Hybrid films of fibroin-polyoxometalate for UVB sensors for monitoring by luminescence Eu^{III}

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Introduction: Phosphomolybdic acid (PMo, $H_3PMo_{12}O_{40}$) is a heteropolyoxometalate with Keggin geometry used in the determination of aromatic residues, such as tyrosine and tryptophan. In the presence of these residues, the PMo can be reduced by short-wave UVB light, which results in different colors for each oxidation state of Mo, i.e. yellow for Mo^{VI} and blue for Mo^{V}. Silk fibroin (SF) is a protein extracted from silkworm cocoons (*Bombyx mori*), composed by ≈5% of tyrosine and tryptophan comparing to the total aminoacid content. Photochromic, insoluble and transparent films based in SF and PMo were studied at this work. The reduction of PMo in the SF was induced under UVB light. Nanoparticles of $YVO_4:Eu^{III}$ displaying a strong red emission were also incorporated into the film. The transition of the oxidation states from $Mo^{VI} \rightarrow Mo^{V}$ in the SF/PMo films was monitored by the variation in the emission intensity of Eu^{III} as a function of the time exposure under UVB light.

Material and Methods: SF was extracted from silk threads of the silkworm cocoon as described by Rockwood et al.[1] The suspension of nanoparticles of YVO4: Eu^{III} was synthesized according with Huignard et al.[2] 3-glycidoxypropyltrimethoxysilane (GPTMS) was added to an aqueous solution of SF 4.5% (w/v) in a ratio of 80:20 (w/w). Afterwards, an aqueous solution of PMo 1.3% (w/v) and $YVO_4:Eu^{III}$ 10% (w/v) were introduced. The pH was adjusted to 5 with an aqueous solution of NaOH 0.5 M. The films were obtained by allowing the mixture to dry at 50 °C for 24 h. A delimited area of the films was exposed to a xenon lamp with λ = 290 nm and power of 0.89 mW for 1 min and 25 s.

Results and discussion: The films formed were insoluble in water and displayed a pale yellow color after drying. After the UVB exposure, the delimited area of the photochromic film showed an evolution of the color since greenish-yellow to blue. In Figure 1a, a decrease in transmittance of the films was observed in the 500-800 nm region due to charge transfer intervalence metal-metal $Mo^{V} \rightarrow Mo^{VI}$bands. It is suggested that the mechanism regards the UVB induced electron transfer from tyrosine and tryptophan residues of SF for the reduction of the PMO ($Mo^{VI} + e^{-} \rightarrow Mo^{V}$). As a result, it is observed in Figure 1b a decrease of the emission intensity at 621 nm corresponding to the $^5D_0 \rightarrow {}^7F_2$ transition of Eu^{III} as a function of the time exposure.

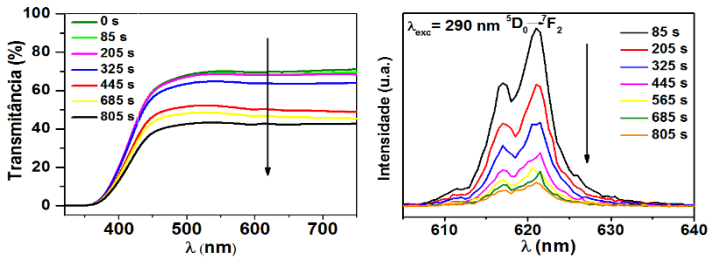

Figure 1. Transmittance (left) and emission spectra (right) of the films as a function of the UVB exposure time.

Conclusions: The luminescence technique offers a very sensitive tool for monitoring the UV light incidence effect in photochromic films of SF/GPTMS/PMo/$YVO_4:Eu^{III}$. The films might be interesting candidates for UVB light sensors by monitoring the luminescence of Eu^{III}.

[1] Rockwood, D. N.; Preda, R. C.; Yücel, T.; Wang, X.; Lovett, M. L.,Kaplan, D. L.; *Nat. Protoc*. **2011**, *6 (10)*, 1612.

[2] Huignard, A.; Buissette, V.; Franville, A. C.; Gacoin, T.; Boilot, J. P.; *J. Phys. Chem. B.* **2003**, *107 (28)*, 6754.

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