

## Uniform Concave Polystyrene–Carbon Core–Shell Nanospheres by a Swelling Induced Buckling Process

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### S Supporting Information

**ABSTRACT:** We have developed a facile procedure that can create asymmetrical building blocks by uniformly deforming nanospheres into  $C_{\infty v}$  symmetry at low cost and high quality. Concave polystyrene@carbon (PS@C) core–shell nanospheres were produced by a very simple microwave-assisted alcohol thermal treatment of spherical PS@C nanoparticles. The dimensions and ratio of the concave part can be precisely controlled by temperature and solvents. The concavity is created by varying the alcohol-thermal treatment to tune the swelling properties that lead to the mechanical deformation of the PS@C core–shell structure. The driving force is attributed to the significant volume increase that occurs upon polystyrene core swelling with the incorporation of solvent. We propose a mechanism adapted from published models for the depression of soft capsules. An extrapolation from this model predicts that the rigid shell is used to generate a cavity in the unbuckled shell, which is experimentally confirmed. This swelling and deformation route is flexible and should be applicable to other polymeric nanoparticles to produce asymmetrical nanoparticles.

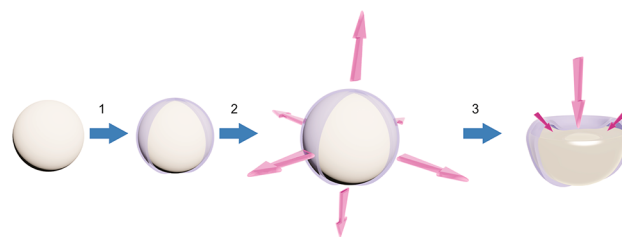
Bowl-shaped particles have recently drawn attention because of their utility in energy storage, photonics, and biomedical applications.<sup>1,2</sup> In particular, polymer particles of this shape are of particular interest because of their potential in drug delivery, developing new assembly structures, and the formation of colloidal surfactants.<sup>2,3</sup> Current methods for producing non-spherical polymer nanoparticles include nanofabrication using dry etching techniques, microfluidics, thermo-mechanical deformation, and single-phase swelling reformation by complex operations, all of which have time, yield, and infrastructure limitations.<sup>2b,4</sup>

One solution to these constraints is through the use of colloidal templates or intraparticle phase separation to chemically synthesize the polymer particles. Various shapes with controllable size and structures, including protrusion, bowl, or other imprinted shapes can be achieved by these embedded templates.<sup>4f,5</sup> Though this strategy can satisfactorily produce nanoparticles in a larger quantity, they are usually limited by the relatively complicated synthesis chemistry as well as other requirements of a rather sophisticated polymerization process that involves careful selection of the seed polymer or monomers.

Hence, there is a need for a simple, cost-effective, and high-yield preparation of uniform, asymmetric polymeric nanoparticles.

The buckling of soft shells outside a soft core is a dynamic but nonselective process that can generate a variety of bowl-shapes without any template. The operation can be achieved by reducing the ratio of the volume of the content to the capsule capacity for micro/nanoscale objects. For instance, the osmotic buckling of micron-sized capsules has been observed *in situ*.<sup>6</sup> However, selectively converting these intermediate shapes into new materials is challenging because the intermediate shapes are unstable, making them difficult to separate and limiting the ability to control the size of the concavity.

In order to develop uniform nanoparticles with controllable concavity, we propose a new route that uses a core–shell nanoparticle and a swelling induced plastic deformation of the shell. Instead of reducing the volume of the encapsulated ingredient, the necessary room for buckling is provided by the plastic enlargement of the shell with a more significant swelling–shrinking process of the core. This volume discrepancy results in a localized compression by the shell and consequent buckling (Figure 1). At the same time, the buckled shell also reshapes the core. This is a facile approach for synthesizing the uniform patterning of an asymmetrical structure with a tunable degree of well-defined concave dimensionality. More specifically, we use the polystyrene@carbon (PS@C) core–shell nanoparticles to demonstrate this concept. In the following discussion, we demonstrate the structure formation, discuss these interactions



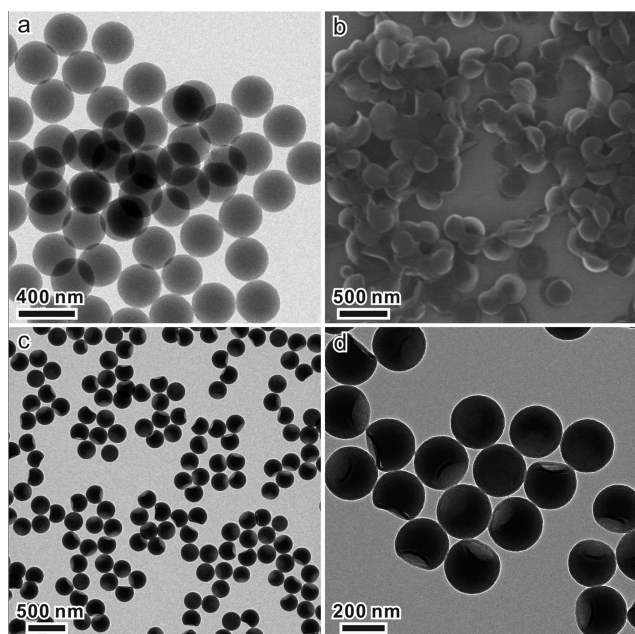
**Figure 1.** Schematic preparation steps of converting a PS nanosphere into the PS@C-K concave nanoparticle: (1) carbon coating; (2) heating process, where PS swelling plasticly enlarges the carbon shell; and (3) cooling process, where deswelling of PS core results in shrinkage. The enlarged shell is pulled in by the core–shell interaction.

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in greater detail, and propose several new structures that might be realized.

Spherical polystyrene particle cores for this swelling-buckling process are prepared by emulsion polymerization initiated with sodium persulfate.<sup>7</sup> Size measurements show that the PS particles have a uniform size distribution of  $210 \pm 9$  nm (Figure S1a). Subsequently, a thin amorphous carbon shell is coated on their surface (Figure S1b) by microwave-assisted hydrothermal carbonization of glucose,<sup>8</sup> forming the shell to be buckled. This shell can be seen clearly after the PS core is dissolved by THF (Figure 2b). The thickness of the carbon shell is tunable by



**Figure 2.** (a) TEM image of monodispersed polystyrene nanospheres without coating. (b) SEM of the carbon shell of PS@C core-shell particle (PS core was removed by THF dissolution). (c,d) TEM of PS@C-K nanoparticles under different magnifications.

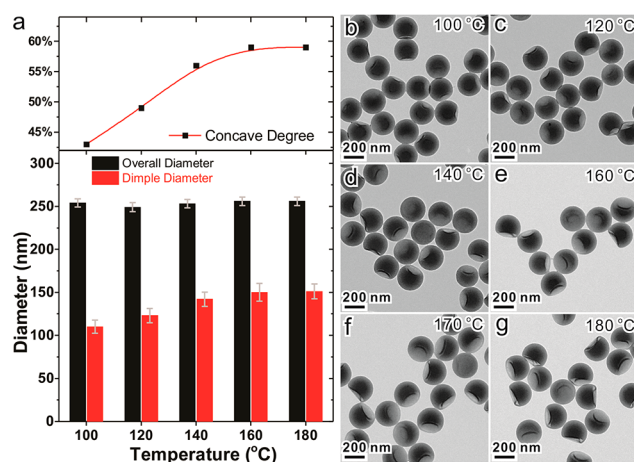
controlling the concentration of glucose, reaction temperature, and time. In the following discussion we focus on creating the concavity using a carbon-shell thickness that is  $20 \pm 5$  nm, which is confirmed by measuring the size distribution of the coated particles (Figure S2). It is noteworthy that deformability of the carbon shell is essential for the formation of concave PS@C. Thicker shells inhibit the creation of the concave structure as discussed in a later paragraph (Figure S3).

The typical concave particles are prepared by an ethanol-thermal treatment of the carbon-coated PS (PS@C) particles at  $170$  °C. Figure 2c,d shows the products of this process. As seen in the TEM images, each particle has a dimpled shape. Particles with this shape are denoted as PS@C-K. By controlling the solvent and treatment temperature, the concave level can be precisely tuned (see below). Size measurements by TEM confirmed that the average diameter of the PS@C particles significantly increased from 230 nm to over 250 nm after the concavity is created. This agrees with our hypothesis that the shell should be enlarged in the synthesis.

In order to estimate the relative volume change in this process, we use the swollen PS core, which has the maximal size in the overall process, as the benchmark (100%). The degree of concavity is defined as the ratio between dimple diameter and the particle overall diameter (particle size). The relative volume

change is estimated by using a geometric model that treats the buckled dimple as a spherical cap (more details for the estimation of relative volume change can be found in Figure S4). Based on the dimple size (110 nm) and particle size (255 nm), the volume change in the formation of the PS@C-K nanoparticles is typically about 15–20%, with consideration of the existence of a hollow cavity. Also, a volume comparison between the PS@C-K with the  $210 \pm 9$  nm PS core also indicates that there is no significant leakage from the shell. In all the experiments that were carried out, the accessible volume change percentage was found to reach about 30% or higher. This volume change is significantly larger than the normal thermal expansion of PS (for instance, one typical thermal expansion coefficient of PS is only about  $8 \times 10^{-4}/\text{K}$ ),<sup>9</sup> which is consistent with the volume increase being due to solvent swelling.

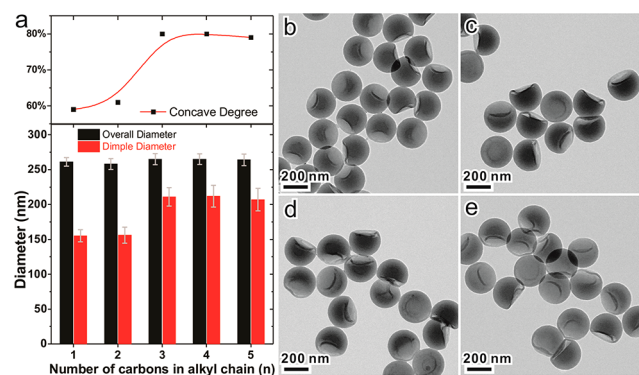
Given the swelling of the PS core confirmed by the volume change, the concavity size should be tunable along with its swelling level. Since higher temperature generally increases the dissolution of solvent molecules in the polymer network and leads to a stronger swelling, we tested a series of temperatures during the synthesis to tune the degree of the buckling. The particle size and dimple diameters of the product both increased with increasing reaction temperature (Figure 3a). Given that the



**Figure 3.** (a) Temperature dependence of particle size and the dimple diameter of PS@C-K nanoparticles prepared by the ethanol-thermal process; the upper panel shows the dimple/particle diameter ratios (denoted as the concave degree). (b–g) TEM images of the corresponding PS@C-K nanoparticles prepared at different temperatures.

glass transition temperature for high-molecular-weight PS is around  $95$ – $100$  °C,<sup>10</sup> the polymer network is significantly expanded under the synthesis conditions. A higher temperature results in more solvent in the PS core, thus creating a stronger tensile stress to the shell and a more significant enlargement. Therefore, it makes sense that samples prepared at  $100$  °C have only a very small dimple since the enlargement of the shell is also minimal (Figure 3b). The overall result is that higher temperatures give a larger swelling volume of the PS core and greater stretching of the carbon shell.

In addition to temperature, another very important factor that controls the polymer swelling process is the type of solvent. In this context we used a series of solvents in the synthesis and characterized the products (Figure 4). The series of solvents includes five homologues of ethanol with small alkyl groups (1–5 carbon atoms). The swelling behaviors of PS are similar for these



**Figure 4.** (a) Solvent dependence of the particle size and dimple diameter of PS@C-K nanoparticles prepared by the alcohol-thermal process at 170 °C; the upper panel shows the concave degree. TEM images of the corresponding PS@C-K nanoparticles using (b) methanol, (c) 1-propanol, (d) 1-butanol, and (e) 1-pentanol.

solvents but have substantial kinetic differences. Also, none of these solvents was able to dissolve the PS nanospheres directly at room temperature. Figure 4a shows the size and concave degree dependence on these solvents. Generally, the concave size increases as the size of the alkyl group increases. The concave size increases from 60% to about 80% from a sample prepared with methanol to one prepared with propanol. According to the molecular structure of PS, alcohols with longer alkyl chains which have lower polarity should have greater affinity to the PS. The trend has been confirmed in previous studies showing that the swelling of PS in alcohols has a positive correlation with the alkyl group chain length.<sup>11</sup>

Our result is generally in accordance with the trend, that the higher alcohols have a better permeability to the PS structure and result in a larger swelling and a larger relative volume change. However, the concave degree stops increasing at about 80% when using a solvent with an alkyl group that is larger than C<sub>3</sub>. In particular, with pentanol, the concave degree decreases slightly. For the swelling of polystyrene in the core-shell nanoparticles, solvents molecules have to permeate through both the carbon shell and the PS network. The discrepancy between this observation and the typical swelling phenomenon may be attributed to the permeability of the solvent through the carbon shell. Since the carbon shell is synthesized from the condensation and polymerization of glucose, its polarity is different from that of PS. The higher alcohols may suffer a greater steric hindrance when diffusing through the carbon shell, although they can permeate more easily through the PS.

On the basis of the product morphology dependence of the synthesis conditions, we propose that the formation of the concavity within the PS@C particles includes two stages. The formation of concavity is the direct result of steps 2 and 3 in the scheme shown in Figure 1 that illustrates the synthesis procedure. The heating process is the first stage (step 2): elevated temperature significantly loosens the polymer network, which allows more solvent molecules to infiltrate into the PS structure. The PS core swells significantly with the inclusion of alcohol molecules. The swollen PS can be regarded as a thick and concentrated solution under this condition with the carbon shell as its differential permeable capsule. The alcohol solvents become hypotonic with respect to the core-shell structure at high temperature. In the second stage, deswelling occurs during the cooling process (Figure 1, step 3). When the nanoparticles are cooled down, the solubility of alcohol molecules in the PS

decreases. Excess alcohol molecules diffuse out from the PS core so that it recovers its original volume. On the other hand, the carbon shell is plastically enlarged, which is in accordance with its glassy 3D network.<sup>12</sup> As the result, the PS core became smaller than the carbon shell. This volume discrepancy establishes room for buckling of the shell to take place at this stage. Our observations suggest that the buckling force should be considered to be the core-shell interface adhesion rather than the capillary force created by the solvent evaporation (further discussion in Supporting Information (SI), page S7).

Elastic energy analysis of soft shells reveals that such an axisymmetric buckling with a single dimple is favored under slow compression.<sup>13</sup> In the synthesis with ethanol, we have not observed any particle with more than one dimple. This suggests that the cooling process is slow enough so that the shell deformation is allowed to establish its lowest energy state, namely the buckled shape with single dimple.

The minimum pressure required for buckling, which depends on the mechanical properties of the shell, is called the critical pressure,  $p_c$  (further discussion of  $p_c$  is included in SI, pages S2–S3). The mechanical model suggests that varying the shell parameters in the experiment may result in different structures. When the shell is too rigid for the internal contraction to overcome  $P_c$ , the core/shell volume discrepancy should only give a cavity, such as the air-cell in the egg. To test this idea, we made PS@C particles with a relative thick shell (over 40 nm) which can significantly increase  $P_c$  and applied the default condition for preparing typical PS@C-K. The predicted unbuckled “air cells” showed up clearly with uniform size (Figure S3). This structure is also reported in a recent study that used a rigid silica shell and mesoporous carbon hemispheres.<sup>14</sup> The partial hollow interior should be an interesting structure for multidrug and multi-transient delivery systems (with two cargos in the hollow and PS side respectively). Another type of similar cases is usually observed in metal-oxide yolk shell structures.<sup>15</sup> The configuration is such that the yolk only has a single connecting point to the shell, which minimizes their contacted area. Both of these cases are the result of lacking core-shell adhesion contraction which supplies the compression force for the buckling. Another type of extreme conditions is when a fast and strong compression is applied to the soft shell, which would then be crumpled at multiple points on its interface with the core. This would result in an appearance similar to that of pepper corn. This condition is discussed in the SI, page S3.

The uniform concave nanoparticles can be used to study colloidal crystallization. Uniform particle assemblies and their derivatives have been widely applied for various applications.<sup>16</sup> Particularly, photonic/colloidal crystals formed using asymmetrical building blocks can promote photonic band gaps with lower refractive index contrasts as well as complete photonic band gaps that can trap photons more efficiently.<sup>17</sup> In this context we assembled PS@C-K nanoparticles in order to get a preliminary perspective of the impact of their concavity on colloidal crystallization. Generally, spherical particles tend to assemble into a close packed lattice (either hcp or fcc). For instance, the starting material of this work, PS spheres can assemble into a highly ordered close packed lattice (Figure S6a). However, as expected, we found that PS@C-K particles cannot easily form this type of lattice. Because of the concave shape, the interaction between particles has an orientation bias when they approach each other. Arrays of a “head-to-tail” configuration are more favorable and observed over a short-range (Figure S6c). Translational symmetric structures are possible in our

conditions, but the domains are very limited in size because of the more complicated interparticle interactions. We have found some long-range ordered structures but only in small areas compared with those observed for the close packing of spheres (Figure S6b). Moreover, the packing density in these assemblies is significantly lower than that for close packed spheres. Some areas clearly appear as a bcc lattice with disordered particle orientations. The PS@C-K particles thus tend to give each other larger space to tolerate their intrinsic asymmetry. Further investigation on how the concave part affects the assembly process and how asymmetric oriented arrays might be vectorially assembled by, e.g., epitaxially induced polar layer assembly or by greater gradient variation of the asymmetric particle surface energy, are needed.<sup>18</sup> One promising approach is to epitaxially initiate the assembly on an appropriate periodically functionalized substrate.<sup>19</sup>

In summary, we have developed a robust method for creating a tunable concave structure for carbon-coated PS particles. The concave evolution can be fine-tuned by varying synthetic conditions such as the temperature and solvent. We propose a mechanism by which the polystyrene core is significantly softened by swelling at a slightly elevated temperature (as low as 100 °C) and behaves like a hypertonic solution within a carbon shell. During this process, the carbon shell is plastically expanded by the tensile stress from swollen PS core. Later in the cooling step, this stress is switched to compression as a result of the PS-carbon adhesion at the core-shell interface. The carbon shell can be readily made with a suitable elastic modulus that fits the requirement of creating buckling of the PS core with a single dimple. Deviation from this mechanism, e.g., air-cell or peppercorn structures, is possible using synthetic procedures with proper core and shell parameters. This demonstration of the ability to engineer polymer nanostructures by a swelling process can be helpful and instructive for the design of new structures with cavity and lower ordered broken symmetries.

## ■ ASSOCIATED CONTENT

### Supporting Information

Synthetic methods, geometric calculations, additional SEM and TEM images, discussion of buckling mechanism. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b05027.

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### Notes

The authors declare no competing financial interest.

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