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Synthesis and Characterization of Organometallic Coordination Polymer Nanoshells of Prussian Blue Using Miniemulsion Periphery Polymerization (MEPP)

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The preparation of organometallic coordination polymer nanoshells is challenging, although the synthesis of metallopolymer in various nanostructures has been explored intensively.¹ Since Mann and his co-workers synthesized nanoparticles (NPs) of cyanometallate coordination polymers of Prussian blue (PB) using reverse micelles for the first time,² a number of materials including polymers, biospecies, and silica have been used as media to confine the growth of the particles for the synthesis.³ In contrast, efforts to vary PB NPs from solid spheres to other nanoshapes are limited despite its importance in the context of nanoscience and material applications.⁴ Talham and his co-workers have prepared two-dimensional PB analogues at the air–water interface using Langmuir–Blodgett techniques.^{5a} Stigman has produced nanocrystalline rods and disks of PB analogues in a silica matrix.^{5b} Porous alumina templates were used to prepare one-dimensional PB nanostructures.^{5c,d} But, to the best of our knowledge, there is no report on the preparation of PB nanoshells. Herein, we report a conceptually new method for the synthesis of PB nanoshells with tunable size using miniemulsion periphery polymerization (MEPP). As shown in Scheme 1, MEPP involves the preparation of miniemulsion droplets using organometallic surfactants, followed by a coordination polymerization at the periphery of the droplets. We also discovered that the resulting shell structure substantially improved the thermal stability of the polymers.

In a typical experiment, miniemulsion droplets with a pentacyanoferrate periphery were prepared from a mixture of water, an organometallic surfactant of poly(ethylene glycol)-*b*-poly(propylene glycol)-*b*-poly(ethylene glycol) terminated with pentacyano(4-(dimethylamino)pyridine)ferrate (EPE-Fe), toluene, and hexadecane (water/EPE-Fe/toluene/HD = 90.8:4:5:0.2 by weight). Upon the addition of Fe³⁺, a dark blue color appeared indicating the formation of PB coordination polymers. The suspension was colloidal stable in water but could be precipitated in methanol. After centrifugation, filtration, and drying, blue powders of PB nanoshells were obtained. In a control experiment, when we added the miniemulsion to methanol before coordination polymerization, no precipitation was observed and the solution became clear, indicating the disassociation of the surfactants.

The coordination polymers were analyzed by using FT-IR, UV–vis, and WAXD measurements. From FT-IR spectroscopy, we observed a CN stretching band shift from 2045 to 2084 cm⁻¹ after the polymerization,⁶ indicating the formation of a cyanide bridge of Fe(II)–CN–Fe(III).⁷ In UV–vis spectra, a strong absorption at ca. 670 nm due to the Fe^{II} to Fe^{III} CT⁸ appeared upon the addition of Fe³⁺.⁶ The intensity of this peak increased in proportion to the amount of Fe³⁺ added,⁶ suggesting the added Fe³⁺ ions were involved in the coordination polymerization. Different from other solid PB NPs,^{2,3} we found that MEPP-produced shells were amorphous probably due to their curved structures.⁶

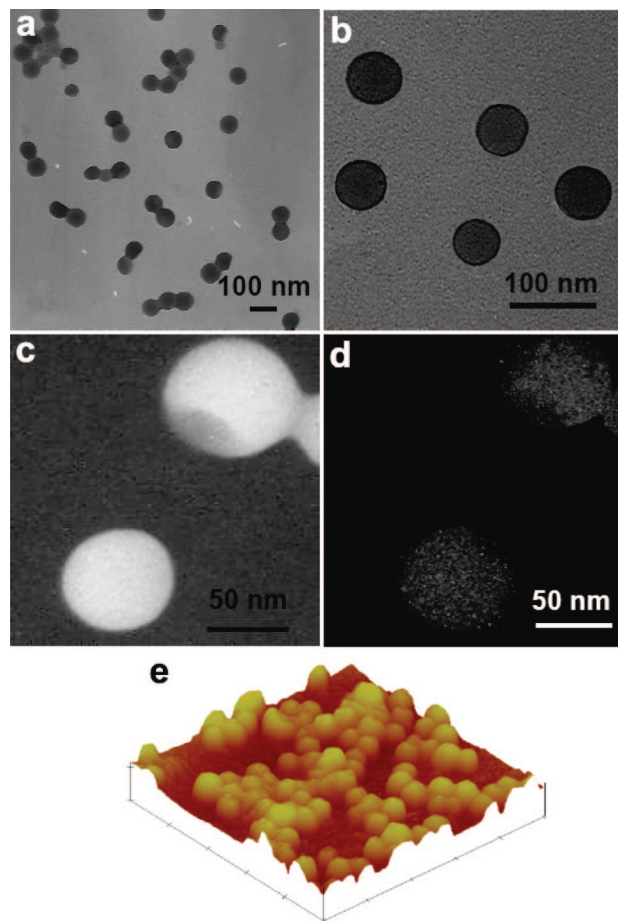
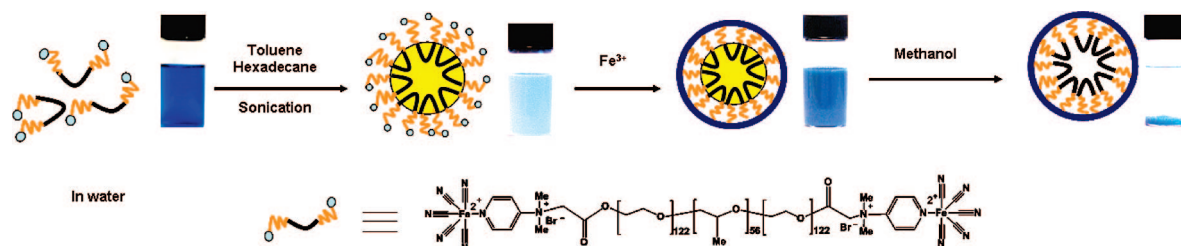


Figure 1. TEM micrographs of the PB nanoshells (a) at lower magnification, (b) at higher magnification, (c) EDX mapping of carbon element, (d) EDX mapping of iron element, and (e) tapping mode AFM image. Image size of AFM micrograph is $1 \times 1 \mu\text{m}^2$. Particle size is determined to be ca. 65 nm.

Figure 1a shows a typical TEM image of the coordination polymer nanoshells with a diameter of ca. 65 nm. However, DLS measurements of the particles in a diluted solution revealed a diameter of 133 nm. These different results may be caused by interparticle coordination. As a matter of fact, the connection of the particles is clearly observed in the TEM image (see Figure 1a). This interparticle coordination could be alleviated by dropwise addition of the miniemulsion to Fe³⁺ aqueous solution instead of adding the Fe³⁺ to the miniemulsion.⁶

A TEM image at higher magnification (see Figure 1b) shows that the particles exhibit a ring-like morphology, typical of hollow shell structures. The thickness of the ring is ca. 2 nm indicating the formation of a thin layer of the coordination polymer with an

Scheme 1. Schematic Illustration of Prussian Blue (PB) Nanoshells Produced through MiniEmulsion Periphery Polymerization (MEPP)

estimated aggregation number of 1106.⁶ EDX mapping reveals that carbon and iron elements (see Figure 1c and 1d) are uniformly distributed over the surface of the shells, confirming the formation of a shell of an organometallic network. A tapping mode AFM was performed, and short rods with hemisphere caps are observed (see Figure 1e). Undeformed shells were also observed from SEM experiments (see Figure 2). The observed rigidity of the shells could be attributed to directional coordination interactions.

We next investigated the coordination polymerization with varied equivalents of Fe^{3+} with respect to Fe^{2+} in the surfactants.⁶ The resulting samples were dried from the solutions and characterized using SEM. The SEM images indicated that a minimum of 1 equiv of Fe^{3+} is required to preserve the shape of the miniemulsion droplets⁶ and hence to generate shell structures.

Synthesis of the shells with varied size using MEPP is possible. In two experiments, we prepared a miniemulsion using the same amount of EPE-Fe (0.5% by weight), but with a toluene content of 5% and 20% by weight, respectively. As characterized by TEM, the particles prepared from the solution containing 20% toluene are ca. 198 nm, which is about twice as large as those in the system with 5% toluene.⁶

The thermal properties of the surfactants and nanoshells were investigated.⁶ As characterized by TGA, EPE-Fe surfactants started to decompose at ca. 150 °C, while the decomposition temperature for PB shells produced from EPE-Fe using MEPP was 360 °C.⁶ Two possible reasons may account for this shell-enhanced thermal stability: (1) the thin layer of PB hollow shells may inhibit heat flow among the particles and therefore may act as insulators; (2) the shell of the PB network prevented the mass loss of EPE polymers. This thermal behavior may be useful for the production of thermal isolation materials or shape-retained nanoceramics.⁹

In summary, we have developed a conceptually new method, MEPP, for the synthesis of PB nanoshells with variable size. The

synthesis involves miniemulsion preparation using organometallic surfactants and coordination polymerization at the periphery of the colloids. The nanoshells were characterized and confirmed by using FT-IR, UV-vis, WAXD, TEM, SEM, and AFM. TGA analysis indicated that the shell structure enhanced the thermal stability of the coordination polymers. Magnetic properties of the shells will be characterized in our further research. The hollow and rigid shells, unlike solid PB NPs,^{2,3} provide possibilities to encapsulate guest materials for various applications such as sensors, biomedicines, enzyme, or catalyst immobilization.¹⁰

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Supporting Information Available: Details of the synthesis and characterization including FT-IR, UV-vis spectra, SEM, TEM micrographs and TGA, WAXD data. This materials is available free of charge via the Internet at <http://pubs.acs.org>.

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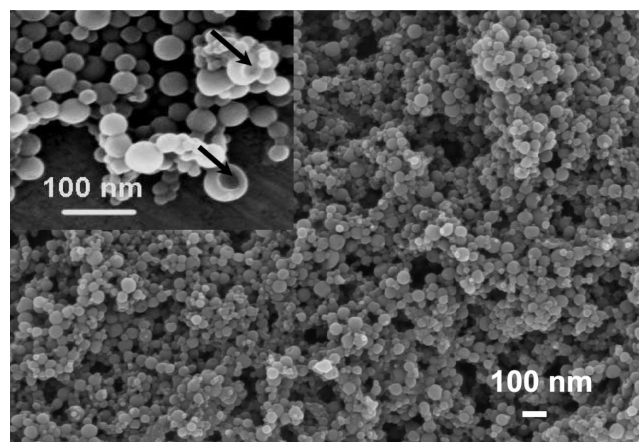


Figure 2. SEM micrographs of the nanoshells. The inset is the SEM micrograph at higher magnification. Arrows denote the collapsed or deformed nanoshells.

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