenomena, like light absorption in electrochromism [1], light emission in electrofluorochromism [2] or light extinction due to plasmon resonance [3]. In all these examples, a reversible switch of the associated property can be easily obtained using an electrochemical signal and devices based on one of this effect [4,5] or a combination of two like absorption and emission [6,7] have been already designed. However, the electrochemical monitoring of light absorption or emission through plasmonic systems is much less common. An example of an electrochromic system interacting with surface plasmon polaritons (SPP) has been recently published [8], highlighting the possibility to tune the optical transmission as the output either by electrochemistry as a first possible input or by plasmon as a second input. In the framework of light emission, many examples can be found of luminescence monitoring by interaction with plasmonic systems, either with colloidal nanoparticles [9] or metallic thin layers [10]. A field where plasmonic properties can be addressed electrochemically is surface plasmon resonance (SPR), a well-known configuration used to design sensors [11]. Coupling electrochemistry and SPR at an interface has been mainly performed in the Kretschmann configuration that is by exciting the plasmon associated to a very thin (a few nm) metallic (Au or Ag) layer by the evanescent wave associated to total internal reflection through a prism. In this configuration, the reflectivity is strongly affected by small changes in the refractive index of the surrounding medium of the metal, these changes being likely to be induced by an electrochemical signal. This modulation of reflectivity associated to SPR at given excitation angle is known as surface plasmon resonance imaging [12] and several examples of this modulation by electrochemical processes can be found in the literature [13,14]. Reciprocally Tao's group has evidenced that the SPR signal could be used to image the electrochemical current with a high spatial resolution and sensitivity [15]. More recently, other configurations have been envisaged, involving nanohole or nanodot arrays which can be excited directly by light and where the output signal is the transmitted light instead of the reflective one [16]. While delocalized propagating plasmons (typical features associated to SPP) are involved in nanometer size metallic layers, with nanodots or nanoholes localized surface plasmons (LSP) are concerned which can radiate on short distances [10]. These recent examples show that light intensity

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can be electrochemically tuned after interacting with plasmonic systems in various configurations (SPP or LSP) and several geometries for excitation and collection.

Nevertheless the electrochemical control of both the luminescence and the plasmonic properties in a single configuration at the same time appears to be a field where experimental results are scarce. An attempt in that direction was made with quantum dots attached to a gold plasmonic surface acting as the working electrode in an electrochemical configuration [17]. On our side, we recently published an investigation of the electrofluorochromic behavior of a dye in solution through a plasmonic electrode made of a gold nanodot array playing the role of a plasmonic grating [18]. Interestingly we found that the excitation light is strongly affected by the interaction with plasmon giving rise to inverted modulation compared to the one of luminescence. To investigate these phenomena, a coupling of fluorescence microscopy in TIRF configuration with an electrochemical cell was implemented [19,20]. This set-up allows the simultaneous record of the luminescence features with the electrochemical current when the potential of the microscope coverslip acting as the working electrode is modulated. Electron beam lithography (EBL) can be used to coat well ordered arrays of metallic nanoparticles of various shapes and sizes thus acting as plasmonic electrodes for the interaction with the fluorophore. An adequate choice of excitation and emission filters allows exciting selectively either the fluorophore or the plasmon or both and then recording the light resulting from these interactions. Thus discrimination between excitation and emission in the output light can be operated and the electrofluorochromic behavior analyzed depending on the interactions involved with the plasmonic electrode. The aim of this paper is to describe the results obtained in that framework, with two kinds of fluorophores: one which can be switched off by reduction (tetrazine derivative), the other which can be switched off by oxidation (iridium complex). In both cases, a dual modulation of reflected and emitted lights by the electrochemical signal has been observed, with either additive or opposite variations according to the type of dye.

2. Experimental section

The synthesis, electrochemical and photophysical features of the tetrazine used in the first part are described in ref. [21]. The maximum absorption and emission wavelengths are equal respectively to 516 and 563 nm. The synthesis, electrochemical and photophysical properties of the iridium complex used in the second part are described in ref. [22]. The maximum absorption and emission wavelengths are located respectively at 475 and 630 nm.

All the experiments are performed with a solution (concentrations typically between 0.1 and 0.7 mM) of the fluorophore in

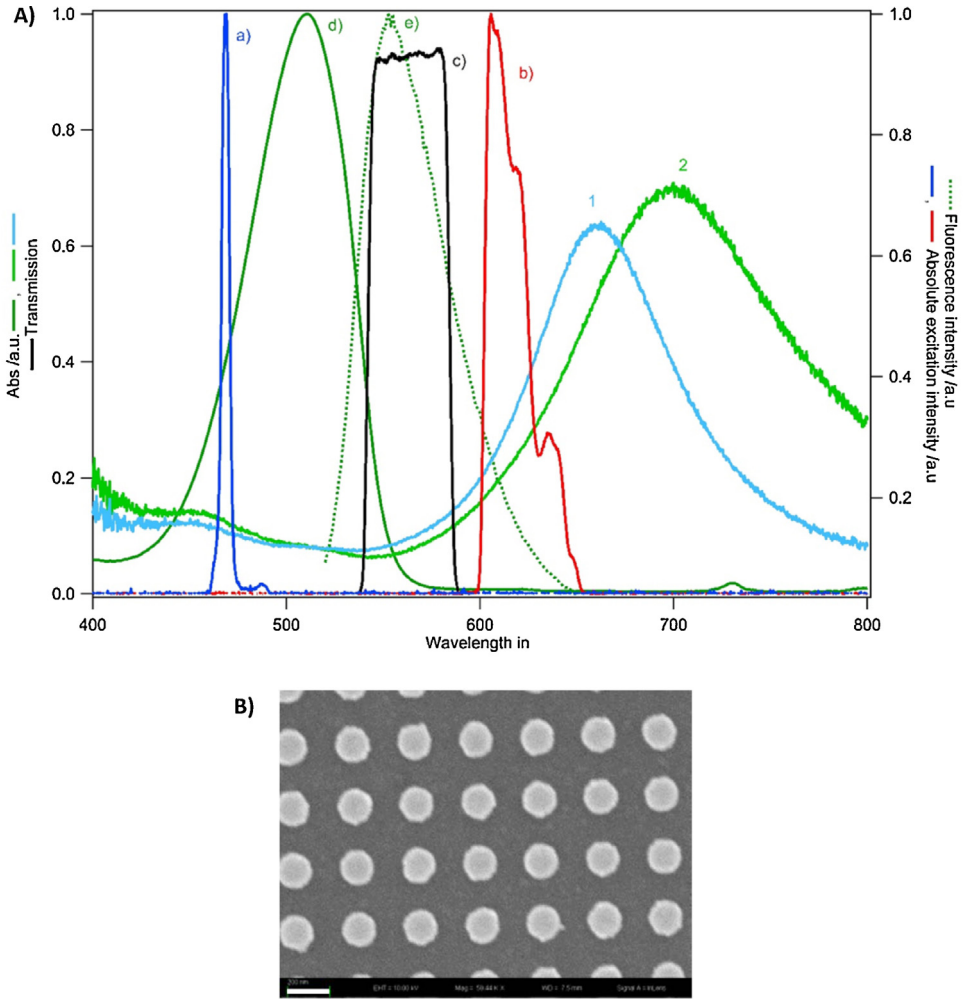

Fig. 1. A) Spectral features of the excitation light (a + b), and emission filter (black line, c) transmittance spectra overlaid with plasmon resonance bands of two investigated gratings (sky blue 1 and green 2). The absorption (green full line, d) and emission (dashed blue line, e) spectra of the tetrazine derivative are also overlaid. B) TEM picture of the grating (scale bar: 200 nm) showing the shape and size of gold nanodots.

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