Photoactive nanoimpellers in sio$_2$ films for controlled drug delivery

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To control, in a non-invasive way, the delivery of drugs in organs affected by cancer or by neurodegenerative diseases is a major issue. It is important to carry the drugs and to release them just in the specific places where drugs are more effective against the diseases, in order to diminish harmful side effects in healthy tissues. The use of SiO_2 as drug carrier is very advantageous due to its chemical stability and its non-toxicity. The release of drugs controlled by light is a good way to deliver the drugs just in selected targeted areas because of its non-invasive nature [1]. We studied the photo-activation of molecular nanoimpellers attached to SiO_2 mesostructured films for the controlled release of drugs. It is convenient to study these systems in the form of transparent films because in this way the optical studies are easier and more confident than in other kinds of materials, even if the surface area of the films is less than the surface area of mesoporous SiO_2 nanoparticles [2].

In this work we studied SiO_2 mesoporous films functionalized with photoactive azobenzene molecules. The films are also doped with Rhodamine 6G molecules, which work as optical probes. The probe molecules are immersed in the pores of the films. The azobenzene molecules attached to the inorganic matrix photoisomerize under illumination, working as nanoimpellers because of their switching movement between trans and cis configurations [3]. The nanoimpellers constant movement under illumination promotes the release of the probe molecules to the environment.

We synthetized the films by the sol-gel method, using functionalized TetraEthylOrthoSilicate (TEOS) as precursor. The TEOS was functionalized with Disperse Red One (DR1) azobenzene molecules. The covalent linkage between both kinds of molecules was confirmed by Fourier Transform InfraRed (FTIR) spectroscopy.

The films were deposited on microscope slides by spin-coating. The mesoporous nature of the SiO_2 films was induced by the use of the CetylTrimethylAmmonium Bromide (CTAB) surfactant molecules during the gelation step of the synthesis. The pores in the films exhibited 1D-lamellar and 2D-hexagonal long-range nanometric order arrangement, with d-spacings equal to 3.3 nm and 4.5 nm respectively, as determined by X-Ray Diffraction (XRD) measurements.

Prior to introduce the Rhodamine 6G molecules inside the pores of the films, the CTAB was extracted from the films using an acidic ethanol solution. The absence of CTAB molecules in the SiO_2 films was confirmed by FTIR spectroscopy, and the presence of DR1 nanoimpellers in the films was confirmed by UV-visible spectroscopy. The UV-visible spectrum of the films showed a broad band centered at around 480 nm, this kind of band is characteristic of films functionalized with high loads of DR1 molecules [4].

The doping of the films with Rhodamine 6G molecules was made by impregnation. The doped films were illuminated with laser light at 532 nm in order to induce the photoisomerization of the DR1 molecules, with the films immersed in water. The DR1 movements due to photoisomerization caused the release of Rhodamine 6G molecules to the water. The relative amount of the released Rhodamine 6G molecules was determined from measurements of their photoluminescence emission intensity at 570 nm as function of the pumping time. The pumping light was at 532 nm. The same wavelength was used to photoisomerize the DR1 molecules and to induce photoluminescence in the released probe molecules. The results were compared with those obtained in darkness for a doped film, in order to determine the efficiency of the photo-activated nanoimpellers.

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References

[1] Lu J., Choi E., Tamanoi F., Zink J. I. Small **4** (2008) 421.
[2] Suh M., Lee H. J., Park J. Y., Lee U. H., Kwon Y. U., Kim D. J. ChemPhysChem **9** (2008) 1402.
[3] Marino I. G., Delmonte D., Pessini F., Lottici P. P., Cristofolini L., García-Macedo J., Franco A., Valverde-Aguilar G. J. Opt. Soc. Am. B **26** (2009) 384.
[4] Priimagi A., Cattaneo S., Ras R. H. A., Valkama S., Ikkala O., Kauranen M. Chem. Mater. **17** (2005) 5798.

Figures

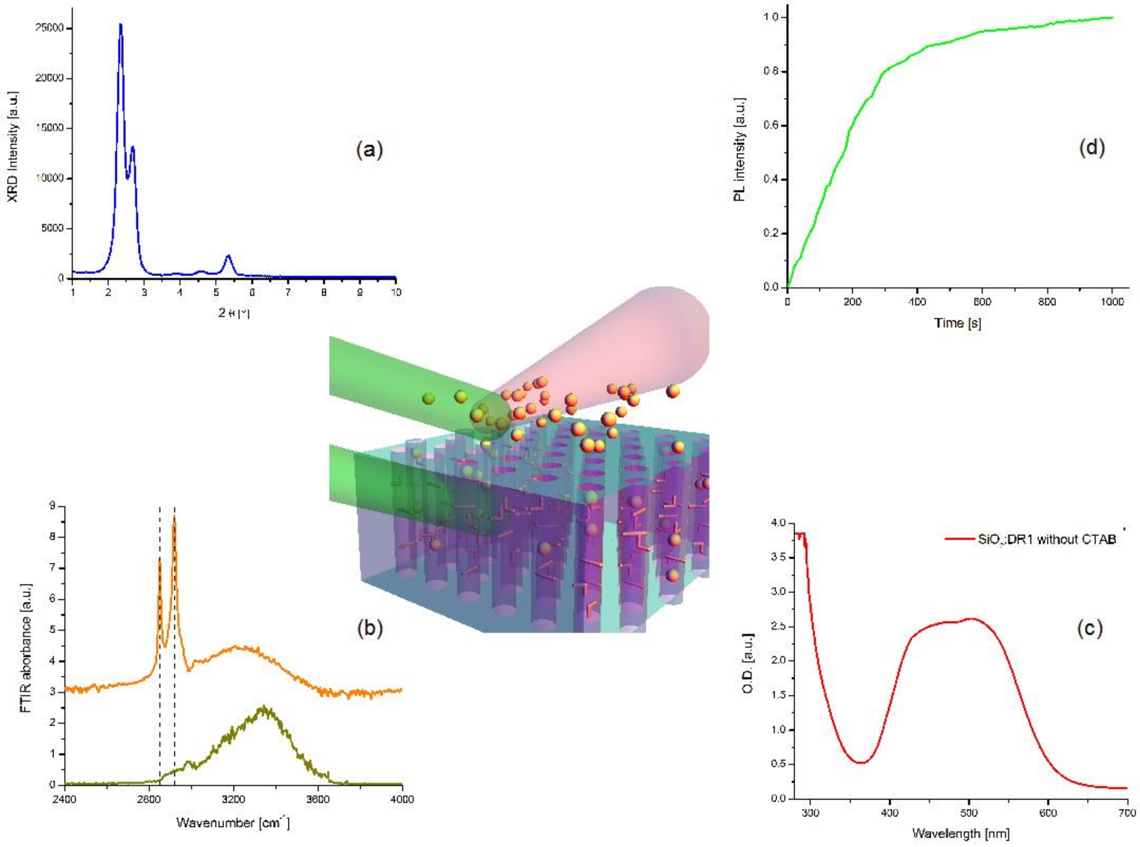

Figure 1. Scheme of a dye doped mesoporous SiO_2 film functionalized with photoactive nanoimpellers. The porous of the film exhibit a periodic ordered arrangement with constant nanometric spacings, as the X ray diffraction pattern of the inset (a) shows. The film is also free of surfactant molecules as the FTIR spectra of the inset (b) make evident. The inset (c) is the UV-visible absorbance spectrum of the film, its shape reveals a high concentration of photoisomerizable molecules. The photoisomerizable molecules are represented by straight (trans configuration) and bent (cis configuration) red tubes inside the pores. The inset (d) shows a typical photoluminescence curve, due to the released dyes, as function of the pumping time. In the scheme, the dyes are represented by orange spheres, the pumping light is represented by the green beams and the luminescent light by the pink one.