

Supplementary information for

One-Step Preparation of Magnetic Janus Particles Using Controlled Phase Separation of Polymer Blends and Nanoparticles

Joonwoo Jeong,^{*a,d} Eujin Um,^{b,d} Je-Kyun Park^b and Mahn Won Kim^{a,c}

^a Department of Physics, Korea Advanced Institute of Science and Technology (KAIST), Daejeon 305-701, Republic of Korea. E-mail: junoo@kaist.ac.kr

^b Department of Bio and Brain Engineering, Korea Advanced Institute of Science and Technology (KAIST), Daejeon 305-701, Republic of Korea.

^c Institute for Soft and Bio Matter Science, Changwon National University, Changwon, Gyeongnam 641-773, Republic of Korea.

^d These authors contributed equally. Present address: (J.J.) Department of Physics and Astronomy, University of Pennsylvania, Philadelphia, PA 19104, U. S. A; (E.U.) Department of Mechanical Engineering, Princeton University, Princeton, NJ 08540, U. S. A.

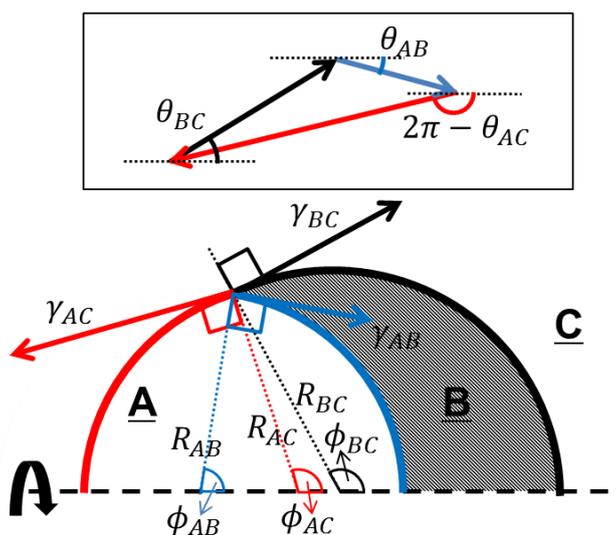


Fig. S1 Schematic diagram of the particle morphology. The rotating arrow on the left of the dashed line shows the rotational symmetry of the particle around the axis. A, B, C represent the PMMA compartment, PVP+PVA compartment, and the continuous phase, respectively. ϕ , R , γ are the arc angle, the radius (the dotted lines), and the interfacial tension of each interface. The inset shows Neumann triangle of interfacial tensions, which represent a balance of interfacial tensions at thermodynamic equilibrium. θ is the angle between the interfacial tension vector and the dotted line which is parallel to the rotational symmetry axis.

Although the system is far from thermal equilibrium due to continuous attrition of solvents, to test the validity of thermal equilibrium assumption, we analysed the morphologies of the particles using Neumann triangle of interfacial tensions. Assuming the morphologies of the particles are at thermodynamic equilibrium,¹⁻⁴ we estimated the interfacial tension ratio between three phases using the measured arc angles ϕ and the Neumann triangle of interfacial tensions as shown in Fig. S1. Equation (S1) shows a relation between the arc angles ϕ and the contact angles θ at the three phase boundary.

$$\theta_{AB} = \phi_{AB} - \frac{\pi}{2}; \quad \theta_{BC} = \phi_{BC} - \frac{\pi}{2}; \quad \theta_{AC} = \phi_{AC} + \frac{\pi}{2} \quad (\text{S1})$$

Under the assumption of thermodynamic equilibrium, the contact angles and the interfacial tensions should satisfy equation (S2), which is equivalent to the Neumann triangle as shown in the inset of Fig. S1.

$$\begin{aligned} \gamma_{BC} \cos \theta_{BC} + \gamma_{AB} \cos \theta_{AB} + \gamma_{AC} \cos \theta_{AC} &= 0 \\ \gamma_{BC} \sin \theta_{BC} + \gamma_{AB} \sin \theta_{AB} + \gamma_{AC} \sin \theta_{AC} &= 0 \end{aligned} \quad (\text{S2})$$

Using the eqn(S1), eqn(S2), and measured ϕ_s from the particle of Fig. 3(a) in the main manuscript, we estimated that the interfacial tension ratios are approximately $\gamma_{AB}/\gamma_{BC} = 0.6$ and $\gamma_{AC}/\gamma_{BC} = 1.6$. From these values of γ_{AB}/γ_{BC} and γ_{AC}/γ_{BC} , we could also calculate the equilibrium shapes of Janus particles of different volume ratios between PVP+PVA and PMMA as shown in Fig. S2.

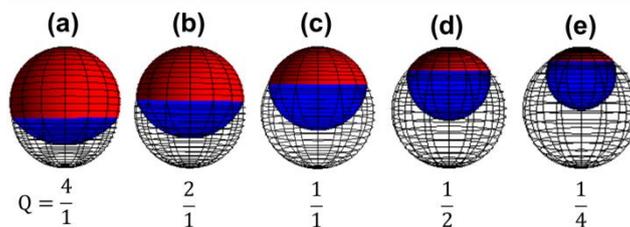


Fig. S2 Simulated morphology of the phase-separated Janus particles in equilibrium as a function of a volume ratio between two compartments. The calculation is based on the values, $\gamma_{AB}/\gamma_{BC} = 0.6$ and $\gamma_{AC}/\gamma_{BC} = 1.6$. The transparent compartment represents PVP+PVA component (B in Fig. 3c), and the colored compartment represents PMMA component (A in Fig. 3c). The blue and red surfaces show two different interfaces. The volume ratio $Q = \text{PMMA}/\text{PVA+PVP}$ is (a) 4/1, (b) 2/1, (c) 1/1, (d) 1/2, and (e) 1/4.

However, as expected, the assumption that the shape of a particle is at equilibrium seems to be invalid in this system. The analysis of the particle in Fig. 3(b) of the main manuscript, which has a volume ratio of PMMA: PVP+PVA= 4:1, showed that the interfacial tension has to be negative, which is physically not possible. In other words, we could not build the Neumann triangle with right directions of the interfacial tension with the particles in Fig. 3(b). Additionally, the shape of the particle in Fig. 3(b) is obviously different from the calculated equilibrium shape of volume ratio of 4:1 in Fig. S2(a). This indicates that the equilibrium assumption is invalid, at least when the volume difference between polymer blends is large.

As pointed out in the main manuscript, the continuous loss of solvents leads to changes in the interfacial tensions, increase of viscosities, and solidification of polymers. These may result in an incomplete phase separation and a pinning of interface. All these invalidate the three phase boundary in thermal equilibrium. Thus, to predict the morphology of the particles fabricated using phase-separation method, we should take non-equilibrium aspects of the phase separation into account.²⁻⁴ However, note that this thermal equilibrium analysis can be valid if the compartments are in liquid phase, such as UV-curable monomer, and have enough time to be relaxed to the equilibrated morphology.

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