

ABSTRACT

Polymer-inorganic hybrid materials offer exciting opportunities as they can exhibit promising properties from both the constituents that are desirable for applications such as sensors, composites, catalysis, energy conversion/storage etc. The self-assembly of block copolymer (BCP) has been one of the fascinating approaches to direct the assembly of inorganic nanoparticles (NPs) for the fabrication of such hybrid materials with well-defined morphologies. In the present work, we demonstrate the self-assembly approach to direct the assembly of quantum dots (QDs) into organized structures. It was further demonstrated that self-assembled morphologies of block copolymer could also be used to obtain isolated photoluminescent core-shell hybrid nano-objects *via* selective solvent approach.

The first part of the present study mostly focussed on the fundamental study on the self-assembly behavior of BCP/QDs hybrids. This involved the investigation on the localization of QDs within the self-assembled structure of BCPs and the effect of QDs *vis-à-vis* its size, shape and surface chemistry on the BCP self-assembly. The cylinder-forming PS-*b*-P4VP block copolymer mixed with TOPO capped CdSe quantum dots of diameter ~3.8 nm was investigated. It was found that quantum dots were enthalpically compatible with P4VP chains *via* ligand displacement of TOPO from the QD surface. However, the QDs were found to localize preferentially at the PS/P4VP interphase plausibly to gain translational entropy in order to further lower the energetics of the self-assembled structure. Interestingly, morphological transformation was observed with increasing weight fraction of the QDs, in the BCP/QD composites, which was driven by the migration of the displaced TOPO from QD surface to the PS phase, effectively raising its total volume fraction. Hence, the PS-*b*-P4VP BCP with PS as the minority block displayed lamellar morphology in its composite with QDs. Most interestingly, it was found that after addition of TOPO capped QDs of diameter ~7.4 nm, the BCP morphology transformed to the perforated lamellar (PL) morphology. Moreover, the QDs were exclusively localized within the P4VP perforations. This is one of the first such observation in the bulk BCP/nanoparticle hybrid systems and the formation of PL morphology was attributed to the alleviation of chain packing frustration after localization of the QDs in the P4VP perforations.

Additionally, to incorporate the quantum dots in the PS phase, QDs were stabilized by thiol terminated PS oligomer *via* ligand displacement approach. It was found that PS-stabilized QDs

also localized in the P4VP phase, driven *via* ligand-displacement of the PS-SH from the QD surface as observed with TOPO coated QDs. This was because of the fact that both TOPO and PS-SH ligands form co-ordinate bond with QD surface and, hence, P4VP was effective, as a multidentate ligand, in displacing them from QD surface. This revealed that the thiol chemistry for binding ligands to QDs behave very differently than that in metallic nanoparticles. Apart from this, self-assembly approach was further used to incorporate anisotropic semiconducting nanoparticles such as nanoplatelets and nanorods with the same surface chemistry, as in QDs, within the self-assembled structure of BCP. It was observed that both nanorods and nanoplates macrophase separated, plausibly due to the stronger inter-rod/inter-platelet interactions in comparison to interaction between P4VP block and ligand bound to the particles surface.

In the second part of this research, the approach was extended to fabricate multifunctional nano-objects by adding second targeted functionality i.e. sulforhodamine 101(S101) during the BCP/QD self-assembly. The organization of two different functionalities within the confined space of the self-organized BCP domains enabled them to localize at distances comparable to their Förster radius enabling an efficient fluorescence resonance energy transfer (FRET) between them. There was a reduction in the mean lifetime and PL quenching of CdSe QDs in the presence of S101 dye, which showed effective energy transfer from donor CdSe QDs to acceptor S101 dye molecules. Similarly, another targeted functionality i.e. Au NPs were also used to fabricate multi-functional nano-objects. The confinement imposed by the nanometer-sized cylindrical core resulted in the localization of the CdSe QDs and Au NPs in close proximity. It was found that photoluminescence properties of QDs could be manipulated by changing the concentration of Au NPs while keeping QDs constant within the nano-dimension geometry of the fibers obtained via self-assembly process of PS-*b*-P4VP BCP. Interestingly, it was observed that PL intensity of CdSe QDs increased at very low weight ratio of Au NPs. On further increasing the amount of Au NPs, the PL intensity decreased and then completely diminished at high ratios.

The present research not only provides fundamental information on the self-assembly behavior of BCP/QD hybrid systems but also has importance for developing nanostructured materials for potential application in sensing, bio-imaging, and functional optoelectronic devices.