

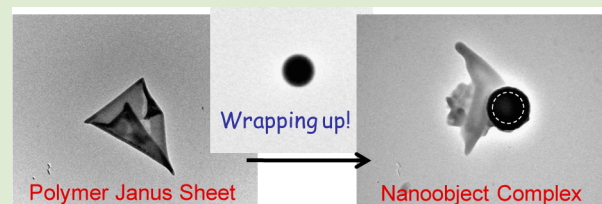
# Dumpling-Like Nanocomplexes of Foldable Janus Polymer Sheets and Spheres

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**S** Supporting Information

**ABSTRACT:** The formation of object complexes between Janus nanosheets and cross-linked polystyrene (PS) microspheres is reported. Sheets with one side tethered with PS chains and the other with poly(2-vinyl pyridine) made from triblock terpolymers were confirmed to be foldable by the addition of acidic water to their dispersion in tetrahydrofuran (THF). When acidic water was added to a THF dispersion of the sheets in the presence of PS spheres of 226 nm, dumpling-like complexes of two different nanoobjects were obtained by wrapping the spheres with the sheets.



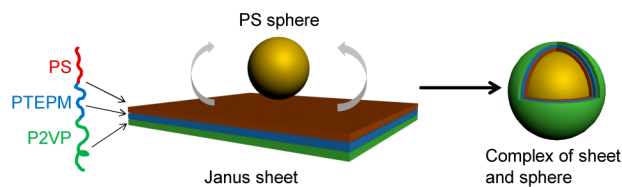
Similar to the atoms and molecules that form molecular crystals and assemblies, nanoparticles or nanoobjects are used as self-assembly building blocks to generate new materials that have attracted much interest over the last two decades. Both macroscale colloidal crystals for photonic materials and colloidal clusters for microscaler assemblies have been produced.<sup>1–5</sup> Controlled interaction of binary nanoparticles using static interactions,<sup>6,7</sup> the depletion effect,<sup>8</sup> and patchy particles<sup>9</sup> has been applied to obtain clusters and assemblies of nanoparticles. It is known that supramolecular chemistry of molecular counterparts is a state-of-the-art achievement of modern molecular science. For example, guest molecules encapsulated with host molecules via noncovalent interaction form supramolecular complexes. However, as far as we know, there is no report of the self-assembly of different shaped nanoobjects to form encapsulated complexes. Herein, we report a foldable Janus polymer nanosheet that enwraps polymer spheres to form a nanocomplex driven by hydrophobic interaction in a selective solvent.

Janus nanoparticles, a class of colloidal materials having two or more areas with different chemical compositions, include spherical, cylindrical, and sheet-like morphologies.<sup>10–13</sup> Among these, two-dimensional Janus nanosheets have an interesting structure with a distinct chemical composition on each face.<sup>14,15</sup> However, relative to Janus nanospheres and nanocylinders, much less research on the preparation and properties of Janus sheets has been performed. Walther et al. prepared polymeric Janus sheets by cross-linking B layers of lamellar microphase-separated ABC triblock terpolymers and then dispersing them in a common solvent of the A and C segments.<sup>14</sup> The obtained nanosheets with a uniform thickness of polymer chain length scale had a blanket-like structure with the A and C segments densely tethered along the two faces. Bending Janus sheets of block copolymers was observed under certain conditions.<sup>16</sup>

In this communication, we generated giant Janus nanosheets from poly(2-vinylpyridine)-*block*-poly(3-(triethoxysilyl)propyl methacrylate)-*block*-polystyrene triblock terpolymer, P2VP<sub>310</sub>-

*b*-PTEPM<sub>58</sub>-*b*-PS<sub>322</sub>, and demonstrated that they were foldable by changing solvent environment. Most importantly, we have demonstrated complexation between the Janus sheets and PS spheres by wrapping self-assembly. The driving force was the hydrophobic interaction of the PS spheres with the PS face of the sheets as shown in Scheme 1. Since the sheets were polydispersed in size, huge sheets capturing one, two, three, or more PS spheres was observed.

## Scheme 1. Schematic Illustration of a Foldable Janus Polymer Sheet, Sphere, and Their Complex by Hydrophobic Interactions



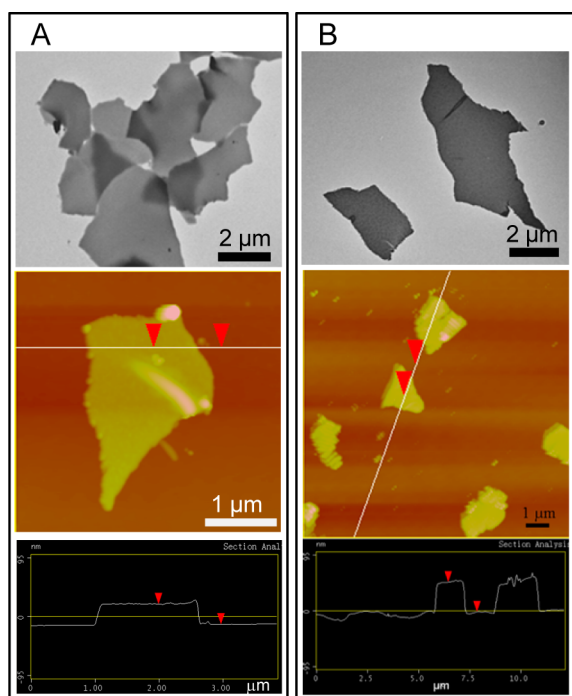
The bulk P2VP<sub>310</sub>-*b*-PTEPM<sub>58</sub>-*b*-PS<sub>322</sub> has a lamellar structure, and cross-linking the PTEPM layers produces sheet-like particles in solvent.<sup>17</sup> The preparation followed a procedure of bulk block copolymer microphase separation, selective cross-linking, and solvent dispersing.<sup>18,19</sup> The bulk structure of P2VP<sub>310</sub>-*b*-PTEPM<sub>58</sub>-*b*-PS<sub>322</sub> was characterized by SAXS and TEM. A highly ordered packed lamellar morphology with a peak position ratio of 1:2:3:4:6 was observed in Figure S1A (in Supporting Information). The domain spacing was calculated to be 52 nm. Without staining, the silica-rich regions of the PTEPM layers were visualized from a microtomed slice by TEM (Figure S1B, Supporting Information). Thus, the basic

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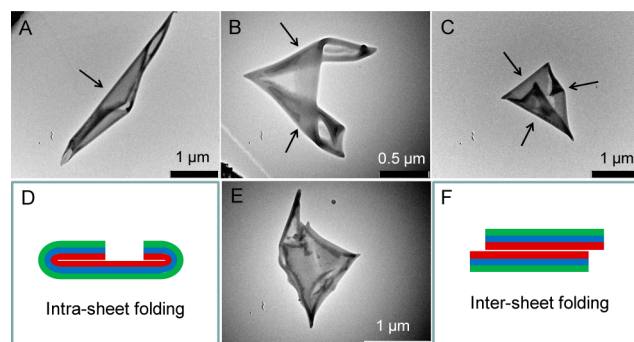
bulk triblock terpolymer layers were 26 nm in thickness, which were stacked back-to-back with similar neighboring layers (Scheme S1A, Supporting Information). The PTEPM middle layer was then cross-linked by silicate gelation, forming Janus sheets with tethered PS chains on one face and P2VP on the other. Since the two faces of single gelated sheets were distinct, different dispersing solvents can have varying effects on the sheet structure. We first dispersed the microphase-separated materials in THF, which is a common solvent of PS and P2VP. TEM and AFM images (Figure 1A and Figure S2, Supporting



**Figure 1.** TEM and AFM height images of (A) Janus sheets obtained from a THF dispersion and (B) bis-sheets from acidic water.

Information) show thin, micrometer-sized sheets with irregular periphery. As revealed by the AFM height image (in Figure 1A), the thickness was ca.  $35 \pm 3$  nm, which agreed with the thickness of unisheets (Scheme S1B, Supporting Information). The bulk materials were also directly dispersed in acidic water which protonates and dissolves the P2VP face. Since the PS layer from one sheet stacks face-to-face with another PS layer in bulk, bis-sheets were obtained in water, a poor PS solvent, as confirmed by TEM and AFM images (Figure 1B). From the height profile, a thickness of  $56 \pm 2$  nm was found, which nearly doubled that of the unisheets from THF. To confirm the P2VP chains located along the two faces of the bis-sheets, gold nanoparticles, ca. 10 nm, were formed in situ by adding Au ions followed by a reduction. Figure S3 (Supporting Information) implies that these gold particles are trapped along the surfaces of the sheets. Thus, the bis-sheets were composed of two unisheets with back-to-back PS layers and protonated P2VP layers exposed to acidic water (Scheme S1B, Supporting Information).

To confirm the Janus structure and its foldability, acidic water (pH = 2), a bad PS solvent, was added to a dispersion of the unisheets in THF. A colloidal dispersion was obtained, and the particle morphology was analyzed by TEM. As shown by TEM (Figure 2A–C) images, these sheets were folded in an intrasheet manner (Figure 2D), which was the morphology

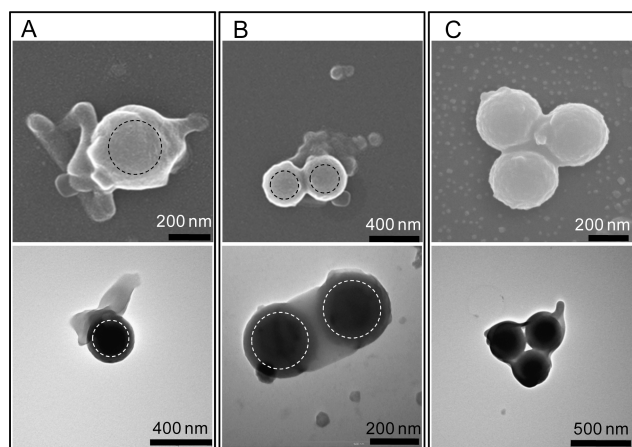


**Figure 2.** TEM images of (A–C) the intrasheet folded sheets and (E) the stacked Janus sheets induced by adding acidic water into a THF dispersion of Janus sheets. (D, F) Schematic representation of folded and stacked sheets. The arrows in A–C indicate the folding direction.

mainly observed. Also, intersheet aggregates were occasionally found (Figure 2E and 2F). Either the intrasheet bending or the intersheet stacking keeps the hydrophobic PS layers wrapped inside to prevent facing the water. Thus, the bending modulus of the block copolymer sheets is not high, and intrasheet folding is a preferential process. Because the size and shape of the Janus sheets were irregular, the sheets were folded irregularly. Further evidence of the amphiphilicity of the Janus sheets was given by the formation of a stable emulsion of toluene in water in the presence of the sheets (Figure S4A, Supporting Information). From SEM (Figure S4B, Supporting Information) and TEM images (Figure S4C, Supporting Information) of dried droplets, it was demonstrated that the Janus sheets were organized along the oil–water interface.

With the above results, amphiphilic, microscale, foldable Janus sheets were obtained and used to capture guest particles through hydrophobic interactions as a sheet-like host. Monodispersed PS spheres (Figure S5, Supporting Information) of 226 nm cross-linked by divinylbenzene (20 wt %) were mixed with the Janus sheets in THF, to which acidic water (pH = 2,  $5 \times$  volume) was added slowly. The colloidal complexes were visualized by SEM and TEM.

Figure S6 (Supporting Information) shows a low-magnification SEM image in which a contour profile of protruding objects of 300–400 nm was observed, along with flat irregular objects along the substrate. Detailed structural information was easily obtained by electron microscopy from the individual complexes in which one, two, three, or more spheres were encapsulated by sheets. For the single sphere case (Figure 3A), both SEM and TEM images demonstrated that the spheres were covered with deformed Janus sheets. The diameter of the spherical complex in a TEM image (Figure 3A, also from different complexes as shown in Figure S7, Supporting Information) was measured to be 310 nm, which is significantly larger than the parent PS sphere (highlighted by dashed circle). The increased size should be attributed to the Janus sheet skin, which had a thickness estimated to be 42 nm, close to the thickness ( $35 \pm 3$  nm) of unisheets measured by AFM. Therefore, a nanocomplex of a Janus sheet and PS sphere was obtained. It is noteworthy that partial sheets did not adhere to the guest sphere (see Figure S7, Supporting Information). This was mainly attributed to the irregular shape of the sheets that was difficult to completely match to the shape of the guest spheres. The images in Figure 3B and 3C demonstrated the complexes could also contain two and three spheres. It seems that two or three spheres were wrapped mainly by one host



**Figure 3.** SEM (top) and TEM (bottom) images of PS spheres complexed by Janus sheets. Dashed circle represents the size of PS spheres in the complexes.

sheet. Moreover, complexes with more spheres were observed from the substrates shown by Figure S8 (Supporting Information) (SEM images) and Figure S9 (Supporting Information) (TEM images). The number of guest spheres may be easily counted from these images. It is also interesting that there were isomer complexes observed. Figure 3C and Figure S9A (Supporting Information) show complexes with three guest spheres that were packed geometrically in two different ways. Five-sphere complexes organized in two ways with Janus sheets were also observed (Figure S9C and 9D, Supporting Information). It is expected that more isomers appear as more guest spheres are included.

The remarkable observations above clearly proved the complexation occurring between different shaped nanoobjects: the foldable Janus polymer sheet as a host and a sphere as a guest. The driving force is based upon the simple hydrophobic interaction between the PS sphere and the PS inner layer of the sheet in a selective solvent. The stiff PS spheres are covered by the PS side of the Janus sheets as much as possible to prevent exposure to water. It is imaginable that one giant sheet may bind one guest sphere, while several small sheets may also stabilize one sphere. For the present system, the spheres were monodispersed, whereas the sheet size was poorly controlled in plane. Thus, the structure of the nanocomplexes was not tailored, which represents our next effort.

In summary, self-encapsulation of polymer spheres by Janus sheets made from block copolymers was reported, and thus the host–guest-like complexes of particles were generated. Though the present complexation model is simple and far from a tailored structure, this finding may open a new area to build complexes of various nanoobjects from one hundred nanometers to micrometers that may demonstrate functions like particle delivery, stimuli-responsive nano-/microself-assemblies, and nano-/microrobot fabrication.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

Experimental, Scheme S1, and Figures S1–S9. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

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