One-step preparation of magnetic Janus particles using controlled phase separation of polymer blends and nanoparticles†

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We present a simple method with the aid of a microfluidic droplet-generation technique to fabricate magnetic Janus particles by utilizing a solvent evaporation-induced phase separation and preferential partitioning of magnetic nanoparticles in the polymer blends. Non-aqueous emulsion droplets of the polymer blends and nanoparticles solution are produced to become Janus particles after the evaporation of the solvent. The stabilizing polymer of the nanoparticles, which is compatible only with one of the polymer blends to be phase-separated, plays a key role in the anisotropic positioning of the nanoparticles in the Janus particles. Using this phase separation-based method and microfluidics, excellent control over the size, size distribution, and morphology of the particles is achieved. Especially, we could control the morphology of the Janus particles easily by varying the volume ratio of the polymers. However, with an analysis of the shapes of resulting Janus particles, we found that non-equilibrium aspects of the evaporation-induced phase separation play a major role in determining the particle morphology. We expect that the versatility of this method in the choice of polymer blends and functional nanoparticles will enable the fabrication of colloids with various functionality and desired morphology.

Introduction

Janus particles are, in a broad sense, particles in which two or more compartments have distinct properties such as shape, chemistry, catalysis and electric/magnetic susceptibility, resulting in anisotropic characteristics.1,2 Since de Gennes raised the concept of Janus particles,3 numerous strategies for the fabrication of them have been developed, and their applications have been expanded into colloid chemistry, optics and biomedicine. For example, stamp coating,4,5 colloidosome,6,7 sputtering,8,9 liquid–liquid dispersion followed by deformation,10–13 cross-linking of liquid crystalline monomer,14 and Langmuir–Blodgett method15 have been employed to fabricate anisotropic particles to be used in rheological fluids,10,16 particulate surfactants,17–19 and electro/magnetophoretic displays.20,21 A number of reviews have been focused on these fabrication methods, their characteristic self-assembly and applications.1,2,22–27

Moreover, we can incorporate anisotropy in field-responsiveness into Janus particles, which enables various kinds of manipulation of the particles. For example, not only orientation and motion of a single particle can be controlled but also field-induced suprastructures can be assembled in a reversible way.8,20,28–37 Particularly, magnetic Janus particles have received remarkable attentions due to several advantages over other types of interaction;28–39 the magnetic interaction is generally not influenced by surface chemistry of particles and characteristics of solvent such as pH, ionic concentration and its dielectric constant as in electric interaction.

Many strategies to prepare field-responsive Janus particles have been developed2,22–24 and include metal evaporation,8 microfluidic co-flow system,20 flame synthesis,30 sonochemical synthesis,39 and biphasic electrified jetting.40 In addition, a phase separation-based method, which is based on the miscibility of two or more materials, has been one of the main schemes for preparation of Janus particles.22,24 Examples include phase separation of polymer blends,41,42 seeded polymerization of monomer on cross-linked polymer particle,28,43,44 and phase separation of a polymer and inorganic nanoparticles.31,36,38 Although the phase separation-based method is one of the most facile and cost-effective way to fabricate Janus particles, preparation processes by emulsion
polymerization or conventional emulsification methods such as homogenization show some difficulties in controlling the size and structure of particles. \(^2,^24\) Microfluidic droplet technology helps production of monodisperse particles but Janus particles usually require multiple inlets of co-flowing system which increases the complexity of the system. \(^2,^20,^31,^32\) The size and the ratio of each compartment can be adjusted only by controlling the flow rates, which are difficult to handle especially when using multiple liquids with different properties such as viscosity and limit the versatility of Janus structures.

In this article, we introduce a new method to prepare magnetic Janus particles by utilizing preferential partitioning of nanoparticles in phase-separated polymer blends confined in microdroplets. The anisotropic positioning of functional nanoparticles in a Janus particle results from the characteristic of the stabilizing polymer which stabilizes the nanoparticles and is miscible only with one component of the polymer blends to be phase-separated (Fig. 1a). This strategy of preferential partitioning with polymer-stabilized nanoparticles to prepare Janus particles has not been reported, and has several advantages over previous methods. First, it is easy to control the internal architecture of Janus particles by simply changing the volume ratio of each component in the polymer blends for phase separation. Second, with the aid of microfluidic droplet generation, the initial size of the emulsion confinement can be monodispersely controlled, and this enables high-throughput production with a single-droplet generation step. Since we only prepare one blend of polymers initially mixed with nanoparticles, we do not need multiple inlets, complex microchannel devices or multi-step processes but a single emulsification step to create variety of structural composition of Janus particles. Besides the advantages of easy implementation of microfluidic technology, there are several other features which give novelty to our method. First, our method allows more choices of polymers and functional nanoparticles. Because our system uses polymer blends we can incorporate various distinct properties such as different degrees of hydrophobicity in one particle, contrary to many previous works in which only use one type of polymer/nanoparticle composite. Furthermore, because this system is based on non-aqueous emulsion using organic solvents, water-soluble polymers and water-insoluble polymers can both be compartmentalized in the same particles. This enables us to remove one of the compartments selectively after synthesis by washing the particles with appropriate solvents. Finally, depending on the surface treatments of nanoparticles, a variety of functional nanoparticles can be incorporated into anisotropic particles and their positions can be controlled accordingly. These strategies gives versatility to the system that it is applicable to numerous combinations of polymers and various functional nanoparticle such as quantum dots and catalytic nanoparticles.

**Experimental section**

**Preparation of PVP-stabilized Fe\(_3\)O\(_4\) nanoparticles in ethanol**

The Fe\(_3\)O\(_4\) nanoparticles of average 10 nm in diameter were prepared by the co-precipitation method according to Massart’s method,\(^45\) and were generously provided by Dr Hyunjoo Park and Prof. David Pine. Fe\(_3\)O\(_4\) nanoparticles, initially dispersed in aqueous phase, were transferred to poly(vinylpyrrolidone) (PVP, average molecular weight \(\sim 10\) k, Sigma-Aldrich)–ethanol (EtOH) solution by repetitive magnetic decantation and solvent exchange. 10 \(\mu\)l of 10 wt\% Fe\(_3\)O\(_4\) nanoparticles aqueous solution was added into 100 \(\mu\)l of 2 wt% PVP–EtOH solution. After magnetic decantation of nanoparticles and removal of supernatant, 2 wt% PVP–EtOH solution was added again. This solvent exchange procedure was repeated three times. The final nanoparticles solution showed no phase separation due to stabilization of nanoparticles by PVP.

**Microfluidic generation of non-aqueous emulsion droplets**

By fabricating a focusing-flow microfluidic channel with poly(dimethylsiloxane) for generation of emulsion droplets,\(^46\) we could produce monodisperse droplets of polymer solution in diameters ranging from 10 to 100 \(\mu\)m with a polydispersity as low as 5% (Fig. 1b). The height of the channel for the injection of the polymer solution was 20 \(\mu\)m, and increased to 60 \(\mu\)m in the flow-focusing region. The dispersed phase is a mixture of three polymer solutions dissolved in dimethylformamide (DMF, Sigma-Aldrich) or EtOH. The first and second
solutions were 4 wt% poly(methyl methacrylate) (PMMA, average molecular weight ~120 k, Sigma-Aldrich) and 2 wt% poly(vinyl alcohol) (PVA, molecular weight 22 k, Junsei Chemical Co., Ltd.) in DMF. The third solution was 2 wt% PVP and approximately 1 wt% Fe$_3$O$_4$ nanoparticles in EtOH. The volume ratio of the PMMA solution to the PVA solution in the mixture was varied between 0 : 1 and 8 : 1 while the volume ratio of the PVA solution to the PVP solution was fixed to 1 : 1. Because the densities of PMMA, PVA, and PVP are very similar as 1.18 g cm$^{-3}$, 1.19 g cm$^{-3}$, and 1.20 g cm$^{-3}$, respectively, all mass-ratios can be considered as volume ratios approximately. There was no observable phase separation in the mixture during the preparation of the samples. The continuous phase was hexadecane (Sigma-Aldrich) which contained 2 wt% non-ionic surfactant (Dow Corning 5200, INCI name: Lauryl PEG/PPG-18/18 Methicone). This surfactant, which is a liquid alkylmethyl silicone polymer copolymer, is amphiphilic to the organic solvent mixture and hexadecane, and guaranteed the stabilization of emulsion droplets during the storage of droplets over 24 h for the evaporation of DMF and EtOH.

Results and discussion

After generating microdroplets from the blend of polymer solution, evaporation of the solvent from the dispersed phase resulted in the size-controlled colloidal particles (Fig. 2). The size and polydispersity of the particles were determined by the initial size of the generated droplets, which was controlled with the flow rates in microfluidic channels. For example, the average diameter of spherical particles in Fig. 2a was 8.7 μm, and the polydispersity was as low as 5.1%. The volume ratio of components in the particles was determined by the concentration of each polymer.

In this experiment, three polymers (PMMA, PVA, and PVP) and Fe$_3$O$_4$ nanoparticles in the emulsion droplets undergo phase separation to make anisotropic particles after the evaporation of solvents. When the composition contains <60 wt% of PVA, PMMA and PVP are incompatible and undergo phase separation after solvent evaporation. PVP is compatible with both PMMA and PVA through dipole–dipole and hydrogen-bonding interaction, respectively. Because the hydrogen-bonding interaction between PVP and PVA can be stronger than dipole–dipole interaction between PVP and PMMA, we expect that most of PVP partition preferentially into the PVA compartment. Thus, after the evaporation of solvents, particles will have two separate compartments, a PMMA compartment and a PVA+PVP compartment, as shown in Fig. 2.

By varying the volume ratio between polymers, we can control the morphology and magnetic anisotropy of the particles. At the same time, we confirm a hypothesis that PVP-stabilized Fe$_3$O$_4$ nanoparticles locate preferentially at the PVP+PVA compartment. The volume ratio between polymers was varied from PMMA : PVA : PVP = 0 : 1 to 8 : 1 : 1, and according to the relative volume ratio of polymers, polymeric particles show different morphologies. The mass ratio between PVP and Fe$_3$O$_4$ nanoparticle was maintained at 2 : 1. When PMMA is absent, PVP+PVA solution makes spherical particles, as shown in Fig. 2a. These spherical particles resemble commercially available magnetic beads. They make straight chains under external magnetic field due to a superparamagnetic property of Fe$_3$O$_4$ nanoparticles (Fig. 2d). When the magnetic field is removed, particles disassemble from the chain structure and re-disperse in the continuous phase.

As the volume fraction of PMMA in the solution increases, the morphology changes from spheres to acorn-like particles as shown in Fig. 2b and 2c. Dark regions of the particles, which are PVP+PVA compartments, result from containing the most of Fe$_3$O$_4$ nanoparticles. Because of induced magnetic dipole–dipole interaction only between PVP+PVA compartments containing Fe$_3$O$_4$ nanoparticles, Janus particles construct zigzag chains under the external magnetic field (Fig. 2e–f).

Judging by more spotted appearance of a dark PVP+PVA compartment in Fig. 2(b) compared to the particles in Fig. 2(a) and 2(d), there seems to be an aggregation of Fe$_3$O$_4$ nanoparticles. However, the particles of the same volume ratio shown in Fig. 4 do not show this aggregation. Presumably this occasional aggregation behavior depends on the fast rate of solvent evaporation.

Fig. 2 Optical microscopy images of magnetic Janus particles with different morphologies. The volume ratio between PMMA : PVA : PVP is (a,d) 0 : 1 : 1, (b,e) 2 : 1 : 1, and (c,f) 8 : 1 : 1. The top row (a–c) shows the particles without external magnetic field. The bottom row (d–f) shows the chains formed by the particles in (a–c), respectively, when magnetic field is applied along the direction of the chain. Fe$_3$O$_4$ nanoparticles are shown at the PVP+PVA compartment (dark region). (g) A size distribution of the spherical particles in (a). The polydispersity calculated is the standard deviation of the diameters divided by the average diameter.
In order to better understand the morphology of polymer-nanoparticle composite from the phase separation, we analysed the shape of resultant Janus particles. As shown in Fig. 3a and 3b, we fit the interfaces between PMMA compartment, PVP+PVA compartment, and continuous phase into three circles. From the microscopic images, we chose the particles in which all three circles meet at one point for analysis, assuming they are in the proper orientation to observe the three-phase boundary and to measure each of three contact angles.

As shown in the schematic diagram of Fig. 3c, we measured the radius of each circle and the arc angles $\phi$ of the three interfaces. Then we calculated the volume ratio of the phase separated regions using eqn (1).\textsuperscript{51}

$$
V_A = \frac{\pi}{3} R_{AC}^3(1 + \cos \phi_{AC})^2(2 - \cos \phi_{AC}) + \frac{\pi}{3} R_{AB}^3(1 - \cos \phi_{AB})^2(2 + \cos \phi_{AB})
$$

$$
V_B = \frac{\pi}{3} R_{BC}^3(1 - \cos \phi_{BC})^2(2 + \cos \phi_{BC}) - \frac{\pi}{3} R_{AC}^3(1 - \cos \phi_{AC})^2(2 + \cos \phi_{AB})
$$

$$
V_B = \frac{\sin \phi_{AC}}{\sin \phi_{BC}} \left( \frac{1 + \cos \phi_{AC}}{2} - \frac{1 - \cos \phi_{AB}}{2} \right)
$$

The volume ratio obtained from the Fig. 3a was 1 : 1, which agrees with the sample volume ratio of PMMA : PVA+PVP, 1 : 1. In the case of the particle in Fig. 3b, the volume ratio was 3.7 : 1, which was a little less than the actual volume ratio of PMMA : PVA+PVP, 4 : 1. This may be the result from the solvent evaporation is too fast for the polymer blends to be separated completely.

Judging by the analysis of resulting particles’ morphologies and the prediction of them with different volume ratios of polymer blends, non-equilibrium aspects of the evaporation-induced phase separation seem to play important roles in determining the particle morphology (see ESI† Fig. S1). Because there is a continuous loss of solvents from droplets to the continuous phase, this system is far from thermal equilibrium. For example, during this evaporation-induced phase separation, the viscosity of each phase and the interfacial tensions between phases change continuously. Furthermore, due to early solidification of polymers, an incomplete phase separation and the pinning of interface also can happen. In fact, an analysis of the shapes of particles, using the Neumann triangle of interfacial tensions and thermodynamic equilibrium assumption,\textsuperscript{51–54} results in unphysical results such as a negative surface tension (see ESI† and Fig. S2). Therefore, to predict the exact shape of particles made by phase-separation-based method, we need to consider non-equilibrium aspects of particle formation.\textsuperscript{51,52,54}

We also demonstrated that one compartment of these Janus particles can be removed selectively to create bowl-shaped morphology. For example, acetone can dissolve PMMA but not PVA. Since acetone is partially miscible with the continuous phase, hexadecane, we can clean the Janus particles with acetone, and re-disperse them into the original continuous phase to find bowl-shaped particles as shown in Fig. 4a. Under magnetic fields, these bowl-shaped particles also make chains (Fig. 4b). However, we could not observe regular zigzag chains such as in Fig. 2e. This irregular chaining seems to result mainly from the complex shape of particles. Without steric repulsion from non-magnetic compartments, particles seem to have various metastable configurations to increase their magnetic dipole–dipole interactions. Additionally, concave shapes of particles can lead to bowl-stacking of particles and hinders their rotation.

Finally, we suggest several applications utilizing interesting features of these Janus particles. According to various choices of polymer blends and nanoparticles, one of compartments can be magnetic, conductive, fluorescent, optically anisotropic, cross-linked, or selectively removed as shown in Fig. 4. Moreover, surface-functionalization of the acorn-like particles followed by the selective removal of one compartment can make particles of anisotropic surface properties with complex shape. This kind of anisotropy in shape and field-responsive-ness may be utilized in the following applications. Particle with complex shape can be a new building block for colloidal assembly such as colloidal clusters and lock-and-key colloids.\textsuperscript{55–56} Field-responsive particles with non-spherical shapes can be used in rheological fluids in which the rheological
behavior can be controlled with external electric/magnetic field.\textsuperscript{10,16} For example, field-induced chains of complex-shaped particles such as in Fig. 4(b) may affect the yield stress of rheological fluids.

Concluding remarks

In summary, we presented a new method of preparing magnetic Janus particles by utilizing evaporation-induced phase separation of polymer blends and polymer-stabilized magnetic nanoparticles in emulsion droplets. Controlling the composition of polymer blends and the stabilizing polymer of nanoparticles, we adjusted the internal architecture of Janus particles and the position of nanoparticles in Janus particles. This preparation method is a one-step process, which simplifies the execution of microfluidic devices for droplet generation, and applicable to any other nanoparticles such as quantum dots if the polymer blends and surface treatment of nanoparticles are chosen appropriately. In addition, the resultant anisotropy of the particles enables construction of interesting field-induced structures and particles of nontrivial morphology. To better understand the morphology, we analysed the shapes of Janus particles. The shapes of particles indicate that non-equilibrium aspects of the evaporation-induced phase separation play important roles in determining the particle morphology. With further understanding of this process of particle formation, we expect this method to be extended to a versatile development of designed structures of colloids with desired functionality and morphology.

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Notes and references