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Surfactant-Free Conjugated Polymer Based Nanoparticles as Smart Photoactive Bio-Interfaces

F. Gobbo,[a,b] I. Abdel Aziz,[a,b] C. Bellacanzone,[a] S. Zappia,[c] M. Diterlizzi,[c] A. M. Ferretti,[c] S. Destri,[c] M. R. Antognazza[a]

[a] *Center for Nano Science and Technology@PoliMi, Istituto Italiano di Tecnologia, Milan, Italy*
[b] *Dipartimento di Fisica, Politecnico di Milano, Milan, Italy*
[c] *CNR-Istituto per lo Studio delle Macromolecole, Milan, Italy*
federico.gobbo@iit.it

Conjugated polymers are emerging as optimal candidates for bio-interfaces, because they are highly biocompatible and they can combine the chemical and mechanical advantages of organic materials with the peculiar optoelectronic properties of semiconductors. Their properties can be easily tuned by proper chemical synthesis, adopting different backbone structures or combining different polymers. In form of nanoparticles (NPs), they can be internalized inside cells and provide a remarkable spatial resolution. They can be prepared in water based solution and in sterile condition, suitable for biological applications. They show high brightness and they are mainly employed for in vivo and in vitro imaging or for drug delivery applications. Only very recently they started to be used as photo-transducers in order to optically modulate living cells activity with reversibility, high selectivity and spatio-temporal resolution, avoiding optogenetic tools [1]. Some recent works have demonstrated their reliability in the modulation of cellular metabolism [2] and even animal behavior [3].
We report on the fabrication and the optoelectronic characterization of biocompatible, low band-gap semiconducting polymer nanoparticles, based on poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b]dithiophene)-alt-4,7(2,1,3-benzothiadiazole)] (PCPDTBT), a polymer extensively studied in bulk heterojunction solar cells as electron donor material. The absorption and emission spectra are located in the far red region of the visible spectrum and in the near infrared (NIR), respectively; at these wavelengths the auto fluorescence of biological matter is lower and the tissue penetration is higher, therefore these NPs are strongly appealing for potential in vivo applications. We synthetized the NPs, through the miniemulsion method, starting from an amphiphilic rod-coil block copolymer composed of PCPDTBT as the rigid block, while the coil segment consists in a short chain of poly-4-vinylpyridine. The latter is hydrophilic and therefore allows to fabricate NPs based on a hydrophobic polymer avoiding the need of surfactant. We also synthetized NPs starting from the pristine PCPDTBT adding a surfactant, polyvinyl alcohol, to investigate the effects of the presence of a surfactant on the optoelectronic properties of the material. NPs were prepared in water, they can be lyophilized and they show excellent colloidal stability. The nano-dimensions of the polymer beads are confirmed by dynamic light scattering measurements and scanning electron microscopy images. Upon illumination with visible light in the correspondence of the absorption peak, NPs dispersed in water generate a photocurrent signal, and the latter has a larger amplitude in case of surfactant free NPs. Also the photoinduced absorption spectroscopy measurements, performed on NPs dispersed in water, show that, in case of surfactant free NPs, the amplitude of the signal attributed to charged states is higher. Thus, the presence of the surfactant limits the capability of the NPs to photo-generate charges.
Secondary line cell models (Human Embryonic Kidney cells, HEK-293) have been treated with NPs. Both the NPs with and without the surfactant internalize within the cell cytosol, without negatively affecting proliferation. The functional interaction between living cells and polymer beads upon optical excitation has been studied by fluorescence imaging experiments. In case of surfactant free NPs, the photo-electrochemical activity of NPs generates intracellular Reactive Oxygen Species (ROS), at non toxic levels. We observed that the polymer beads are internalized also in more significant cellular model, as rat cortical neurons, without exhibiting cytotoxic effects. ROS regulate different biological functions as signal transduction, blood pressure modulation, immune system control and metabolism regulation; alteration in their concentration might lead to pathological conditions as autoimmune, cardiovascular and neurodegenerative diseases [4]. Therefore, the capability of polymer NPs to optically modulate ROS balance by on-demand illumination might open the path for studying biological processes with a minimally invasive procedure and with unprecedented spatiotemporal resolution, laying the foundation for developing novel therapeutic approaches.

References

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