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Fluorescence of polyaniline films on platinum surfaces. Influence of redox state and conductive domains

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Abstract

The photoluminescence of polyaniline films onto platinum electrodes has been studied as a function of the polymer oxidation state between the fully reduced (leucoemeraldine) and half oxidized (emeraldine) forms. The fluorescence emission spectra have been corrected for absorption and reflection from the underlying metal surface. From these results the quantum yield relative to the reduced state as a function of electrode potential has been obtained. This quantum yield is maximum for the reduced state and decays between ca. 0.3 and 0.4 V in the standard hydrogen electrode scale, reaching a minimum value. This behavior is interpreted in terms of three oxidation states: leucoemeraldine, intermediately oxidized protoemeraldine and emeraldine, each having different absorption and emission behavior. In the emeraldine form, the presence of conductive, quasi-crystalline domains is considered to fully quench emission from excitons located both inside the domains and within a range equal to the exciton delocalization length. A good agreement with the experimental data is found.

Keywords: Conducting polymer; Metal surface; Photoluminescence; Quantum yield; Quenching

1. Introduction

Conducting polymers show interesting optical properties (such as fluorescence, electrochromism, etc.) leading to a number of proposed applications such as sensors, displays and other optoelectronic devices [1–9]. Aryl amine polymers, such as polyaniline (PANI), show photoluminescence in their reduced state, which decreases when the polymer is oxidized [10–14]. Even when the quantum yield is small, the study of these properties is interesting because it will give insight into the electronic structure of these materials. There are few studies concerning the photoluminescence of PANI and similar polymers. Son et al. [10] studied the fluorescence quenching of PANI upon oxidation, and developed a simple model assuming that charge carriers (polarons) are responsible for quenching, allowing for overlapping between quenching centers. Thorne et al. [11] studied the time-resolved fluorescence of the reduced form of PANI, leucoemeraldine (LE), and explained the time decay curves as due to the diffusion in one dimension of randomly located traps, postulated to be short segments of the oxidized, emeraldine (EM), form of PANI. Ram et al. [12] applied fluorescence microscopy to study the ageing of PANI films in room atmosphere, and explained the observed decay in terms of a diffusion phenomenon. Recently [14] the fluorescent emission of PANI in different redox states was studied, measuring the quantum yield of the base forms of LE and EM in solution with *N*-methylpirrolidinone as solvent. The quantum yield for both forms were found to be $\phi_{\mathrm{LE}} = 1.2 \times 10^{-3}$ and $\phi_{\mathrm{EM}} = 1.0 \times 10^{-3}$. Also, the fluorescent behavior of PANI films supported on platinum electrodes was studied qualitatively; it was found a complex thickness dependence of the fluo-

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rescent emission, and a potential dependence similar to that previously reported [10].

The redox behavior of aryl amine polymers such as PANI is usually interpreted in terms of three redox states, the reduced leucoemeraldine, half oxidized emeraldine and fully oxidized pernigraniline, the conversions between them involving two-electron reactions [1–3,15–23]. The conversion between LE and EM (known as redox switching) is the most important because pernigraniline is unstable in aqueous solution. It involves an intermediate state, usually known as radical cation or polaron state, which shows unpaired spins in EPR measurements [24–26] and is often considered to be a transient one. However, one of the first studies on PANI chemistry [27] described it as a distinct, stable, oxidation state called protoemeraldine (PE), and recently it was also considered to be a stable state, explaining the temperature dependence of the PANI magnetic susceptibility in terms of the LE–PE–EM equilibrium [26]. More recently, the same scheme was successfully applied to explain the electrochemomechanical behavior of thick PANI films [28], considering the presence of a distribution of formal redox potentials for the PE to EM oxidation [29–31]. From a structural point of view, it has been proposed [32] and recently shown [33,34] that in the conductive (doped emeraldine) state, PANI films are actually composed of small, highly interacting, quasi-crystalline, conductive domains separated by low conductivity regions; it has been also proposed [35] that conduction is achieved through resonance tunneling between the conductive domains.

In this work the potential dependence of the relative quantum yield of PANI films supported on platinum electrodes is studied. The fluorescent emission is measured, corrected for absorption and the quantum yield, relative to the potential of maximum emission, is obtained. We will present first the correction procedure, then the experimental methods, afterwards the results will be discussed and finally the conclusions will be enumerated.

2. Relative quantum yield of films supported on metals

In the analysis of photoluminescence of solid films, it must be considered the absorption of both the excitation and emission beams by the film material in order to have quantitatively correct results. When a fluorescent film of thickness L, supported on a reflective surface, is irradiated with an excitation beam of intensity I_0 (of wavelength λ_0) there is, in principle, reflection of both the excitation and the emitted beams. Fig. 1 illustrates a volume element in the film in this situation. The emitted intensity measured at the detector I_m, at a given emission wavelength λ, will have two contributions: directly emitted I_{ed} and reflected I_{er}. Each of these two will in turn have two contributions: emission due to the direct excitation beam I_{0d} and that due to the reflected beam I_{0r}. In general absorption by the film will be present with extinction coefficients α_0 at λ_0 and α_e at λ. Considering the symmetry of the problem, it can be written for the total intensity at a given wavelength $\delta I_e(\lambda)$ emitted from a layer of thickness dx:

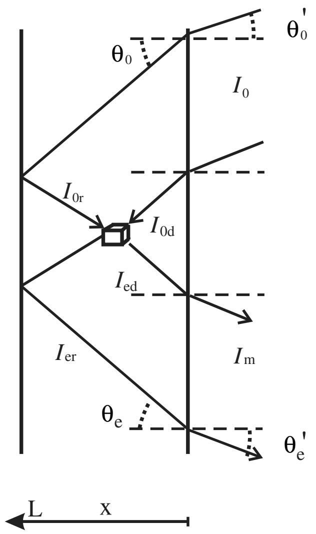

Fig. 1. Optical paths in the fluorescence of metal supported emitting films. See text for details.

$$\delta I_e = \varphi(\lambda) I_0 \left[\exp\left(-\frac{\alpha_0 x}{\cos\theta_0}\right) + f_0 \exp\left(-\frac{\alpha_0(2L-x)}{\cos\theta_0}\right)\right] n_c A\,\mathrm{d}x \tag{1}$$

where $\varphi(\lambda)$ is the fluorescent emission relative to I_0 at wavelength λ, f_0 is the metal reflectance at λ_0, n_c is the chromophore concentration and A is the area covered by the excitation beam. The intensity reaching the detector δI_m will be:

$$\delta I_m = \omega \delta I_e \left[\exp\left(-\frac{\alpha_e x}{\cos\theta_e}\right) + f_e \exp\left(-\frac{\alpha_e(2L-x)}{\cos\theta_e}\right)\right] \tag{2}$$

where ω is a geometrical factor depending on the instrument and f_e the metal reflectance at λ. The corrected emission intensity per unit thickness, $I_{m,c}$, can then be obtained after integrating over the film thickness, assuming that the quantum yield is independent of thickness, resulting in Eq. (3):

$$\begin{aligned} I_{m,c} = I_m \Bigg\{ & \frac{1}{\left(\frac{\alpha_0}{\cos\theta_0} + \frac{\alpha_e}{\cos\theta_e}\right)} \left[1 - \exp\left(-\frac{\alpha_0 L}{\cos\theta_0} - \frac{\alpha_e L}{\cos\theta_e}\right)\right] \\ & + \frac{f_e \exp\left(-\frac{2\alpha_e L}{\cos\theta_e}\right)}{\left(\frac{\alpha_0}{\cos\theta_0} - \frac{\alpha_e}{\cos\theta_e}\right)} \left[1 - \exp\left(-\frac{\alpha_0 L}{\cos\theta_0} + \frac{\alpha_e L}{\cos\theta_e}\right)\right] \\ & + \frac{f_0 \exp\left(-\frac{2\alpha_0 L}{\cos\theta_0}\right)}{\left(-\frac{\alpha_0}{\cos\theta_0} + \frac{\alpha_e}{\cos\theta_e}\right)} \left[1 - \exp\left(\frac{\alpha_0 L}{\cos\theta_0} - \frac{\alpha_e L}{\cos\theta_e}\right)\right] \\ & + \frac{f_0 f_e \exp\left(-\frac{2\alpha_0 L}{\cos\theta_0} - \frac{2\alpha_e L}{\cos\theta_e}\right)}{\left(\frac{\alpha_0}{\cos\theta_0} + \frac{\alpha_e}{\cos\theta_e}\right)} \left[\exp\left(\frac{\alpha_0 L}{\cos\theta_0} + \frac{\alpha_e L}{\cos\theta_e}\right) - 1\right] \Bigg\}^{-1} \end{aligned} \tag{3}$$