

## Structured Organic-Inorganic Hybrids Prepared Through Block Copolymer-Metal Complexation

Organic–inorganic hybrid (OIH) nanomaterials are an important class of functional materials that find applications in advanced batteries, where these nanohybrids improve efficiency and lifespan by enhancing the physical and chemical properties at the nanoscale as well as their applications in drug delivery systems, where these hybrids can be used to create targeted and controlled release mechanisms for therapeutic agents.

Hybrid nanomaterials are commonly synthesized through post-polymerization self-assembly techniques, which involve several steps, including block copolymers synthesis, associating guest molecules in a suitable solvent, and triggering the self-assembly of the block copolymers. A key limitation of this approach is the low product concentration (<1 wt%) and the multi-step nature of the process, which complicates scale-up. In recent years, the one-pot polymerization-induced self-assembly (PISA) method has been developed, allowing for the production of block copolymer nanomaterials with higher concentrations (10–50% w/w solids) and diverse morphologies such as spheres, worms, vesicles, and nanotubes. However, despite these advantages, the synthesis of organic-inorganic hybrid nanomaterials via PISA is not without challenges. For instance, achieving precise control over polymer chain length, composition, and architecture is crucial to directing the self-assembly process. The reactions often require fine-tuning of conditions such as monomer concentration, solvent composition, temperature, and initiator type, all of which significantly impact the resulting morphology.

Polymers such as polyvinylpyridines (PVPs) have been extensively investigated for their ability to form coordination bonds through the lone pairs on the nitrogen atoms of the pyridine rings, which rapidly interacts with various inorganic precursors. In our approach to synthesizing organic-inorganic hybrid (OIH) nanomaterials, we utilize coordination chemistry through block copolymer complexation. Specifically, we introduce an inorganic precursor, such as trichlorosilane, into a solution of block copolymers like polystyrene-*b*-poly(4-vinylpyridine) (PS-*b*-P4VP). The precursor selectively interacts with the P4VP block via  $\pi$  interactions, promoting chain crosslinking and resulting in the formation of assembled nanostructures. A key insight in our project is that structural variation is not solely governed by changes in the volume fraction of the block copolymer components but can also be finely tuned by altering the concentration of the block copolymer solution. Typically, block copolymer morphology is influenced by the relative volume fractions of the blocks, with different ratios leading to distinct nanostructures such as spheres, cylinders, or vesicles. However, our work demonstrates that even with a fixed volume fraction, the concentration of the block copolymer solution alone can dramatically affect the resulting morphology. We demonstrate that, at higher solution concentrations, the system favors the formation of large worm-like vesicles, which likely arises from chain aggregation in the confined concentrated environment. Conversely, at lower concentrations, we observe a shift towards the formation of discrete nanoparticles. This is likely due to the polymer chains having less kinetic constraints allowing them to self-assemble into compact, stable structures that minimize surface energy.

Advanced characterization techniques, including transmission electron microscopy (TEM) and atomic force microscopy (AFM), are employed to probe the morphology and structural properties of these OIH nanomaterials. In sum, by systematically altering the block copolymer composition and concentration we gain insight into the tunability of the self-assembled nanostructures, enabling the design of materials with specific properties for targeted applications.