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Formation of Nanostructured Materials via Coalescence of Amphiphilic Hollow Particles

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The formation of nanostructured materials via molecular self-assembly has attracted increasing attention throughout the past decade, driven by a wide range of possible applications for such materials in science and technology.[1] Polymer nanotubes are of particular interest because of their potential in diverse fields.[2] Most nanotubes have been prepared using template techniques.[3] However, there are a few reports of their preparation via polymer self-assembly in dilute solutions.[4] Eisenberg et al. utilized the self-assembly of amphiphilic block copolymers with long hydrophobic blocks and very short hydrophilic segments to form "crew-cut micelles" in *N*,*N*-dimethylformamide (DMF). Bilayer aggregates, such as tubules, vesicles, and lamellae, formed when water was added to the micelle solution.[5] Manners and Winnik et al. prepared organometallic poly(ferrocenyldimethylsilane-*b*-dimethylsiloxane) (PFS-*b*-PDMS) copolymers with block ratios of 1:12 that formed hollow nanotubes in *n*-hexane and *n*-decane.[6] Liu et al. also prepared monolayer nanotubes from triblock and tetrablock copolymers.[7] The multiple block copolymers self-assembled in methanol or water to form core−shell cylindrical micelles. After the shells of the cylindrical structures were photo-cross-linked, the cores were degraded via ozonolysis. Wooley et al. prepared an amphiphilic triblock copolymer, poly(acrylic acid)$_{90}$-*b*-poly(methyl acrylate)$_{80}$-*b*-polystyrene$_{100}$, that self-assembled to form supramolecular structures having a rod-like morphology in a 33 vol % tetrahydrofuran/water solvent system.[8]

Herein, we describe a novel and convenient approach to prepare various nanostructured materials via the aggregation and coalescence of amphiphilic, hollow particles in aqueous solution. Well-defined amphiphilic core−shell particles are first prepared. The homopolymer in the polymer core is then removed by extraction with dichloromethane (DCM) to produce hollow particles, which are induced with water to form various nanostructured materials, such as nanotubes, microfibers, and microrods.

Thus, an amphiphilic poly(ethyleneimine)(PEI)-*g*-poly(methyl methacrylate) (PMMA) copolymer was first prepared by an aqueous free radical polymerization.[9] The copolymer self-assembled to form core−shell nanoparticles with PEI shells and PMMA cores. The cores also contained PMMA homopolymer that was also generated in the polymerization. The mean number-average hydrodynamic diameters (D_n) of the PMMA/PEI particles were less than 150 nm, and the particle size distribution (D_v/D_n) was between 1.08 and 1.10. Transmission electron microscopy (TEM) images of the particles clearly revealed that the particles had a well-defined core−shell morphology (Figure 1a). The average diameter of the PMMA cores was approximately 90 nm, while the average PEI shell thickness was 23 nm. The PMMA cores contained approximately 50−60 wt % grafted PMMA and 40−50 wt % homo-PMMA. The weight ratio of the grafted PMMA to that of the PEI in the backbone of the graft copolymer varied from 2:1 to 2.5:1.

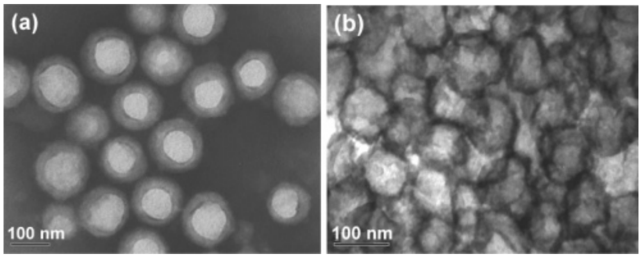

Figure 1. TEM images of (a) PMMA/PEI core−shell particles; (b) PEI-*g*-PMMA hollow particles.

We first attempted to slightly cross-link the PEI shell, which contained free amino groups, by treating the PMMA/PEI particles with a 1% glutaraldehyde solution for 2 h at room temperature. After repeated washings with water and acetone, the particle dispersion was freeze-dried. The fine powder was then stirred in DCM for 3 h to extract the PMMA homopolymer in the cores. The viscosity of the solution increased due to the dissolution of the PMMA. Water was then added, and the heterogeneous mixture stirred. The aqueous phase was isolated, diluted with water, dried on a copper grid at room temperature, and stained with a 2% phosphotungstic acid (PTA) solution. TEM images showed that the majority of particles were hollow, and some were fused together in a continuous mass (Figure 1b). The shells were distorted, indicating that they were flexible upon removal of the cores.

To our great surprise, a small amount of other nanostructures were also present, such as linear and worm-like nanotubes (Figure 2). The diameters of the nanotubes were between 60 and 100 nm, and their wall thickness was approximately 10 nm (Figure 2a and 2b). It is proposed that the nanotubes were formed through particle aggregation and coalescence. Some evidence for this formation mechanism is provided in Figure 2d, which shows two short tubes that have aggregated and fused to form what appears to be an intermediate structure in long nanotube formation. Figure 2b (at the lower right corner) also reveals a similar aggregation intermediate where boundaries can still be observed. Another worm-like nanotube structure that formed is shown in Figure 2c. In this case, the diameter of the nanotube is approximately 23 nm, while it is microns in length.

The discovery of the nanotubes prompted us to investigate other experimental conditions that affect their formation. When we directly extracted the PMMA in the cores of PMMA/PEI particles without prior cross-linking the shells and used different approaches to remove the DCM in the water/DCM mixture, fiber and rod-like structures that were microns in length were produced in high yield.

Examination of various ratios of water to DCM (20:80, 50:50, 70:30, and 95:5 vol %) revealed that a volume ratio of 70:30 was

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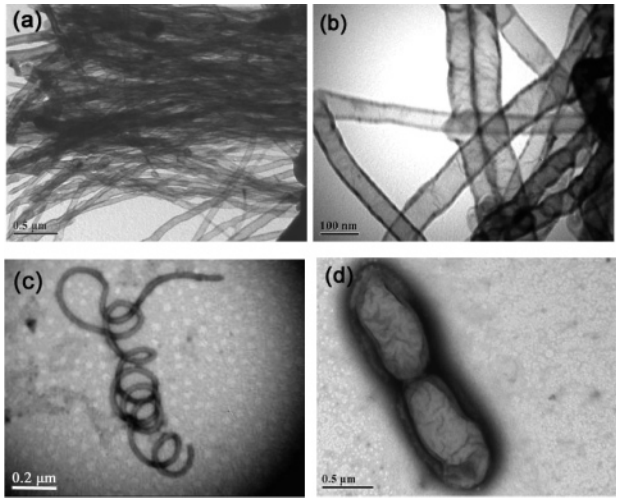

Figure 2. TEM images of nanotubes formed from PEI-*g*-PMMA hollow particles.

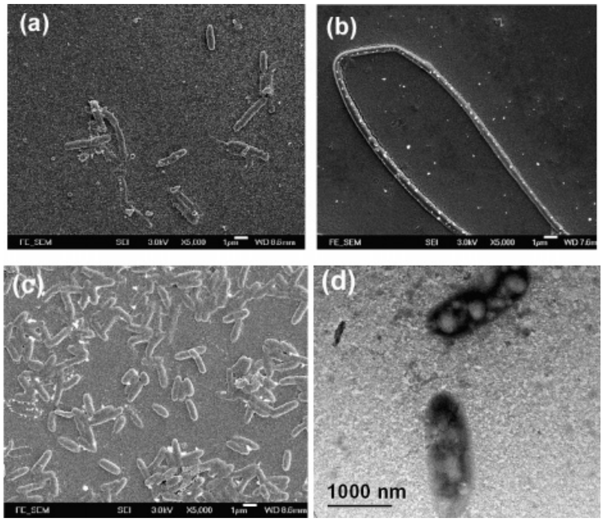

Figure 3. SEM images of assembled structures formed through a slow DCM evaporation in water (DCM:H_2O = 30:70 v/v%). (a) Microrods formed during stirring at 150 rpm. (b) A microfiber formed during stirring at 350 rpm. (c) Microrods formed during sonication. (d) TEM image of the microrods prepared via ultrasonic treatment.

optimum for micromaterial formation (Figure 3). The length of assembled structure could be controlled by varying the rate and manner in which the water/DCM mixture was stirred during DCM evaporation. A slow stirring rate of 150 rpm resulted in the formation of microrods between 1.5 and 4 μm long (Figure 3a). Individual particles were still observed, indicating that the conversion of hollow particles to the rods was incomplete. An increase in the stirring rate to 350 rpm resulted in the transformation of all the hollow particles to microfibers ~550 μm long with diameters of 0.5 μm (Figure 3b). The vigorous stirring of the hollow particle dispersion might have assisted their formation through shear induced coagulation.

When the particle dispersion in water/DCM mixture was agitated in an ultrasonic bath and DCM evaporated gradually, highly uniform microrods approximately 1.5 μm long and 0.4−0.6 μm in diameter were produced (Figure 3c). SEM images indicated that all the particles were converted to the microrods. Particle size measurements showed that the peak corresponding to the original particle sizes had totally disappeared. TEM micrographs of the microrods, which were stained with 0.5% PTA solution for 1 min, showed that the microrods contained several PMMA nanodomains (Figure 3d). Thus, it appears that the microrods were formed from a few hollow PEI-*g*-PMMA particles, but they were not hollow due to the aggregation of the PMMA grafts. In fact, when the microrods were treated with DCM, they separated into individual core−shell particles.

In summary, a novel route to nanotubes, microfibers, and microrods has been developed that does not involve the utilization of block copolymers. Instead, well-defined, amphiphilic core−shell particles were first prepared by a simple graft copolymerization, followed by removal of the homopolymer in the cores. The resulting hollow particles were induced to aggregate and coalesce to form various nanostructured materials. The sizes and shapes of the assembled materials could be controlled by varying the experimental conditions. It is speculated that the driving forces for the nanostructured materials include the reduction in surface energy associated with the partially exposed PMMA grafts gained by reducing the surface area. This process is facilitated by the softness of the hollow particles and the interdiffusion of the PEI chains. Detailed studies of the effects of other experimental variables on the morphologies obtained, their formation mechanisms, and the applicability of this method to prepare similar morphologies with other core−shell particles are currently in progress.

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Supporting Information Available: Experimental data for the syntheses; FTIR spectra of the isolated copolymer and homopolymer; SEM images of the particles, microrods, and microfibers; and a compilation of the morphologies obtained under different conditions are available. This material is available free of charge via the Internet at http://pubs.acs.org.

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