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FUNCTIONAL NANOCOMPOSITES FROM SELF-ASSEMBLY OF BLOCK COPOLYMERS WITH NANOPARTICLES

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Abstract
This dissertation studied the proper distribution and location control of nanoparticles (NPs) within block copolymer (BCP) templates. A facile ligand exchange reaction was introduced for the hydrophilic magnetic NPs (MNPs) that are readily dispersed in polar solvents with outstanding stability. Small molecule ligands were selected to associate strongly with particle surfaces, provide hydrophilic termini for polarity matching with polar solvents, and offer the potential for hydrogen-bonding interactions to facilitate NP incorporation into polymers. Areal ligand densities of NPs indicated a significant increase in the ligand coverage after the exchange reaction.

Hydrophilic MNPs were shown to drive the self-assembly of BCPs via favorable H-bonding interactions between the NP and hydrophilic polymer domains, leading to enhanced segregation strength and long-range order of the nanocomposites. Extremely high loadings of NPs were selectively confined within the target domain with no macrophase separation observed. Polymer domain width (*L*) and maximum incorporated NP size (*d*) were correlated to reveal much higher *d/L* ratios for blends with favorable interactions. In addition, FePt NPs were confined in the hydrophobic domain or at the interface by using polystyrene as the ligand.

Progressively, magneto-dielectric metamaterials were fabricated in a bottom-up fashion by using orthogonal interactions (H-bonding and π-π stacking) from block copolymer/NP self-assembly, with MNPs and dielectric NPs (DNP). The spatial distribution of DNPs in the BCP template were controlled by the use of additives and surface modification of DNPs.

Finally, BCP/MNP nanocomposites were used to fabricate functional materials. First, the vertical ordering of BCP/MNP thin films were improved, taking advantage of the tendency of MNPs aligning to form lines in the direction of an external magnetic field. Second, ordered mesoporous carbon/iron oxide composites were achieved by cooperative self-assembly of PtBA-*b*-PAN block copolymers with iron oxide NPs followed by carbonization. The resulting electrode material exhibit high specific surface areas and pore volumes that contribute to an over 50% increase in the specific capacitance upon NP loading. Third, mesoporous silica/MNP composites containing high concentrations of NPs within the silica walls was presented via $scCO_2$ infusion of TEOS, which can potentially be used at the catalyst for carbon nanotube growth.