Surfactant-free miniemulsion approach for low band gap rod-coil BCP water-processable nanoparticles: synthesis, characterization and application.

D2. Microscopy at the Forefront of Nanostructured Materials Characterization and Correlation with Modelling

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Introduction/Purpose

The assembly of hydrophobic conjugate polymers into water-processable nanoparticles (WPNP) is a new technology with a large number of applications in optoelectronics, biology, and medicine. We based our studied on four amphiphilic low band gap rod-coil block copolymers (BCPs) composed by a rigid hydrophobic p-type semiconductor polymer, PCPDTBT, and 4-vinylpyridine-based (4VP-based) coil block that interacts with water and has different molecular structure and length for each BCP used. The insertion of polar tailored segment in the polymeric backbone prevents the surfactant addition during the aqueous nanoparticle fabrication

Methods

Stable in water WPNS were synthesized by mean a surfactant-free miniemulsion approach, thanks to the presence of the coil block in the BPC backbone, that stabilizes the nanostructure. The BPC with five 4VP repeating units was mixed with an electron acceptor fullerene derivative ([6,6]-phenyl-C61-butyric acid methyl ester, $PC_{61}BM$) to achieve blend WPNPs. The WPNPs and b-WPNPs were fully characterized by TEM, STEM-EDX, EFTEM, AFM, and DLS in order to clarify the influence of the 4VP-based coil blocks on the WPNP morphology and stability, and to identify where the PCBM is located in the b-WPNP.

Results

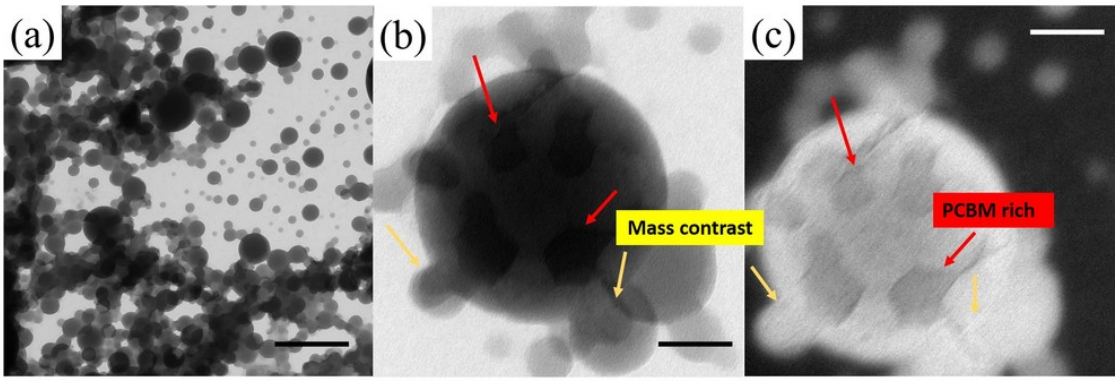
The morphological characterization confirmed the WPNP spherical shape. The STEM-EDX analysis revealed the WPNP internal composition, in particular, that the rod blocks, rich in sulfur, aggregates mainly in the core of the WPNPs, while the 4VP-based coil tends to locate on the edge.
The EFTEM images of the b-WPNPS showed the presence of PCBM rich insiede them.

Conclusions

We developed a new surfactant-free approach to prepare BCP-based WPNPs in aqueous suspensions using amphiphilic low band gap rod-coil BCP, thus avoiding purification steps and obtaining a more sustainable process. B-WPNP were applied as active layer in working organic solar cells fabricated through sustainable processing (PCE 2.5%).

Selected references

[1] S. Zappia, G. Scavia, A. M. Ferretti, U. Giovanella, V. Vohra, S. Destr *Adv. Sustainable Syst.* **2018,** 1700155 DOI: 10.1002/adsu.201700155. [2] A.M. Ferretti, S. Zappia, G. Scavia, U. Giovanella, F. Villafiorita-Monteleone, S. Destri, *Polymer*,**2019** under revision



TEM images of the a) BCP5:PC61BM (1:3) blend NPs, b) detail of one blend nanostructure, and c) corresponding EFTEM image where it is evident a difference in contrast between the PCBM rich zone (the darker area highlighted bye the red arrows) and the others.. The scale bars are (a) 500 nm and (b,c) 50 nm, respectively.