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Droplet-assisted Fabrication of Colloidal Crystals from Flower-shaped Porphyrin Janus Particles

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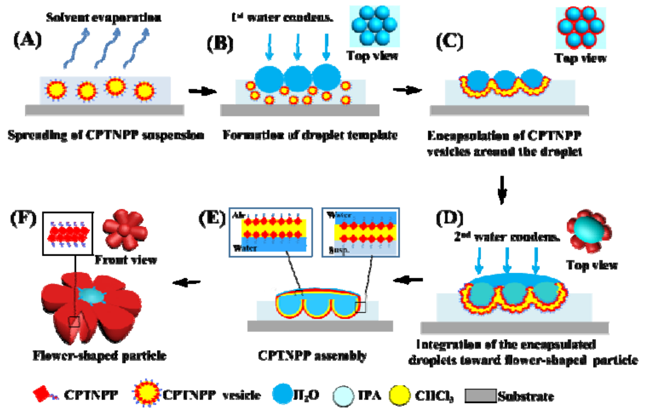
A facile fabrication of flower-shaped porphyrin Janus colloids with oriented arrangement was demonstrated based on the interfacial assembly and water droplet template. The as-fabricated colloidal crystals from flower-shaped Janus particles show special optical signal resulted from the hierarchical structures.

The anisotropy of Janus particles[1-2] has attracted wide interest owing to their unique applications[3-11] in self-assembled hierarchical structures,[3a-b,6a,7a] solid surfactant,[6a-b] asymmetric catalytic systems,[8b] spatially-controllable chemical reactions,[11b] optic materials[10a,11a] and etc. During the past decade, numerous techniques have been established to synthesize Janus particles,[3-11] including electro-hydrodynamic jetting,[3a,8b,11b] microfluidics assembly,[9c] emulsion polymerization,[5a-b,6b] layer by layer assembly,[9a-b] masking coating,[4a,c], and micro-contact printing.[4b] These progress contributes to the successful fabrication of a plethora of Janus particles with controllable size/shape. However, there remains a challenge to fabricate Janus particles with hierarchical structure and keep orientated arrangement, using a facile protocol.[12-13] Droplet template[14-15] has became an effective approach for the formation of porous film to deposit nanoparticles, proteins, and quantum dots. Herein, we demonstrated one-step fabrication of flower-shaped Janus particles with orientated assembly by droplet template method, it was expected that the colloidal crystals assembled from flower-shaped Janus particles may produce an unique optic property[16] based on the hierarchical structures.

In this paper, a physical-anisotropic flower-shaped Janus particles with orientated assembly is facilely achieved from the porphyrin derivative of 5-(4-(ethylcarboxypropoxy)phenyl)-10,15,20-tri(naphthyl) porphyrin (CPTNPP) based on the two-step water droplet condensation process. As shown in Scheme 1, the 1st water condensation in Scheme 1B resulted in the formation of the Janus petal microparticles. The Janus characteristic of petals is stemmed from the distinct encapsulation of CPTNPP around the two interfaces of droplet in Scheme 1C: the concave side is formed at the water-suspension interface, while the flat side is produced at the air-water one. The subsequent 2nd condensation of droplet (in Scheme 1D) induces the integrated aggregation of the Janus petals toward the flower-shaped particles. The orientated arrangement of flower-shaped Janus particles can be attributed to the well-ordered assembly of the droplet template, with its concave side toward suspension phase and its flat side toward the air phase. Importantly, the colloidal crystals resulted from orientated assembly of flower-shaped Janus particles, contribute to the multi-wavelength optical signal. The work provides not only a facile approach for the fabrication and assembly of Janus particles, but also an important insight for the creation of novel optical materials.



Scheme 1. Schematic illustration of the formation process of flower-shaped porphyrin Janus particles. The process includes spreading CPTNPP suspension onto the substrate (A), formation of water droplet template (B), encapsulation of the water droplet template by CPTNPP vesicles (C), the integration of the encapsulated droplet toward flower-shaped Janus particles (D), and the resultant CPTNPP assembly in the particles (E, F). The inserted scheme is to guild the understanding of the formation process of the particle.

Scheme 1 presents the typical formation process of flower-shaped Janus particles from CPTNPP. Firstly, CPTNPP suspension was spread onto the hydrophobic substrate at 0℃ with the humidity of 50% in Scheme 1A. The suspension was prepared by mixing the chloroform solution (10^{-5}~10^{-6}mol/L) of CPTNPP into isopropyl alcohol (IPA), forming the CPTNPP vesicles (confirmed from Figure S1 in the supporting information). Subsequently, the droplet template formed on the interface of air-suspension, arousing from the 1st water condensation owing to the solvent evaporation in Scheme 1B, yielding a new water-suspension interface (confirmed from Figure S2B and S3). Followed by the encapsulation of the water droplet by CPTNPP vesicles at both interfaces of air-water and water-suspension, hemispheric Janus petals were produced from droplet template in Scheme 1C. Afterwards, 2nd water condensation integrated all of these petals altogether with consistent orientated arrangement (in Scheme 1D), similar to a flower stalk connecting all of Janus petals toward flower-shaped particles. Finally, the interfacial assembly of CPTNPP contributed to the flower-shaped particles in Scheme 1E and 1F, with complicated morphology, i.e., integrating flat and concave into one large particle (as shown in Figure 1B).

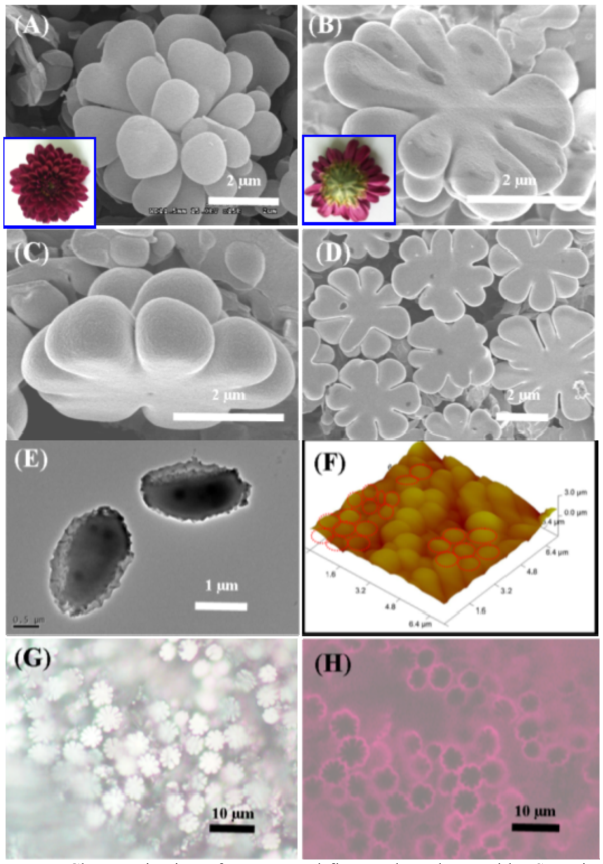


Figure 1. Characterization of as-prepared flower-shaped assembly. SEM images of front side (A), back side (B), cross-section (C) and aggregation (D) of as-synthesized flower-shaped particles. (E) TEM and (F) AFM image of flower-shaped particles, the inserted red circle is to guide the observation. (G) optic-microscopy and (H) fluorescent image of the large-scale flower-shaped particles. The inserted photos in left bottom of Figure 1A and B are the front side or back side of the actual flower, to comparing the as-fabricated flower-shaped particles.

Figure 1 presents the morphology characterization of the as-formed flower-shaped Janus porphyrin particles. Clearly, the flower-shaped particles show a distinct structure between its front and back side. Its front side looks like a vivid blossom multi-layered flower in Figure 1(A), containing of the aggregation of many micropetals, similar to the actual flower inserted in left bottom of Figure 1A. While its back side shows the flat contour structure produced from the fusion of flower petals microparticles in Figure 1(B). The blurring interface in the center can be attributed to the fusion effect of the 2nd water condensation, similar to a stalk integrating the micropetals around the center, as inserted flower in the left bottom of Figure 1B. These can be confirmed from the cross-section image in Figure 1(C): a clear 3-dimensional structure of the flower-shaped particles with smooth back side and the concave front side of the particles, suggesting the two-faceted property, i.e., Janus characteristic of the whole particle. TEM image in Figure 1(E) shows different dark shade, indicating the hollow cavity structure of the flower-shaped particles (confirmed from Figure S4). Its wavy-like brim can be attributed to the aggregated structures from microparticles. AFM image in Figure 1(F) proves that the flower-shaped particles are actually the aggregation of the porphyrin nanoparticles, with a typical 6~7 particles surrounded around one centered particle acting as the stamen, while the surrounding particles served as flower petals. Optic photo in Figure 1(G) and fluorescent image in Figure 1(H) demonstrate large-area flower-shaped Janus particles. Importantly, the flower-shaped Janus particles show well-orderly directional-assembly, spanned more than hundreds of micrometers, with its flat back-side orientated toward the air, while the concave front side toward the substrate.

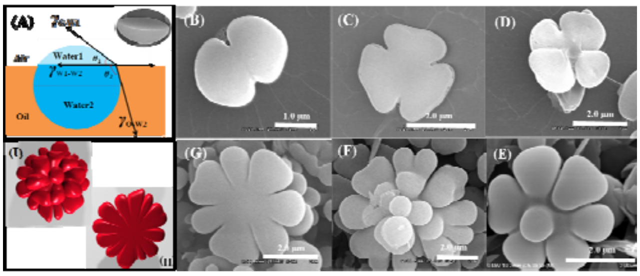


Figure 2. (A) Schematic illustration for the formation of Janus petals, the inserted is the SEM image for the Janus petals. (B-G) SEM images of the flower-shaped particles with different petals, (B) two-, (C) three-, (D) four-, (E) single-layer flower, (F) multi-layer flower, (G) back side of the flower. And (H) and (I) scheme for the back and front side of the flower.

Droplet template condensation plays a crucial role on the formation of Janus petals and their integrated aggregation toward the flower-shaped particles. The formation of Janus petals can be attributed to the 1st condensation of droplet template (in Scheme 1B), while the integrated aggregation of petals toward flower-shaped particles is aroused from the 2nd droplet condensation (in Scheme 1D). When the 1st droplet condensation occurs to the suspension in Scheme 1B, producing new interfaces of suspension-water and air-water as shown in Figure 2A (confirmed in Figure S3). The encapsulation of CPTNPP at both interfaces promotes the production of the uneven particles owing to the different interfacial tension.[14a] Concretely, the shape of the two interfaces can be predicted by the modified Young's equation,[17] indicated by θ_1 and θ_2 respectively in Figure 2a (the detailed derivation process can be seen in the supporting information, Scheme S3, equation S1~S5). That is, the resultant petal particle is a combination of the two parts. The flat structure is obtained at the air-water interface, while the concave structure is formed at the suspension-water interface indicating the formation of Janus petals (as shown in inserted SEM image in Figure 2a). In our system, the value of $\cos\theta_1/\cos\theta_2 = -\gamma_{w\text{-}O}/72$ (the derivative process in the supporting information). Since the $\gamma_{w\text{-}O}$ is smaller than 29.49 (seeing Table S1 in the supporting information), $\cos\theta_1/\cos\theta_2$ is smaller than 0.41, implying the Janus characteristic of the as-formed petal particles.

The 2nd condensation of droplet (in Scheme 1D and E) acts as a flower stalk that integrates the petals together toward the flower-shaped particles, blurring the interface among the micropetals in Figure 1B. Simultaneously, 2nd condensed droplet induces the deformation of the petals to fit the flower-shaped particles as shown in Scheme 1D and 1F. Clearly, different deformation of the petals is observed for one-, two-, three-, four-, five-, or even seven-petal single-layer flower-shaped aggregates in Figure 2A-E. In the process, the aggregated particles acted as the flower petal or flower stamen in Figure 2E. Furthermore, the complicated multi-layer aggregation is produced by gathering together of petals simultaneously. Figure 3 exhibits an *In-situ* optical images for the formation process of flower-shaped particles after 2nd water condensation accompanied with increased growing time, that is taken from high-speed camera (see Figure S5). At first, no obvious image is observed for the water droplet template forming at the suspension in Figure 3A. Subsequently, an enhanced and spreading shinning part is seen with an increased exposing time after 2nd water condensation in Figure 3B and 3C. When taking a close at the shinning part, beautiful flower-shaped particles can be observed as shown in the inserted image in the left bottom of Figure 3 C, that arousing from the aggregate structure of different petals. Figure 3E-F show a detailed description of the influence of the 2nd water condensation on the flower-shaped particles (indicated by the blue circle). Obviously, the condensation process directionally aggregated the petals toward the center, leading to the deformation of the particles from hemispherical to the extended one, accompanied with a simultaneous melt and coagulation among petals as indicated by blue circle in Figure 3E-3F. In contrast, the petals kept separated and perfect hemispheric structures (red circled in Figure 3F) in the absence of the 2nd condensation process. It should be emphasized that the 2nd condensed process endows the resultant aggregate with the two-facelet characteristic, i.e. Janus property. The front side of the particles looks like a blossom flower in Figure 1(A) and 2(F), remaining an intrinsic and separate shape/property of the petals. While the back side of the particles just shows the flat contour structure (Figure 1B, 2G) left by the aggregate petals, keeping the composite shape/ property of the petals.

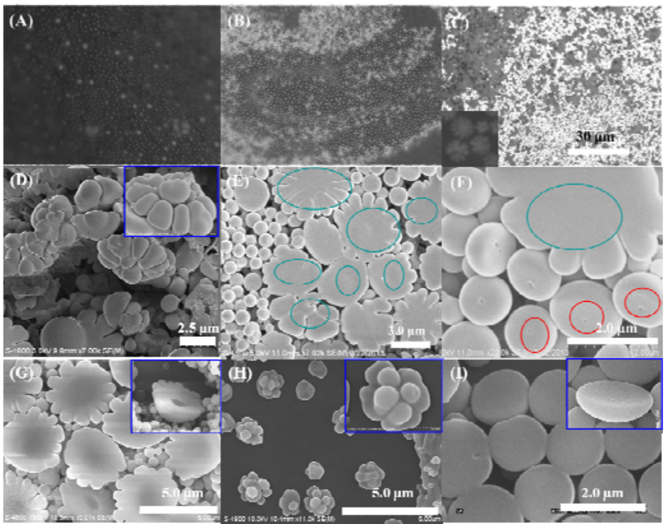


Figure 3. (A-C, E-F)Influence of the 2nd water condensation on the formation of flower-shaped particles. (A-C) *In-situ* optic images of the formation process for the particles after 2nd water condensation accompanied with prolonging growing time. (E-F) Typical SEM images for the aggregation and deformation of Janus petals toward flower-shaped particles. The blue circle indicates the 2nd condensed droplet, red circle indicates the particles in the absence of the condensation process. (D,G)SEM images of flower-shaped particles produced from CPTNPP suspension with IPA fraction of 70% (D) and below 30% (G) at the humidity of 50%. And SEM images of the flower-shaped particles produced from IPA fraction of 50% at the humidity lower than 30% (H) and over 80% (I).

The detailed shape of petal particles can be adjusted by changing the droplet template based on the modulation of solvent component and environmental humidity as shown in Figure 3D, G and Figure 3H, I respectively. Figure 3D and G show the influence of IPA fraction in CPTNPP suspension on the resultant petals particles and the flower-shaped particles. Clearly, when the sample is assembled from CPTNPP suspension with higher IPA fraction, such as 70%, a sheet-like flower-shaped particle is obtained in Figure 3D; while foot-morphology of flower-shaped particles are obtained when the sample is assembled from CPTNPP suspension with lower IPA fraction, i.e., 30% in Figure 3G. The influence of IPA fraction in CPTNPP suspension can be attributed to the influence on the interface tension between water droplet and suspension based on the modified Young equation[17] (the detailed explanation can be seen in Scheme S3). Increased IPA fraction in CPTNPP suspension results in a decreased interface tension between water droplet and suspension (see Table S1 in the supporting information), leading to the water droplet with low contact angle (CA). Which causes sheet-like petals and the corresponding flower-shaped particles in Figure 3D. While the decreased fraction of IPA leads to an increased CA of water droplet on suspension, getting a fat petals and the corresponding foot-morphology of flower-shaped particles in Figure 3G. The suitable IPA fraction in the mixture is helpful for the formation of flower-shaped aggregation owing to full contact and easy entanglement of the porphyrin molecule around the water droplet with smaller CA. Otherwise, environmental humidity affects the flower-shaped particles by modifying the amount of water droplet formed on the suspension. Tiny flower-shaped particles are obtained with the humidity below 50% in Figure 3H, while the continuous films assembled from cake-shaped particles are prepared at the humidity over 80% in Figure 3I. The flower-shaped particles are obtained under suitable humidity of 50%-70% in Figure 1.

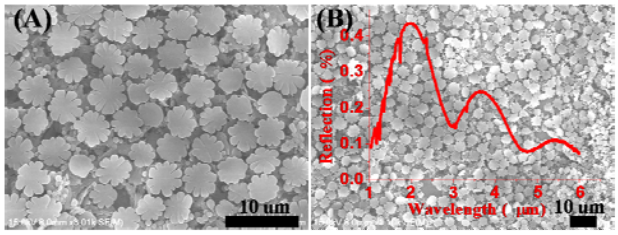


Figure 4. Large-area flower-shaped assembly with orientated arrangement and its optic properties. (A-B) SEM images of large area of the as-synthesized flower-shaped particles. The inserted in B is the reflection spectrum of the samples

Importantly, the as-fabricated flower-shaped Janus particles keep directional orientation at the interface of air/suspension, which can be attributed to well-ordered arrangement of the water droplet template in Figure 4(A), (B). The orientated assembly of the flower-shaped particles toward the colloidal crystals contributes to the special optic properties as shown in Reflection spectrum inserted in Figure 4(B)(measured from FTIR (Bruker, VERTEX 70, 36×, NA = 0.5). The three-wavelength spectrum are corresponding to the integration effect of the building blocks of nanopetals, one-layer and multi-layer flower-shaped particles respectively.

According to Bragg reflection: [13a,18]

$$\lambda_{max} = 2dn_{eff} \sin\theta$$

where λ_{max}, the wavelength of the diffraction peak; *d*, the thickness of the building blocks in large-area flower-shaped assembly. In our case, d_{petal} = 0.5~0.8 μm, $d_{one\text{-}layer\ flower}$ = 0.8~1.5 μm, $d_{multi\text{-}layer\ flower}$ =1.5~2.5 μm, the data is read out in Figure S6; θ is an angle of incidence, and $\theta = 90°$ in our experiment; n_{eff} is the effective refractive index of the hollow CPTNPP flower-shaped particles. The calculated λ_{max} is 1.9, 3.6 and 6.1 μm respectively, the data are close to that measured one from the spectrum (λ_{max} = 2, 3.6, 5.5 μm, detailed calculation in Scheme S4).

Conclusions

In conclusion, flower-shaped Janus particles with oriented arrangement were successfully fabricated by the combination of water droplet template and interface assembly. The as-prepared flower-shaped colloidal crystals show a multi-wavelength optical signal produced from the hierarchical structures. This fabrication of flower-shaped Janus particles not only provides a new approach for the design and assembly of Janus particles, but also is of great importance for the construction of novel assembly structure. And it may bring about some potential applications in optic devices.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [Materials, experimental section, characterization and the analysis for the flower-shaped assembly and the optic property of the resultant film]. See DOI: 10.1039/c000000x/

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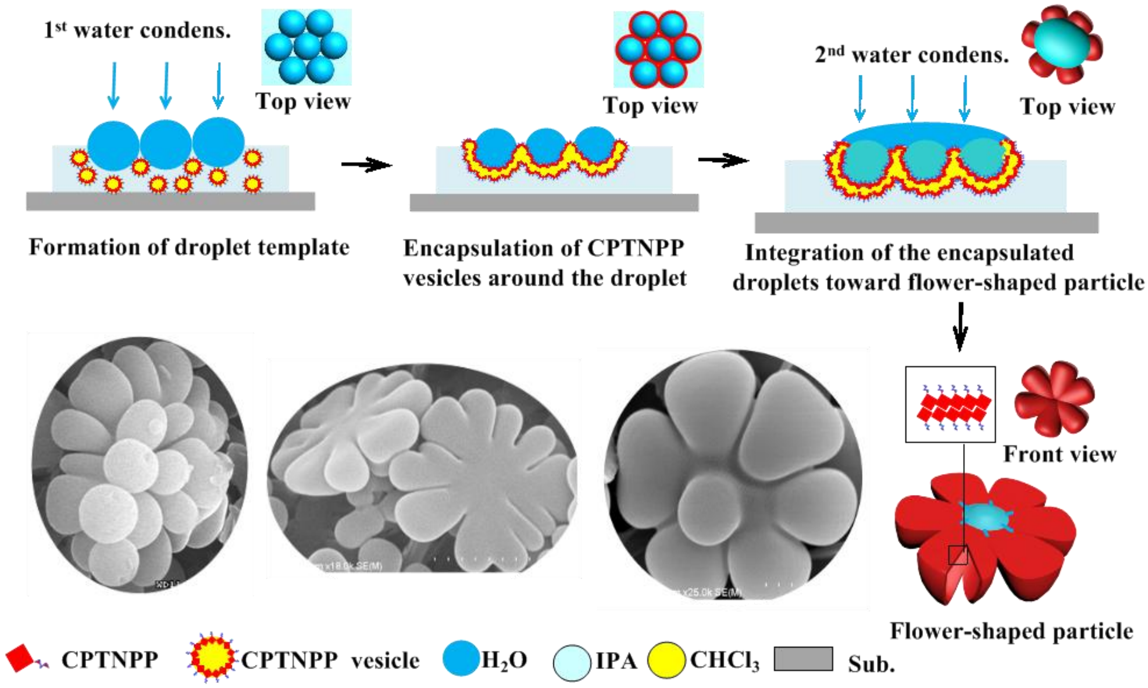

A porphyrin colloidal crystals flower-shaped Janus particles were fabricated by two-step droplet condensation.