Tuning of the photophysical properties of core-shell silica nanoparticles for bio-imaging and photodynamic therapy

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Abstract Spherical core-shell silica NPs with an external surface functionalized by amino groups and with an optimal average size around 50 nm, suitable for biomedical applications, have been successfully synthesized by a Stöber-modified method.[1] An optimization of the properties of fluorescent dye embedded in their core and of various photosensitizers (PS) grafted on the shell was carried out. By the encapsulation of fluorescent Rhodamines in the core at an optimal concentration to limit reabsorption, relatively high fluorescence quantum yields ($\phi_{fl} \geq 0.3$) were obtained, which allowed their tracking by fluorescence microscopy techniques and improved the time scale for detection due to the increase of dye photostability. A careful investigation of the stability of NPs suspensions showed a strong modification upon grafting of the PS. By covalent grafting of original lab-made halogenated 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (BODIPY) photosensitizers to the external shell of silica, good singlet oxygen quantum yields (Φ_Δ ~ 0.35-0.40) were obtained in ACN and chloroform solvents. Such quantum yields are globally much higher than those of similar NPs using grafted Rose Bengal (RB) as PS (Φ_Δ ~ 0.10-0.27). The resultant singlet oxygen quantum yields were related to the agglomeration of NPs, which depends both on the type of photosensitizer and on the amount of grafted PS. Finally, by the combination of two chromophores with overlapping absorption bands and complementary actions, namely a rhodamine with high fluorescence efficiency in the silica core and a BODIPY or RB with a high singlet oxygen quantum yield grafted on the shell, NPs with dual functionality were characterized (ϕ_{fl} ~ 0.10-0.20, Φ_Δ ~ 0.16-0.25), opening the route for theranostics (bioimaging and PDT).[2] Accordingly, by proper choice of the dyes, of their concentration inside and onto the NPs and of their grafting method, fine-tuning of singlet oxygen production and fluorescence emission is made possible. Further experiments will be soon carried out to improve the stability of the NP in polar solvents, and particularly in aqueous suspension, in order to be able to design "in vitro" phototoxicity experiments.

References

[1] W. Si-Han, M. Chung-Yuan and L. Hong-Ping, Chem. Soc. Rev., 42 (2013) 3862-3875
[2] Nerea Epelde-Elezcano, Ruth Prieto-Montero, Virginia Martínez-Martínez, María J. Ortiz, Alejandro Prieto-Castañeda, Eduardo Peña-Cabrera, José L. Belmonte-Vázquez, Iñigo López-Arbeloa, Ross Brown and Sylvie Lacombe (Submitted)

Figures

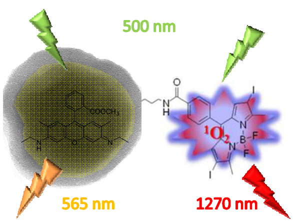

Figure 1: Schematic illustration of Silica nanoparticles with fluorescent Rhodamine embedded in the core and BODIPY photosensitizer grafted on the shell, generating fluorescence emission and singlet oxygen, respectively, under green excitation light