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Nanoparticle templating by block copolymer micelles: how polymer self-assembly controls nanoparticle size and substructure

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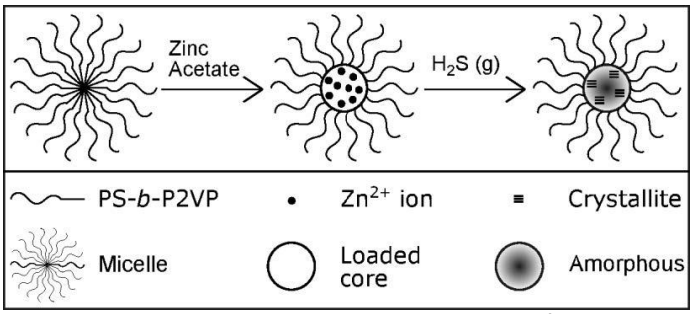
Block ionomer micelles have been widely used to generate self-assembled nanomaterials with precisely-tuned regularly-spaced nanoparticles, with applications across biological physics, optics and magnetism[1–3]. One of the most popular block copolymer systems used for nanoparticle synthesis is that of poly(styrene)-*block*-poly(2-vinyl pyridine) (PS-*b*-P2VP), which forms spherical micelles when dissolved in an aromatic solvent. The size of the formed micelles is controlled by tailoring the lengths of the individual polymer chains, while the ability of the polar core of the micelle to form complexes with metal ions allows for the production of a variety of nanoparticles with controlled diameters. Along with elemental nanoparticles such as gold[4], oxides of iron[5], zinc[6] and titanium[7] have also been formed. However, despite its wide application as a template for nanoparticle synthesis, the mechanism of nanoparticle growth within the PS-*b*-P2VP core is not well understood. In particular there is a lack of direct *in situ* characterisation of the transition between metal-loaded micelle and the final nanoparticle, which is a complex, system-dependent process.

We present herein, for the first time, the application of BCMs as templates for the synthesis of zinc sulfide (ZnS) nanoparticles with a unique composite nanocrystal substructure consisting of small crystallites existing within a larger amorphous organic-inorganic matrix. Through a combination of advanced characterization techniques, including high resolution analytical transmission electron microscopy (ATEM) and solution-phase small-angle X-ray scattering SAXS, we identify a distinctive pathway for nanoparticle formation: Zn^{2+} ions are distributed throughout the micelle core, which solidifies as a unit upon sulfidation. In this way, the overall size of the nanoparticle is found to be determined directly by the size of the original micelle core. We contrast this with measurements of the better-known synthesis of gold nanoparticles in identical polymer micelles, where the forming nanoparticle condenses out of the core, with its size controlled purely by the amount of metallic precursor.



Scheme 1. Schematic showing the mechanism of ZnS nanoparticle synthesis: 1) Zn^{2+} ion encapsulation within core of micelles, 2) Treatment with H2S generated *in-situ* and 3) Formation of single ZnS nanoparticle with composite sub-structure in core of micelles

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