Angewandte Chemie

DOI: 10.1002/anie.200703032

Nanostructures

Interfacial Assembly of Nanoparticles in Discrete Block-Copolymer Aggregates**

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The ability to control the assembly structure of nanoscale materials is critical to understand their collective properties and to develop new materials and devices from nanoscale building blocks. In nature, lipid membranes function as structural scaffolds to organize nanoscale intercellular components. This role of lipids originates from their tendency to self-organize into diverse supramolecular aggregates including micelles, bilayers, vesicles, and liquid-crystalline phases. Amphiphilic block copolymers, man-made analogues of lipids, are becoming increasingly important for the synthesis, manipulation, and assembly of nanoparticles. They have been demonstrated to be effective solubilizing agents to transfer organic-phase nanoparticles into water.[1–4] Preorganized spherical or cylindrical block-copolymer micelles have been actively explored as a type of confined reactor for the controlled synthesis of nanoparticles.[4,5] However, in most of the solution-phase studies, the nanoparticles were considered as simple solutes, and the efforts in directing the arrangement of nanoparticles using block copolymers have been largely limited to two-dimensional systems.[6,7]

Herein, we describe a novel solution-phase assembly of CdSe quantum dots (QDs) and a prototypical amphiphilic block copolymer, poly(acrylic acid)-*block*-polystyrene (PAA-*b*-PS). Importantly, this study demonstrates that the interactions between nanoparticles and block copolymers can drastically alter the morphology of block-copolymer aggregates and can lead to a unique three-dimensional assembly structure of nanoparticles (a nanocavity in the present study) with controllable assembly parameters. Coassemblies of PAA-*b*-PS and organic-phase nanoparticles, including QDs and magnetic particles, have been prepared previously.[3,4] However, in those studies, the nanoparticles were passively incorporated into the coassemblies by acting as simple solutes, and they were evenly distributed in block-copolymer micelles. Herein, we show a unique example in which nanoparticles act as active components for the assembly formation. Moreover, we demonstrate that one can control the three-dimensional assembly structure of nanoparticles inside discrete block-copolymer aggregates by manipulating the interfacial energy of the composite system.

In typical experiments, PAA_{41}-*b*-PS_{193} (0.3 $mg\,mL^{-1}$) was first dissolved in dimethylformamide (DMF; 500 μL) and mixed with trioctylphosphine oxide (TOPO)-stabilized CdSe/ZnS core–shell QDs (3.2×10^{-6} M) in chloroform (25 μL). Then, additional DMF (950 μL) was added to the solution with stirring. To induce the assembly of the block copolymer and the QDs, water (300 μL, 18 MΩ) was slowly added to the mixture at the rate of 10 μL per 30 s. The solution was stirred for 15 h, and then dialyzed against water for 24 h. Finally, the assemblies were purified by a series of centrifugations.

Transmission electron microscope (TEM) images reveal that the QDs are incorporated in well-isolated block-copolymer aggregates (Figure 1 A,B). The nanoparticle–block-copolymer assemblies (NBAs) are composed of three parts: an outer polymer shell, an inner polymer core, and QDs arranged in a spherical configuration at the interface between

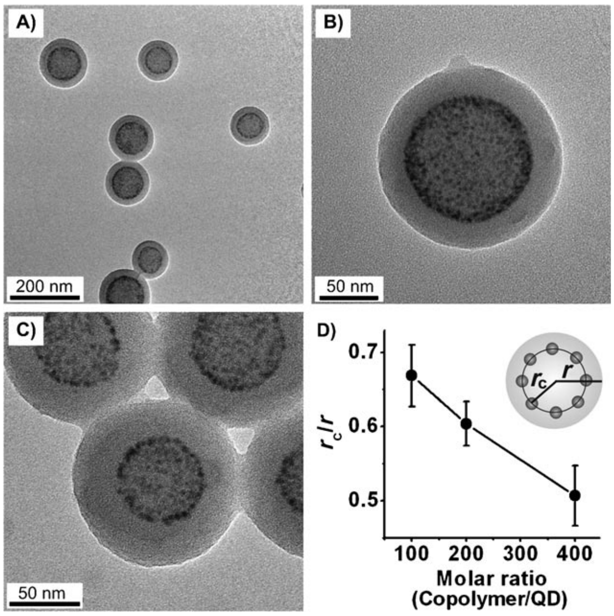

Figure 1. A) TEM image of assemblies of CdSe/ZnS QDs and PAA-*b*-PS. B) High-magnification TEM image showing individual QDs (dark dots) imbedded inside a block-copolymer aggregate. C) TEM image of assemblies formed with a four-times larger amount of the copolymer and the same amount of the QDs. D) Plot of the radial position (r_c/r) of the QDs against the molar ratio of the copolymer to the QDs. The radial positions were determined with approximately 120 assemblies for each sample.

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[**] This work was supported by the University of Pennsylvania, an MRSEC seed award (DMR 05-20020), and NSF-CHE-0501198.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

the polymer core and the polymer shell. The average diameter of the assembly and the polymer-shell thickness were determined to be (129 ± 18) nm and (21.1 ± 1.9) nm, respectively (see the Supporting Information). While the size distribution of the assembly is rather broad, the thickness of the polymer shell is highly uniform, and it is shorter than the length of a fully stretched PS segment (49 nm). This observation suggests that the outer shell is composed of a monolayer of block copolymers with PAA at the exterior, which stabilizes the assembly in water. The radial position (r_c/r) of the QDs inside the block-copolymer aggregate could be easily controlled by varying the molar ratio between the copolymer and the QDs (Figure 1 C,D). A TEM image of the assemblies formed with a four-times larger amount of block copolymers is presented in Figure 1 C, which clearly shows that the radial position of the QDs is shifted towards the center when the amount of polymer is increased.

Note that the structure of the NBAs reported herein is distinct from the previously reported composites in which hydrophobic nanoparticles were evenly embedded in PAA-*b*-PS block-copolymer micelles.[3,4] In the present case, the edge of the core region appears darker than the middle, indicating that the QDs are radially arranged at the interface between the polymer core and the shell, as illustrated in Figure 2 A,B.

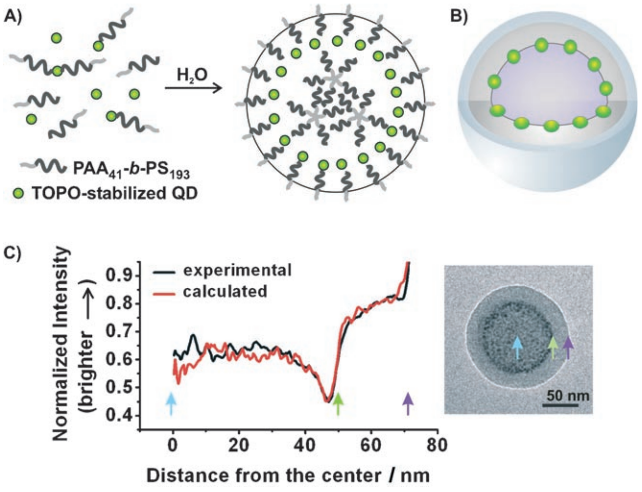

Figure 2. A) Schematic description of the cross-sectional structure of the NBA. B) Three-dimensional representation of the NBA. Green dots represent the QDs assembled at the spherical interface between the polymer core and the shell. C) Experimental and calculated radial intensity profiles of TEM images of NBA. Right: The TEM image used in the analysis. The colored arrows indicate corresponding positions.

The morphology of the polymer core inside the QD nanocavity is difficult to characterize, but we hypothesize that the core is composed of aggregates of reverse micelles. Overall, the morphology of the polymer comprising the assemblies resembles that of a large compound micelle (LCM) as described by Zhang and Eisenberg,[8] which is composed of multiple reverse micelles encased in a layer of PAA-*b*-PS. It is interesting to note that the localization of the QDs at the spherical interface allows the visualization of the internal structure of the polymer aggregate, which is difficult to image otherwise. To analyze the assembly structure further, radial intensity (gray-scale) profiles of TEM images were obtained and compared with calculated profiles (Figure 2 C). The calculated intensity profiles were generated by assuming that the QDs are located strictly at the interface (see the Supporting Information). Figure 2 C confirms that the simulated intensity profile based on the model described in Figure 2 A matches well with the experimental result. It is also important to note that the QDs are completely excluded from the polymer shell (Figure 1 B,C). These results support a model in which the QDs are entrapped exclusively at a spherical interface inside the polymer aggregate.

Significantly, the QDs in the assemblies were highly luminescent in water. The photoluminescence (PL) intensities of prepared NBA solutions varied from batch to batch, but the average quantum yield (QY) of the QDs in the NBAs estimated from five different samples was 37 %, which is slightly higher than that of the original TOPO-stabilized QDs in chloroform (34 %, Figure 3 A; see the Supporting Information for details on the QY calculation). Moreover, the PL intensities from single assemblies without any optimization were comparable to those of commercial fluorescent microspheres (Molecular Probes, 100 nm in diameter; Figure 3 B). This is a significant improvement compared to previous studies,[4,9] where QDs were synthesized inside block-copolymer aggregates and then organized into bigger assemblies. Although these studies were elegant investigations of the synthesis and assembly of QDs, the QDs synthesized inside block copolymers were not as bright as the TOPO-stabilized QDs. In addition, the emission bandwidth is similar before and after encapsulation, indicating that the nanoparticles remain intact after the encapsulation (Figure 3 A). A slight red-shift of the PL peak positions was observed, presumably because of the changes in the dielectric constant of the medium and energy transfer to larger QDs within the assemblies.

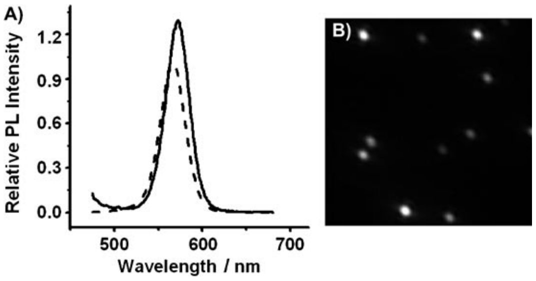

Figure 3. A) PL spectra of the NBAs dispersed in water (solid line) and of the TOPO-stabilized QDs in chloroform (dashed line) at the same QD concentration. B) PL microscope image (10×10 µm^2) of the NBAs spread on a polylysine-coated glass coverslip under illumination with an argon-ion laser (514 nm).

Another very interesting characteristic of the assembly formation is that the nanoparticles were found to be a necessary component to form the type of block-copolymer assembly described above. When the same procedure was repeated in the absence of nanoparticles, the resulting polymer aggregates were mostly composed of a mixture of rod-shaped micelles and lamella (Figure 4A). On the other hand, similar types of large spherical polymer aggregates were obtained by using tetrahydrofuran (THF) as the solvent instead of DMF (Figure 4C). It is well-known that the morphology of block-copolymer aggregates can be controlled by many factors including solvent composition.[10,11] Since THF is more hydrophobic than DMF, the hydrophobic domain of the polymer aggregates is initially larger in THF. Thus, block copolymers lower the free energy by adopting inverted micelles, which are subsequently solubilized by a layer of block copolymers.[10,12] It is quite intriguing to note that, in the presence of the nanoparticles, the large compound assemblies are formed even in DMF (Figure 4B), because the hydrophobic nanoparticles bind to the PS chains and increase the effective size of the hydrophobic domain of the block copolymers. This observation demonstrates that nanoparticles can play an active role in the block-copolymer assembly processes, rather than simply being incorporated passively in the hydrophobic domain as solutes. In thin-film systems, the cooperative assembly of nanoparticles and block copolymers has been shown to modulate the orientation of copolymer domains normal to the surface and to cause phase transitions of the block-copolymer morphology.[6,13,14] It is also interesting to note that the incorporation of the nanoparticles significantly narrows the size distribution of the copolymer assemblies (Figure 4B,C).

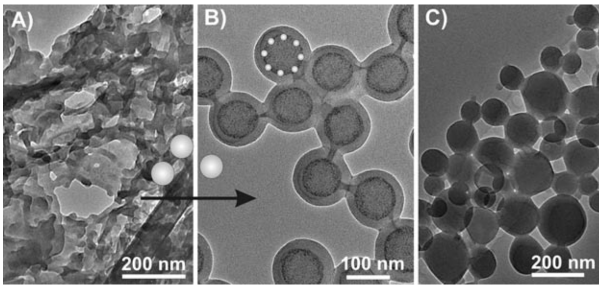

Figure 4. TEM images of A) the PAA-*b*-PS aggregates formed in the absence of nanoparticles, B) the NBAs showing a morphological transition by the addition of nanoparticles, and C) the PAA-*b*-PS aggregates formed in the absence of nanoparticles by using THF rather than DMF as the solvent.

The precise mechanism of the radial nanoparticle assembly is not yet understood, but the resulting assembly structure should be a manifestation of the minimized free energy of the system. We hypothesize that the TOPO-stabilized QDs are initially included in different parts of the PS domains of the block copolymers to avoid contact with water. As the assemblies are formed, and the polymers and QDs reorganize within the assemblies, the QDs are pushed out of the PS chains and assembled at the interface between the polymer core and the shell. This hypothesis is consistent with a theoretical simulation showing that nanoparticles form a nanosheet within a polymer lamella structure to reduce the loss of conformational entropy of polymer chains.[15] The study described herein deals with alkyl-terminated particles and PS; thus, both enthalpic and entropic effects can contribute to the phase segregation and the unusual assembly formation. Indeed, it has been shown that PS and alkyl-terminated nanoparticles phase separate when they are mixed and spin-coated on a substrate.[16]

In summary, we report the first example of a solution-phase assembly of nanoparticles and block copolymers in which the two components cooperatively self-organize into a novel assembly structure. Importantly, this study demonstrates that the manipulation of the interactions among nanoparticles, block copolymers, and solvent can lead to unique assembly structures that are not possible by a simple solubilization approach. In addition, we have shown that one can obtain desired radial distributions of nanoparticles by simply changing the molar ratio of copolymers to nanoparticles. The QDs incorporated in the polymer assemblies are highly luminescent, retaining the QY of the original nanoparticles in chloroform, and they are very stable in aqueous solution over a period of months, showing promise for their use as PL imaging probes. One might find the assemblies useful in other applications in which the radial assembly structure is critical to function, as in the case of whispering-gallery-mode lasing.[17] This approach should be applicable to other types of materials, and we are currently evaluating various types of nanoparticles and polymers, including biologically active block copolymers to generate multifunctional biological imaging probes.

Experimental Section

Poly(*tert*-butyl acrylate)$_{41}$-*block*-polystyrene$_{193}$ (PtBA$_{41}$-*b*-PS$_{193}$) was synthesized by the sequential reversible addition–fragmentation chain transfer (RAFT) polymerization of *tert*-butyl acrylate and styrene.[18] Subsequently, PtBA-*b*-PS was hydrolyzed by HCl to generate PAA-*b*-PS.[19] The PS end of the polymer is terminated with a dodecyltrithiocarbonate group introduced from the RAFT catalyst.

TOPO-stabilized ZnS-coated CdSe nanoparticles (4.6 nm in diameter) were synthesized by a modified literature method.[20]

Typically, the NBAs were isolated from large block-copolymer aggregates by centrifuging the solution at 7000 rpm for 10 min and discarding the precipitates. Then, the supernatant was centrifuged again at 16000 rpm for 1 h, and the precipitates were collected and redispersed in water (1 mL). For further purification, the solution was centrifuged for 1 h at 16000 rpm after stirring for 24 h. Finally, the precipitates were collected, redispersed in water (100 μL), and analyzed by TEM.

Received: July 7, 2007
Revised: September 25, 2007

Keywords: amphiphiles · block copolymers · nanostructures · quantum dots · self-assembly

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