Selective Synthesis of Carbon Nanorings via Asymmetric Intramicellar Phase-Transition-Induced Tip-to-Tip Assembly

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ABSTRACT: The selective synthesis of energetically less favorable ring-shaped nanostructures by liquid phase synthetic chemistry is a huge challenge. Herein, we report a precise synthesis of carbon nanorings with a well-defined morphology and tunable thickness based on asymmetric intramicellar phase-transition-induced tip-to-tip assembly via mixing hydrophobic long-chain octadecanol and block copolymer F127. This orientational self-assembly depends on the hydrophobicity difference of the intermediate’s surface, which triggers directional interactions that surpass the entropy cost of undesired connections and help assemble intermediates into defined ringlike structures. Based on a ringlike template, carbon nanorings with adjustable sizes can be attained by changing synthetic variables. More importantly, diverse units including crescentlike, podlike, and garlandlike nanostructures can also be created through controlling the kinetics of the self-assembly process. This discovery lays a solid foundation for the challenging construction of such a precise configuration on the nanoscale, which would not only promote fundamental studies but also pave the way for the development of advanced nanodevices with unique properties.

INTRODUCTION

The past two decades have witnessed the explosion of synthetic methodologies that allow nanostructured carbon materials to be precisely engineered.1−3 This has greatly enriched the family of carbon nanomaterials as well as promoted research on structure–function relationships.4−7 Among diverse nanostructures, the ringlike shape is critically required as one of the model systems of 2D carbon materials for fundamental studies, such as negative magnetoresistance,8 electromechanical effects,9 and magnetic responses.10 Nevertheless, carbon rings with a regular morphology and hollow open interior have not been synthesized yet via liquid phase synthetic chemistry.11

In aqueous solutions, the principle of minimization of interfacial energy tends to produce isotropic morphologies, and this has been widely used, especially to prepare carbon nanospheres.12,13 To overcome the limitation of this primary principle, additional strategies, e.g., controlled phase transition14 or cooperative coassembly,15 have been applied to induce anisotropic nucleation and growth, and several novel nanoparticles including bowl-like, flakelike, or walnutlike nanoparticles have been prepared.16−20 However, the efficient synthesis of bespoke carbon nanomaterials with well-defined ringlike morphology is still a huge challenge.21−23 Despite the achievement of ringlike micelles made of several specific copolymers, a complete separation of micelles from solution remains unsolved, let alone a conversion into carbon nanorings due to their structural and thermal instability.

In this study, we describe a selective synthesis of well-shaped carbon nanorings based on a simple two-surfactant system by mixing hydrophobic long-chain octadecanol with block copolymer F127 in aqueous solutions, via asymmetric intramicellar phase-transition-induced tip-to-tip assembly and a carbonization procedure. Noticeably, besides carbon nanorings, versatile asymmetric nanostructures including crescentlike, podlike, and garlandlike nanoparticles were simultaneously produced, which further indicates the effectiveness of this kinetic controlled synthesis.

RESULTS AND DISCUSSION

Carbon nanorings were synthesized by using the commercially available surfactants octadecanol and triblock polymer F127 as the template. As a typical example, octadecanol/F127 mixed micelles with a ringlike morphology were prepared through emulsification and a subsequent incubation process. After the

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addition of monomers (resorcinol/formaldehyde/propylamine) into the micelle solution, polybenzoxazine-based polymer nanorings were obtained, which faithfully copied the ringlike morphology of the template through the interface assembly. Subsequently, carbon nanorings with a well-preserved structure were achieved by pyrolysis of the polymer counterparts.

As shown in the scanning electron microscopy (SEM) images in Figure 1a,b, polymer nanorings were formed with a diameter of 782 ± 83 nm and a thickness of 183 ± 11 nm. The Fourier transform infrared spectroscopy (FTIR) spectrum of polymer nanorings (Figure S1) showed typical bands of benzoxazine monomer at ∼1109, 1228, and 950 cm⁻¹ and bands of benzoxazine ring-opening polymerization at ∼3210 and 3390 cm⁻¹. After pyrolysis at 600 °C in an argon atmosphere, the carbon nanorings (Figure 1c,d) retained the undamaged ringlike shape corresponding to their polymeric counterparts. The diameter and the thickness after thermal treatment were 640 ± 67 and 155 ± 8 nm, respectively, while the circumference shrinkage was 18.2%. The X-ray diffraction (XRD) pattern indicated that the as-prepared carbon nanorings are of amorphous state carbons (Figure S2). In addition, the CO₂ adsorption isotherm (Figure S3) of the carbon nanorings showed a typical type I curve, indicating the microporous feature. The specific surface area and total pore volume of the carbon nanorings are 772 m² g⁻¹ and 0.22 cm³ g⁻¹, respectively. The pore size distribution curve derived from the adsorption branch indicated that carbon nanorings have a homogeneous pore size distribution of 5–6 Å.

The presence of octadecanol is decisive to the formation of a ringlike morphology. We found that a high concentration of octadecanol, namely, a high molar ratio of octadecanol/F127, would accelerate the cyclization process and improve assembly kinetics. In the absence of octadecanol, uniform nanospheres with an average diameter of ∼127 nm were obtained (Figure 2a). This observation agrees with our previous report.²⁴ When a tiny amount of octadecanol was used (the octadecanol/F127 molar ratio is 0.5:1), nonspherical nanostructures appeared. This phenomenon indicated that the hydrophobic octadecanol would interact with F127 micelles, causing the deformation of spherical micelles (Figure 2b). When the molar ratio of octadecanol/F127 was increased to 1:1, the coexistence of diverse special species including crescentlike, podlike, and garlandlike nanostructures was observed (Figure 2c). The crescentlike units bridged with each other through the tips, describing a curving podlike structure (Figure 2c, green arrow). All of these nanostructures are intermediates of the “cyclization reaction” of nanoring formation. However, the merging process was nonsynchronized. Catching up with the dynamic evolution of the growth process would collect a big variety of intermediate nanostructures with varied dimensional morphologies, including crescentlike, podlike, and garlandlike nanostructures. When the joint neck between two units was not tightly formed, the combined arc could not hold its morphology due to the capillary cohesion during evaporation for SEM measurements (Figure 2c, yellow arrow).

![Figure 1. SEM images of (a, b) polymer nanorings and (c, d) carbon nanorings.](Image)

![Figure 2. SEM images of nanostructures prepared with different molar ratio of octadecanol/F127: (a) 0:1, (b) 0.5:1, (c) 1:1, (d) 5:1, (e) 10:1, and (f) 17.5:1.](Image)
Figure 3. SEM images of polymer nanorings prepared with an incubating time of (a) 0 h, (b) 24 h, (c) 48 h, and (d) 72 h. (e) XRD pattern of the template with an incubating time of 0 h. (f) XRD pattern evolution of the template with incubating time. (g) Size evolution of the template with incubating time. (h) Proportion of the nanostructure evolutions as a function of incubating time.

In order to facilitate the kinetics of assembly process, we increased the molar ratio of octadecanol/F127 to 5:1. As a result, intact nanorings with a diameter ranging from 520 to 890 nm and smooth surfaces were synthesized. Meanwhile, a number of nanospheres still existed (Figure 2d). When the molar ratio of octadecanol/F127 reached 10:1, nanorings were recognized as the main product, while a smaller proportion of nanospheres was also observed (Figure 2e). Considering the solubility limitation of the octadecanol in the F127 micelles, the highest molar ratio of octadecanol/F127 can only reach 17.5:1. In this case, remarkably, nanorings were the net products (Figure 2f).

These results demonstrated that the phase transition of octadecanol could induce the deformation of F127 micelles and drive the transformation from a spherical to crescentlike shape. Then, the anisotropy crescents self-assembled into a ringlike morphology by the unique tip-to-tip fusion process. We envisage that, with the increased amount of octadecanol added, more amphiphilic F127 molecules would be consumed, thus stabilizing the hydrophobic phase. Moreover, it also means that fewer F127 spherical micelles could form. When the amount of octadecanol reached maximum solubility, namely, the octadecanol/F127 molar ratio of 17.5:1, only polymer nanorings were observed as expected.

To capture the formation process of the ringlike template, six intermediate samples incubated at 28 °C for 0, 24, 48, 72, 96, and 120 h were accordingly extracted. It should be noted that the morphology of the octadecanol/F127 toroidal template is not easy to observe by SEM directly because the template is too soft and vulnerable under an electron beam (see Figure S4). Therefore, we decided to use a polymer coating as an indirect but easy method to freeze the morphology of the template during the growth process. All samples were prepared by keeping the octadecanol/F127 molar ratio at 5:1. As seen in the SEM images of Figure 3a, a number of half-moon-like nanostructures with a length of ~111 nm and width of ~74 nm were instantly generated when the microemulsion solution was cooled down to 28 °C. From the XRD pattern of the template in Figure 3e, two main diffraction peaks that appeared at 21.8° and 24.7° are assigned to the γ phase of an octadecanol crystal, which means that the anisotropic morphology might be strongly bridged through octadecanol via its phase transition from liquid to crystal inside the F127 micelles.

After 24 h, previous elementary nanostructures totally disappeared, which were replaced by slender and curving crescentlike nanostructures. In addition, some of them assembled into podlike and garlandlike nanostructures (Figure 3b). These nanostructures, though the morphology differs, are all intermediates from the same process toward nanoring structures. The presence of podlike nanostructures with a groove area between two or three units indicated the unique tip-to-tip assembly and ring-closing process from crescents to garlands (Figure 3b,c by the blue arrow). The slender and curving crescents have an approximate width of 87 nm, which is close to the width of the nanostructures in Figure 3a. Hence, their production can be reasonably attributed to the tip-to-tip fusion of elementary nanostructures formed initially.

The intermediates went through a further transformation with prolonged incubating time. Crescentlike nanostructures nearly disappeared while garlandlike nanostructures became well-rounded, and podlike nanostructures still existed at 48 h (Figure 3c). Besides these intermediates, an unusual two-crescent-aggregate also coexisted (as indicated in Figure 3b,c by the yellow arrow), which might be derived from the drying effect during the sample preparation for SEM observation.

The ring-closing fusion entered its mature period after 72 h, and other intermediates were scarcely observed (Figure 3d). Integrated nanorings with smooth surfaces were finally acquired. Noticeably, their sizes were significantly larger than those of the rings formed after 48 h, indicating a continuous fusion process owing to Ostwald ripening. When the incubating time is further extended to 96 or 120 h, the morphology and diameter of the nanorings basically showed no obvious change (Figure S5a,b). Along with the morphology transition, the diffraction peaks at about 24.2° and 21.5° of the XRD pattern evolution from 24 to 96 h ascribed to the β phase of octadecanol became stronger, indicating a polymorphic transition of octadecanol from γ phase to β phase in micelles (Figure 3f). The nanoring formation process was further revealed by dynamic light scattering (DLS) measurements of the template, in which the size distribution increased with the incubating time until reaching a steady state after 48 h (Figure 3g). The mixed octadecanol/F127 micelles are larger than pure
F127 micelles in size, indicating that octadecanol molecules have entered into the hydrophobic interior of the micelles. This further demonstrates the swelling effect of the long-chain fatty alcohols.

In addition, we managed to capture the podlike and garlandlike intermediate morphology using in situ transmission electron microscopy (TEM) (as indicated in Figure S6 by the yellow arrow). In order to present the ringlike morphology of the octadecanol/F127 template, we have grafted octadecanol with 7-(diethylamino)-coumarin-3-carboxylic acid to trace the fluorescent signal of the template solution. A fluorescent ring with a diameter of 2 μm was observed, strongly proving the existence of the ringlike template (Figure S7).

Based on the above observation and statistical analysis of 100 samples, we presented a growth map to describe the ring cyclization process (Figure 3h). The elementary nanostructures were consumed to extinction (0%) in 24 h, and intermediates increased sharply to a maximum (100%) simultaneously. The rings began to form after 24 h at the expense of these intermediates and subsequently reached 26%, 90%, and 100% within 48, 72, and 96 h, accordingly.

Unlike the assembly of isotropic particles, the crescents with two tips are actually patchy structures; thus, the assembly occurs only via the tip-microzone, and any connections in other regions are invalid. The anisotropic particle–particle interactions were probably derived from the affinity of the hydrophobic molecule octadecanol, ultimately leading to the orientational assembly.

The formation of elementary nanostructures and their subsequent ring-closing assembly are two key processes for the achievement of the ringlike template. Therefore, we propose an asymmetric intramicellar phase-transition-induced orientational self-assembly process for the formation of octadecanol/F127 ringlike micelles, as depicted in Figure 4.

First, as hydrophobic octadecanol is added into a surfactant F127 aqueous solution by vigorous stirring, mixed octadecanol/F127 micelles with PEO as the shell and a PPO cross-linked octadecanol network as the core are formed via noncovalent bonding. By quenching the hot microemulsion from 80 to 28 °C, octadecanol can nucleate and crystallize quickly into the imperfect monoclinic γ phase, within the confined space of F127 micelles. Driven by interfacial tension, the interior rigid crystal network impels the deformation of the original sphericity toward anisotropy nanostructures. As a result, elementary micelles with a larger surface area, higher aspect ratio, and an intrinsic curvature are formed.

Meanwhile, the growth of an octadecanol crystal may crack the hydrophilic PEO surface layer, which serves as an encapsulating agent of the octadecanol crystal, and cause the mixed micelles to expose two hydrophobic tiplike termini at the interface. The convex shape of such a terminus feels strong pressure from the convexlike distributed water molecules in its vicinity and tends to fuse with other micelles that it may access to eliminate the unbalanced force at the micelle–water interface. The fusion of two or more micelles via their hydrophobic tips offers a gain in solvation free energy and stabilizes the newly formed crescentlike, podlike, and, further, garlandlike nanostructures. These nanostructures interact with the water molecules in their vicinity via the hydrophilic chains of F127 on the surface and enthalpically adapt better with the aqueous environment.

Once the hydrophobic tip is captured by another brother unit, a groove between neighboring crescents is consequently formed, which is gradually smoothed through subsequent epitaxial alignment and crystallization of octadecanol molecules. During the self-assembly process, the XRD diffraction peaks ascribed to the β phase octadecanol become stronger along with incubating time. The polymorphism evolution of octadecanol indicates the phase transition of octadecanol from the γ phase to β phase in the micelles. This kind of orientational assembly of a highly organized ringlike superstructure is proved to be favorable not only in thermodynamics but also in kinetics. As is known, with the increase of the assembly unit number of a target structure, the probability of a correct-at-once connect decreases exponentially.26 Strong interaction is required to surpass the entropy cost for the formation of the correct and orientational combination. Therefore, the high yield of the target nanorings (∼100%)
depends significantly on the directional hydrophobic interactions for specific connections between the crescentlike units. However, due to the randomness of each particle’s Brownian motion and the presence of multiple intermediates in aqueous solution, the ring-growth process is out of sync to some extent, resulting in the coexistence of crescentlike, podlike, and garlandlike nanostructures.

Moreover, the assembled ringlike template is still open to merge with other residual units through Ostwald ripening, resulting in a continuous increase of diameter. As time goes on, the ring-expansion gradually stagnates and reaches a plateau until the ever-dwindling units disappear. In summary, a ring’s diameter is decided by the size of each section and the amount of available residuum through ripening.

The thicknesses of the polymeric nanorings were tunable by simply varying the monomer concentration during the polymerization assembly reaction. By preserving the ratio of resorcinol/formaldehyde/propylamine, and concurrently varying the molar ratio of octadecanol/resorcinol in the order of 0.035, 0.069, 0.104, and 0.138, the thickness of obtained polymer nanorings can be adjusted to 183 ± 11, 127 ± 8, 104 ± 4, and 96 ± 8 nm (Figures 1a, 5a,b, and 2f). Using experimental data of the molar ratio and thickness with the polynomial fitting, a good quadratic equation of thickness vs molar ratio is obtained (Figure 5c). After pyrolysis at 600 °C, their carbonized productions preserved a perfect toroidal morphology, indicating the good thermal stability of the polybenzoxazine-based nanorings (Figures 1c and 5d–f). The thickness of carbon nanorings was decreased to 86 ± 7, 95 ± 10, 113 ± 6, and 155 ± 8 nm, and the linear shrinkage was 10.4%, 8.7%, 11.0%, and 15.3%, correspondingly. Like their polymer counterparts, the thickness of carbon nanorings also preserved a quadratic function relation with the octadecanol/resorcinol molar ratio (Figure 5c).

The effect of the F127 concentration on the morphology of the polymer nanorings was also investigated. When maintaining the octadecanol/F127 ratio, as the mass fraction of F127 decreased to 0.5 wt % and after incubating for 120 h, only podlike nanostructures were observed, implying that the toroidal micelles were not completely assembled (Figure S8a). However, at high F127 concentrations (e.g., 1 wt %), nanorings with intact architectures were obtained (Figure S8b), which illustrates that the concentration of F127 affects the self-assembly rate from crescentlike units to nanorings. In addition, we have attempted using the other amine, such as dimethylamine, as the reagent during the polymerization process. As presented in Figure S9, the sample maintained a regular ringlike morphology with a diameter of 810 ± 70 nm and thickness of 150 ± 9 nm, indicating that the variation of amine is possible with the proposed synthetic method.

### CONCLUSION

In summary, carbon nanorings with a well-defined morphology and tunable thickness have been successfully synthesized by asymmetric intramicellar phase-transition-induced tip-to-tip assembly, involving the use of commercially available surfactants octadecanol and F127. The two-step assembly of the octadecanol/F127 ringlike template has been illustrated: crescentlike nanostructures created by the asymmetric octadecanol phase transition inside mixed micelles could further orientationally self-assemble to nanorings during the incubation process. Based on the well-shaped ringlike template, polybenzoxazine-based polymer and carbon nanorings were successfully derived. The obtained carbon nanorings are uniform in shape and have a high surface area. We believe that this discovery of carbon and polymer nanorings may inspire further studies of new methods and principles of building anisotropic carbon materials for more applications that take advantage of their different physicochemical properties.

### EXPERIMENTAL SECTION

**Chemicals.** Resorcinol (99.5%), ammonia solution (25 wt %), propylamine (98.5 wt %), formaldehyde (37 wt %), and octadecanol were obtained from Sinopharm Chemical Reagent Co., Ltd. Pluronic F127 was purchased from Sigma. All chemicals were used as received.
Preparation of F127/Octadecanol Ringlike Micelles. Typically, 0.8 g of F127 was first dissolved in water at 40 °C and then heated up to 80 °C. Then, 0.3 g of octadecanol was added to the hot aqueous solution followed by vigorous stirring for 3 h to form a clear translucent microemulsion. After incubation at 28 °C for 120 h, an emulsion of ringlike F127/octadecanol micelles with a weak liquid crystal phenomenon was achieved.

Preparation of Carbon Nanorings. 0.44 g of resorcinol and 584 μL of formaldehyde were dissolved in 390 mL of water at 20 °C. After 1/2 h, 10 mL of the suspension of the template was added. Then, 1 mL of propylamine solution (1 M) and 1 mL of ammonia solution (1.5 M) were added in sequence with gentle stirring for 1 h. The white solution was further heated to 70 °C for 4 h to solidify the polymer. Finally, the polymer nanorings were obtained after centrifugation, rinsing three times, and freeze-drying. Carbon nanorings were obtained by pyrolysis of polymer nanorings at 600 °C for 2 h under an argon atmosphere.

Characterization Methods. SEM images were conducted by a Hitachi S-4800 instrument. In situ TEM images were carried out by an FEI Tecnai G2 F20 microscope operating at 300 kV. DLS tests were obtained by a Malvern Zetasizer NanoZS instrument at 28 °C. XRD patterns were performed with a Panalytical X’pert Pro Super X-ray diffractometer using Cu Kα radiation (40 kV, 40 mA, λ = 0.154 18 nm). The FTIR spectrum was collected on a Nicolet 6700 FTIR spectrometer. CO₂ adsorption isotherms were measured with the Autosorb instrument. DLS tests were obtained by a Malvern Zetasizer NanoZS instrument at 28 °C. XRD patterns were performed with a Panalytical X’pert Pro Super X-ray diffractometer using Cu Kα radiation (40 kV, 40 mA, λ = 0.154 18 nm). The FTIR spectrum was collected on a Nicolet 6700 FTIR spectrometer. CO₂ adsorption isotherms were measured with the Autosorb instrument.

FTIR spectrum of the polymer nanorings; XRD pattern and CO₂ adsorption isotherm of the carbon nanorings; SEM images of the template solution, samples fabricated after adding propylamine and adding ammonium hydroxide; SEM images of polymer nanorings prepared with an incubating time of 96 and 120 h; in situ TEM images and confocal laser scanning microscopy images of the octadecanol/F127 template; SEM images of the polymer nanostructures prepared with different concentrations of F127; and an SEM image of the polymer nanorings prepared with dimethylamine as the reagent.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscentsci.1c00735.

Notes
The authors declare no competing financial interest.

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