Nanoimaging: photophysical/ technological characterization of PLGA nanoparticles engineered with Quantum Dots

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Purpose: In this research we aimed to functionalize polymeric nanoparticles (NPs) with quantum dots (QDs) by means of two different formulation procedure and to characterize the polymer/QDs architecture by assessing their chemico-physical, morphological and photophysical features. We tried also to establish if a quenching phenomena caused by the "packaging" of QDs in a polymeric matrix and the recovery of their fluorescence after reverting polymer in the linear form could exist.

Methods: NPs were obtained in accordance with the nanoprecipitation procedure and in particular we achieved two different QDs-modified NPs typologies (pre-formulation and post-formulation). Nanoprecipitation of PLGA and PLGA-PEG-QDs mixture in organic solvent produced PRE-FORMULATION QDs-MODIFIED NPs (PLGA-PEG-QDs was previously synthesized starting from PLGA503H with EDC-NHS technology) while reaction between preformed PLGA- NPs and the amino-group of QDs-PEG-NH_2 produced POST-FORMULATION QDs-MODIFIED NPs. Size, z-potential (ζ-pot), morphological (SEM, AFM, TEM) and photophysical [confocal microscopy, fluorescence lifetime imaging microscopy (FLIM)] analysis of all the samples were performed.

Results: The most significant differences between the two categories of QDs-modified NPs consisted in their inner structure and in the maintenance or loss/shift of emission signals. In particular, POST-FORMULATION QDs-MODIFIED NPs, which exhibits QDs anchored onto the NPs surface level, maintained those photo-physical characteristics peculiar of QDs (brilliant color under UV exposition and identical emission spectra), demonstrating the successful and the feasibility of surface modification. On the other hand, PRE-FORMULATION QDs-MODIFIED NPs showed an "un-usual" morphological aspect, also revealing uncommon photo-physical behaviors. These observations can be explained by the different polymeric environment inducing "defects" in QDs-PEG-NH2 surface or, somehow ,decreasing the quantum yields of free QDs-PEG-NH2.

Conclusions: These findings evidenced for the first time the importance of considering polymeric influence using QDs probe and may induce a new way for different NPs characterization by

analyzing QD fluorescence spectrum. NPs labeled with QDs, if safe and properly characterized, can represent useful tools for treatment, diagnosis and monitoring of biological systems and dynamics.