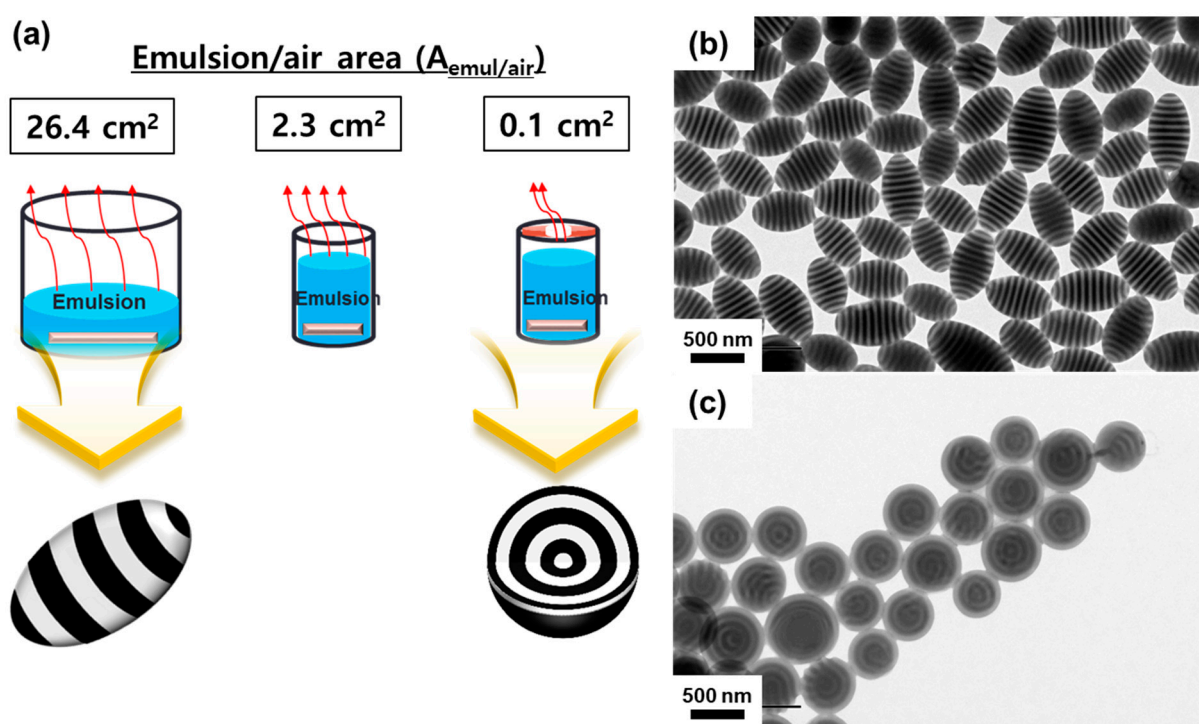


# Morphological Evolution of Hybrid Block Copolymer Particles: Toward Magnetic Responsive Particles

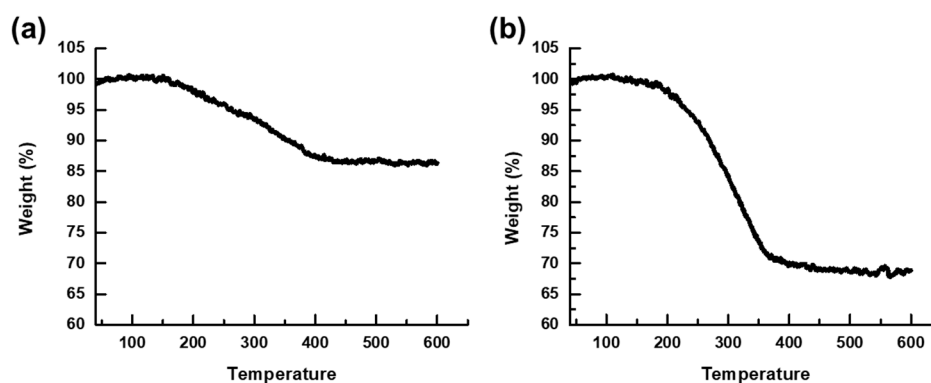
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**Figure S1.** (a) Illustration showing the control of the evaporation rate of toluene by varying the emulsion/air interfacial area ( $A_{\text{emul/air}}$ ). Low-magnification TEM image pristine PS-*b*-PB of (a) ellipsoidal particles ( $A_{\text{emul/air}} = 26.4 \text{ cm}^2$ ), and (b) onion-like particles ( $A_{\text{emul/air}} = 0.1 \text{ cm}^2$ ).



**Figure S2.** TGA traces of (a) Au NPs and (b) Fe<sub>3</sub>O<sub>4</sub> NPs.

**Table S1.** Physical properties of Au and Fe<sub>3</sub>O<sub>4</sub> nanoparticles.

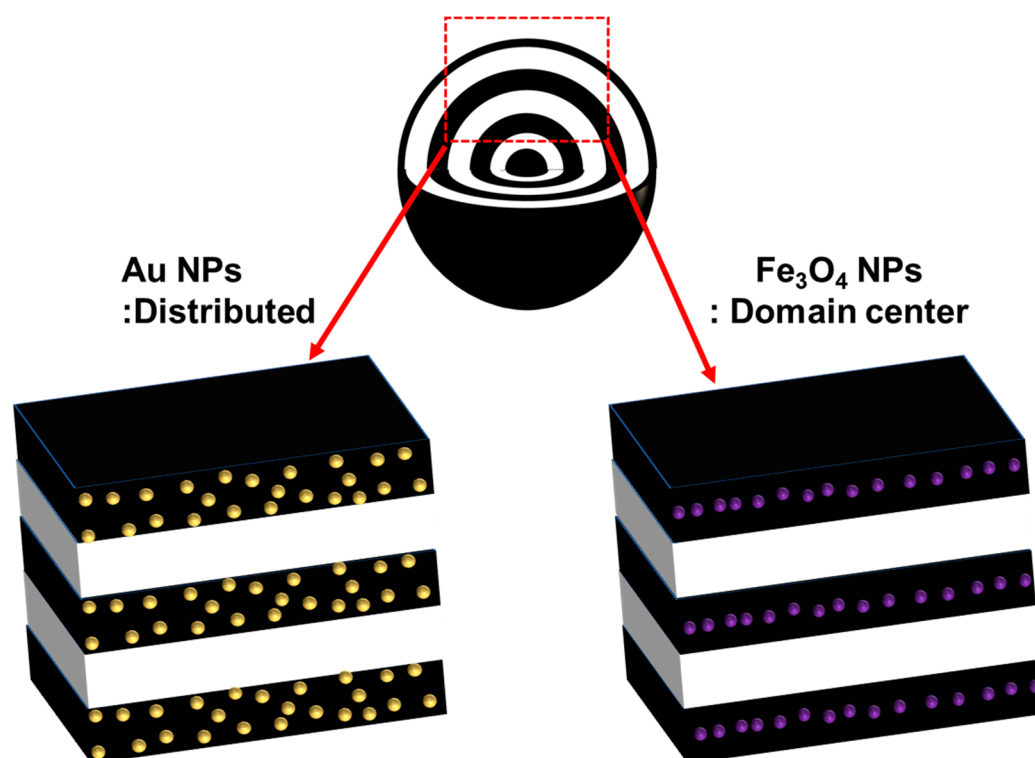
	$d_{core}$ (nm)	$d_{(core+shell)}$ (nm) <sup>a</sup>	$W_L$ <sup>b</sup>	$\sigma$ (chains/nm <sup>2</sup> ) <sup>c</sup>
Au	$4.8 \pm 0.5$	8.1	0.14	6.02
Fe <sub>3</sub> O <sub>4</sub>	$5.3 \pm 0.5$	8.2	0.32	4.56

<sup>a</sup>  $d_{core+shell}$  was calculated by  $d_{core} \times \left( \left( \frac{\rho \times W_L}{\rho_L \times (1 - W_L)} \right) + 1 \right)^{1/3}$ ; <sup>b</sup> Based on the weight loss measured in TGA.

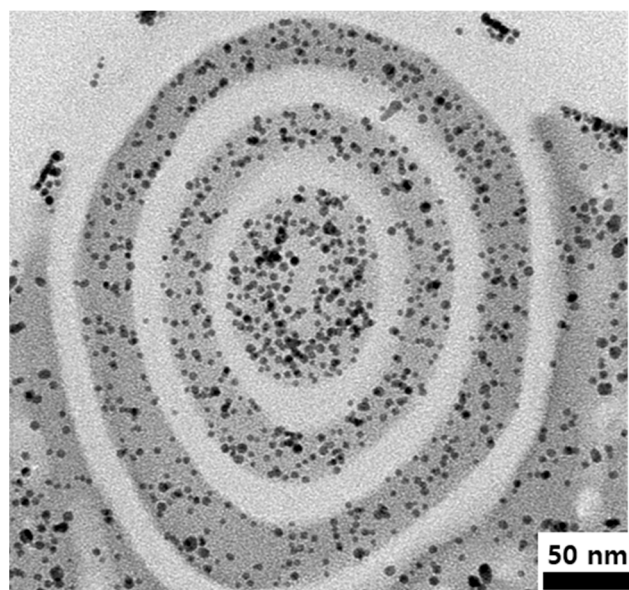
<sup>c</sup> Grafting density ( $\sigma$ ) of the ligand was calculated based on following equation:<sup>1-3</sup>

$$\sigma = \frac{W_L \times N_A \times \rho \times d_{core}}{6 \times MW \times (1 - W_L)}$$

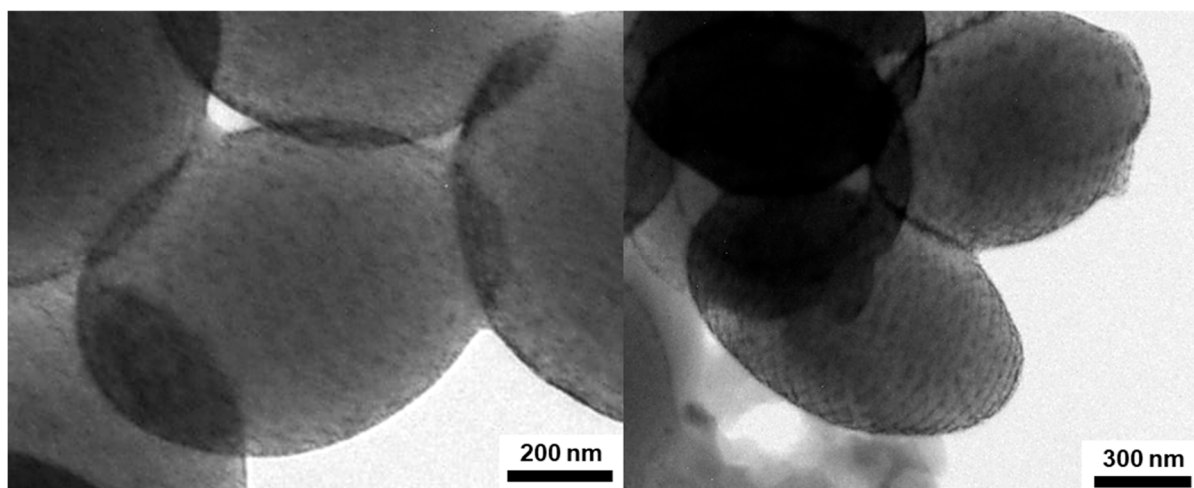
where  $W_L$  is weight fraction of the oleic ligands determined by TGA,  $N_A$  is the Avogadro constant,  $\rho$  is the density of metals (19.32 g/mL for Au and 5.15 g/mL for Fe<sub>3</sub>O<sub>4</sub>),  $d_{core}$  is the diameter of metal core and  $MW$  is the molecular weight of the ligands (i.e. 282.5 g/mol for oleic acid).



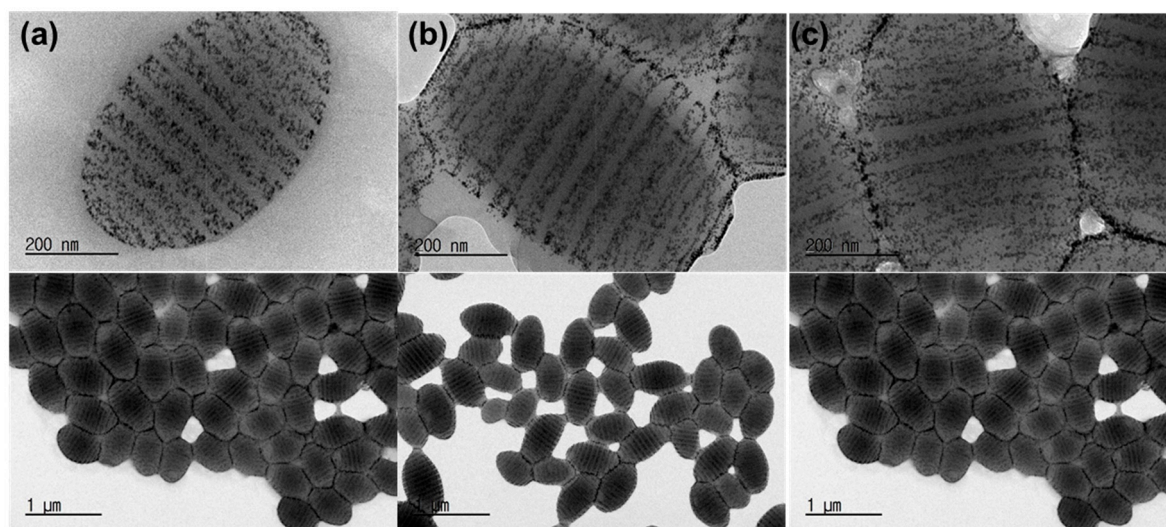
**Figure S3.** Schematic illustration showing the difference in the distribution of NPs inside the PB domains.



**Figure S4.** Cross-sectional TEM images of onion-like PS-*b*-PB/Au hybrid particles.

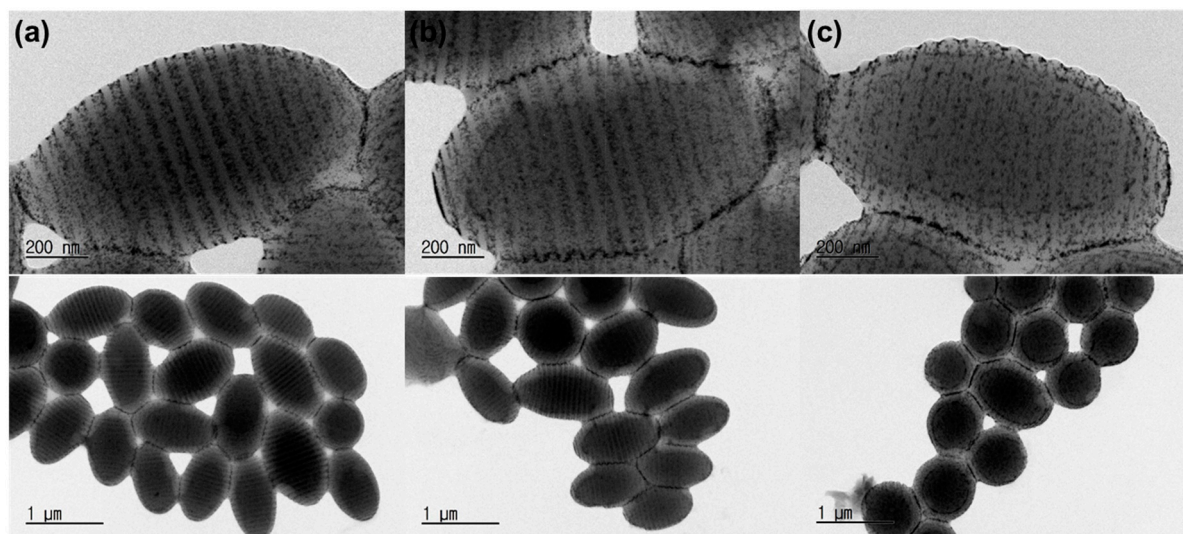


**Figure S5.** TEM images of tilted PS-*b*-PB/Au ellipsoids.  $\phi = 7.0$  vol%.

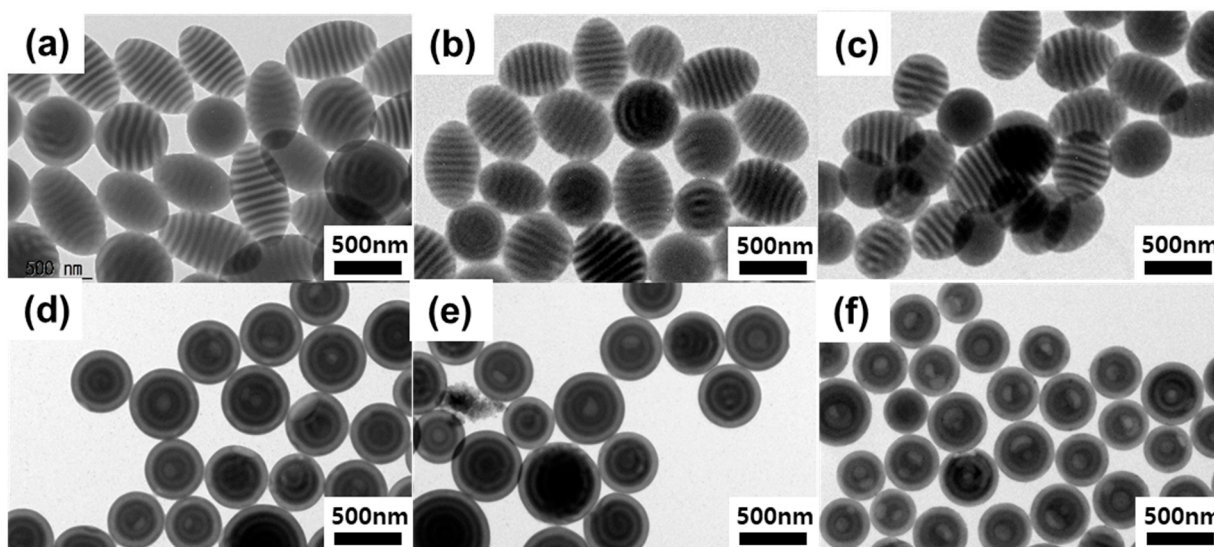




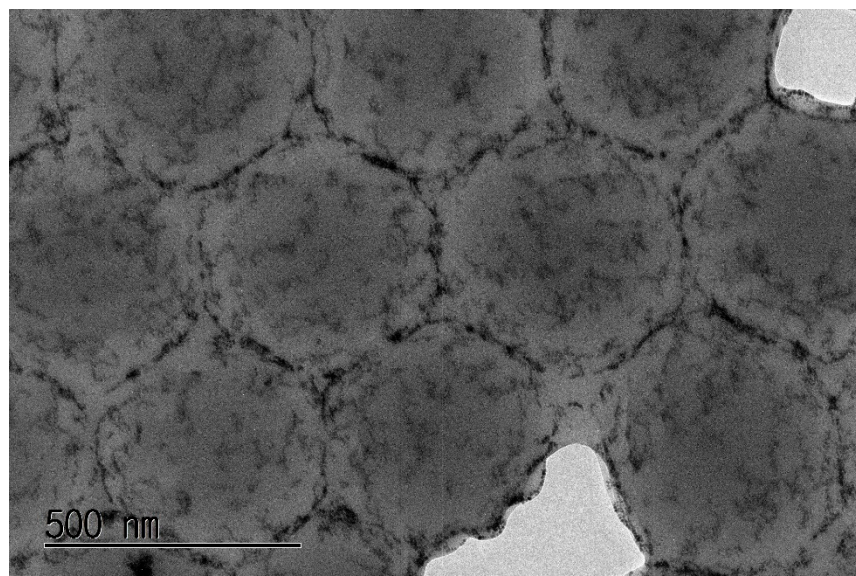
**Figure S6.** Magnified (upper) and low-magnification (lower) TEM images of hybrid PS-*b*-PB/Au striped ellipsoids as a function of solvent evaporation rate. (a)  $A_{\text{emul/air}} = 26.4 \text{ cm}^2$ , (b)  $A_{\text{emul/air}} = 2.3 \text{ cm}^2$ , and (c)  $A_{\text{emul/air}} = 0.1 \text{ cm}^2$ .  $\phi = 7 \text{ vol}\%$ . Particles were observed without any staining.



**Figure S7.** Magnified (upper) and low-magnification (lower) TEM images of hybrid PS-*b*-PB/Au striped ellipsoids as a function of solvent evaporation rate. Larger-sized ellipsoids were produced by using a 2.1  $\mu\text{m}$  SPG membrane. (a)  $A_{\text{emul/air}} = 26.4 \text{ cm}^2$ , (b)  $A_{\text{emul/air}} = 2.3 \text{ cm}^2$ , and (c)  $A_{\text{emul/air}} = 0.1 \text{ cm}^2$ .  $\phi = 7 \text{ vol}\%$ . Particles were observed without any staining.



**Figure S8.** TEM images of hybrid PS-*b*-PB/ $\text{Fe}_3\text{O}_4$  particles as a function of  $\phi$ . (a-c)  $A_{\text{emul/air}} = 26.4 \text{ cm}^2$ , (d-f)  $A_{\text{emul/air}} = 0.1 \text{ cm}^2$ . (a, d) pristine PS-*b*-PB particles, (b, e)  $\phi = 1.4 \text{ vol}\%$ , and (c, f)  $\phi = 3.5 \text{ vol}\%$ . PB domains were stained with  $\text{OsO}_4$ .



**Figure S9.** TEM images of hybrid PS-*b*-PB/Fe<sub>3</sub>O<sub>4</sub> were obtained by freeze-drying the emulsion after evaporation of toluene for 6 hr.  $A_{\text{emul/air}} = 26.4 \text{ cm}^2$

## References

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3. Xu, M.; Ku, K. H.; Lee, Y. J.; Shin, J. J.; Kim, E. J.; Jang, S. G.; Yun, H.; Kim, B. J., Entropy-driven assembly of nanoparticles within emulsion-evaporative block copolymer particles: crusted, seeded, and alternate-layered onions. *Chem Mater* **2020**, *32*, 7036–7043.