Electronic Supplemental Information

Magnetic nanoparticles-induced anisotropic shrinkage of polymer emulsion droplets

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Experimental Section

Materials. All chemicals and reagents were purchased from Sigma-Aldrich Co.. Toluene, hexane, Iron (Ш) acetylacetonate, phenyl ether (99%), oleic acid (90%), oleylamine (>70%) , 1,2-hexadecanediol (97%), and sodiumdodecylsulfate (99+%) were used as received. Polystyrene (Mn=40.000, 1.05) was purchased from Polymer Source Co.

Experimental.

Synthesis of magnetic NPs. Magnetic NPs were synthesized according to the reported method by Sun et al [1]. In brief, Fe(acac)$_3$ (706 mg), 1,2-hexadecanediol (2.86 g), oleic acid (1.7 g), oleylamine (1.6 g) , and benzyl ether (20 ml) were added into a 100 ml of flask and magnetically stirred after vacuum-argon circulation for 10 times. The mixture was heated to 50℃ for 5 min, and 100℃ for 5 min, and 150 ℃ for 5min, and 200 ℃ for 30min. Then the mixture was heated to boiling for 40 min. The black-colored mixture was cooled to room temperature under argon. Under ambient conditions, 40 ml of ethanol was added to the mixture, and the black precipitate was separated by centrifugation at 5000 rpm for 10 min. Then the precipitate was redispersed into hexane with the presence of oleic acid (5mg/ml) and oleylamine (5mg/ml). Then the mixture was precipitated again. The washing process was repeated for three times. Another centrifugation was performed to remove any undispersed residue. Finally, the particles were dispersed into hexane containing oleic acid (5mg/ml) and oleylamine (5mg/ml).

Two different washing procedures were performed for the following experiments:

1) For the shrinkage experiments of emulsion droplets, the above as-prepared NPs were precipitated with ethanol and separated by centrifugation, and then redispersed in pure hexane. The process was repeated for three times. Finally, the product was dried to powder by evaporating hexane at room temperature.

2) For the DLS and TEM controlled experiments, the above as-prepared NPs solution was precipitated with ethanol and separated by centrifugation, then redispersed in pure hexane. The product was dried to powder by evoporating hexane at room temparature.

Liquid droplets shrinkage experiments

A given amount of magnetic NPs powder was added into 500 μl of PS toluene solution, and then was dispersed homogeneously with the help of ultrasound. The mixture was then added into 12ml of SDS aqueous solution (1 wt.-%) and emulsified by a homogenizer for 3 min. The emulsion was sealed with a plastic lid. On the lid, a small hole was made by a 0.45 mm of syringe tip. The emulsion was then placed into an oil bath at 70℃ for 12 h. All the experiments were performed along a similar procedure except for different amounts.

Characterization.

SEM imaging was performed by using field-emission scanning electron microscopy (Gemini LEO 1550) operated at 3 kV. TEM imaging was performed by using Zeiss EM912 Omega microscope at an acceleration voltage of 120 kV. CLSM images in transmission mode were obtained by confocal microscopy (Leica DM IRBE). Thermogravimetry Analysis was performed by a NETZSCH TG 209 F1 under N_2 flow and 5K/min. The size distribution of the NPs in toluene was measured by a Malvern Zetasizer Nano ZS. The static interfacial tension was measured by pendant drop method (OCA 15, DataPhysics). The oscillating drop experiments was preformed using Drop and Bubble Profile Analysis Tensiometer PAT-1 (Sinterface Technologies, Berlin, Germany). The magnetization curve was measured using an Alternating Gradient Magnetometer (Micromag 2900, Princeton Measurements Corporation).

Calculation 1:

The surface ligand number of NPs based on TGA results: Here R_{n1} is the average radius of the NPs, V_{n1} and S_{n1} are the volume and surface area of a single nanoparticle, ρ_{n1} is the density of NPs. V_{nt} and S_{nt} are the total volume and total surface area. The ligand content is φ and the initial mass is 1g, so the mass of pure iron oxide is $(1- \varphi)$. For simplicity, we suppose it is equally adsorbed on the NPs surface for OA and OLA, M_a is the average mole mass of the ligand. N_A is Avogadro's number.

The number of NPs:

$$N = \frac{1-\varphi}{\frac{4}{3}\pi R_{n1}^3 \rho_{n1}} = \frac{3(1-\varphi)}{4\pi R_{n1}^3 \rho_{n1}} \tag{1}$$

The total surface area:

$$S_{nt} = 4\pi R_{n1}^2 N = \frac{3(1-\varphi)}{R_{n1}\rho_{n1}} \tag{2}$$

The ligand number per nm^2:

$$n = \frac{\varphi(1-\varphi) N_A R_{n1}\rho_{n1}}{3M_a} \tag{3}$$

Radius of NPs: Based on TEM images shown in Fig. 1, we got an average size by measuring 300 NPs with the help of the software Image J. For the NPs in Fig.1b, the average diameter is about 5.5 nm, and for NPs in Fig. 1d, the average diameter is about 6 nm.

The ligand number per nm^2:

Here if ρ_{n1} is 5.18 g/cm^3, according to the calculation by formula (3), the ligand number is 4.9 chains/nm^2 and 4.37 chains/nm^2, separately.

Calculation 2:

The relationship of NPs concentration and liquid droplet diameter when NPs form a monolayered or multilayered structure on the liquid droplet surface

Here R_l, S_l, V_l are the radius, surface area, and volume of single liquid droplet, separately. C, r, ρ are the concentration, average radius, density of NPs, and S_n, V_n are the surface area and volume of single nanoparticle. a is the area correction factor of a single NP because of packing void when NPs form a monolayer on the liquid droplet surface.

The surface area of a single droplet:

$$S_l = 4\pi R_l^{\ 2} \tag{4}$$

The volume of single droplet:

$$V_l = \frac{4}{3}\pi R_l^{\ 3} \tag{5}$$

The volume of single NP:

$$V_n = \frac{4}{3}\pi r^3 \tag{6}$$

The occupied area of a single NP on liquid droplet surface:

$$S_n = a\pi r^2 \tag{7}$$

The necessary number of NPs to form a monolayer:

$$n_1 = \frac{S_l}{S_n} = \frac{4R^2}{ar^2} \tag{8}$$

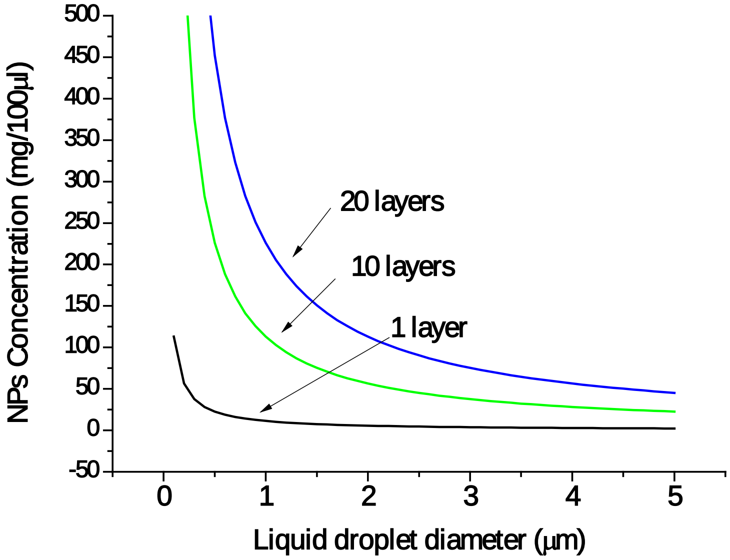
The NPs number in a single liquid droplet:

$$n_2 = \frac{V_l C}{V_n \rho} = \frac{R^3 C}{r^3 \rho} \tag{9}$$

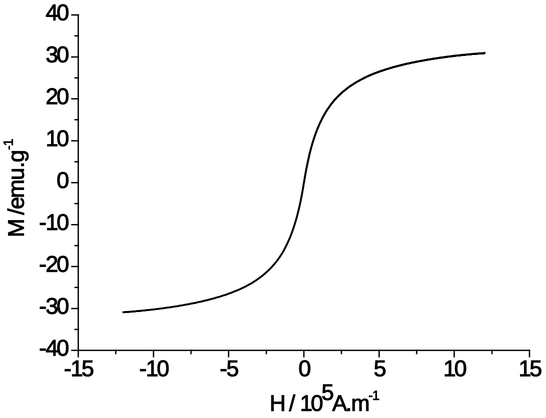
So, we can get the relationship between R and C when NPs number is low to form only a monolayer (n_1=n_2),

$$RC = \frac{4r\rho}{a} \tag{10}$$

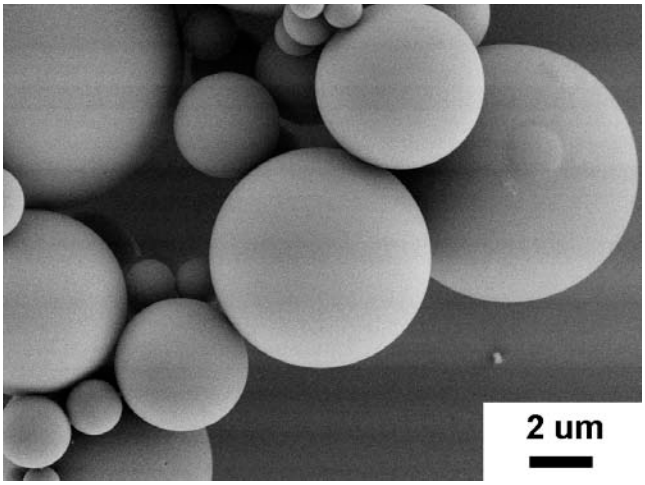
That means that it is a constant once we chose the NPs. It illustrates that, to form a monolayered or multilayered structure, small droplets need a higher NPs concentration. Here if *r* is 6 nm, and *d* is 5.18 g/cm^3, and *a* is 1.1 (calculation by hcp packing), we get the following critical curves :



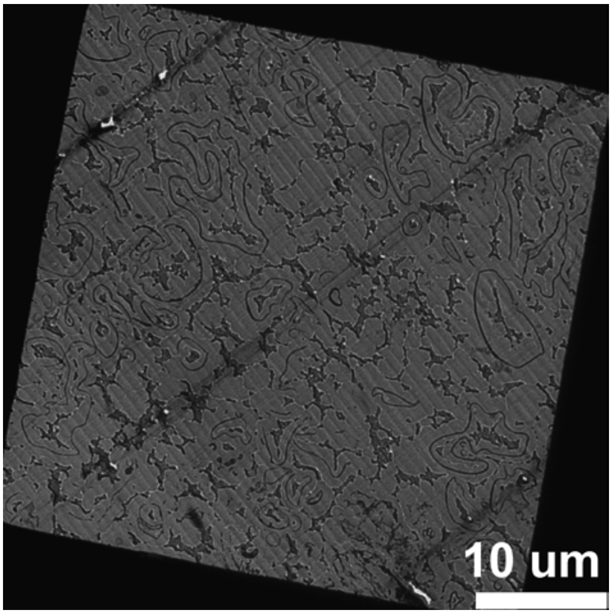
Therefore, if the multi-layered structure is favorable for the occurrence of buckling, the buckling of small liquid droplets requires to the evaporation of a bigger solvent fraction. If the required solvent fraction is above the solvent content, only solid spheres can be obtained. This model is simple, many factors are not considered, however, it could provide qualitatively an explanation why the bigger particles collapse but small particles remain as solid spheres.



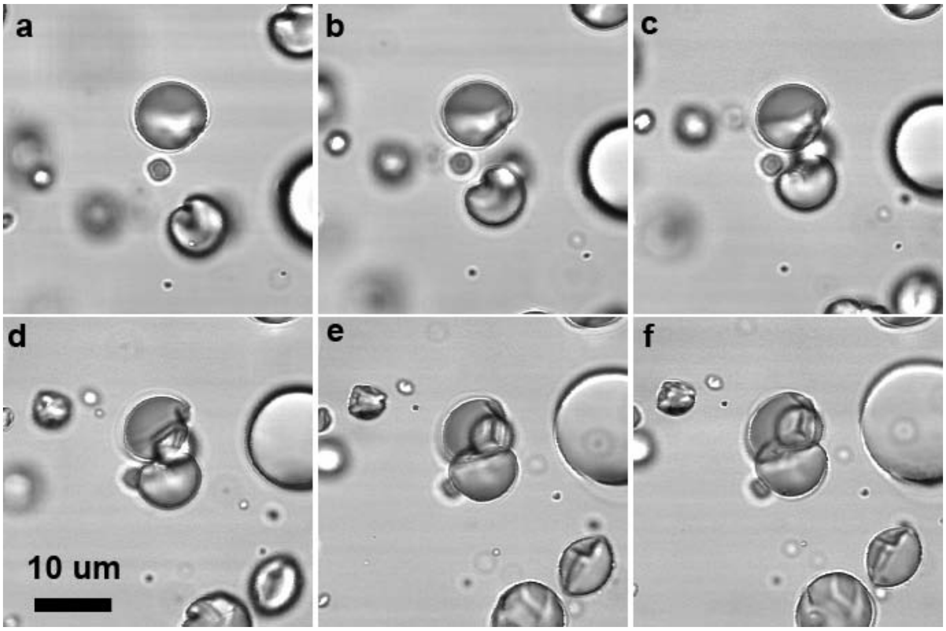
SI Figure 1 Room temperature magnetization curve of the as-prepared ligand-deficient NPs



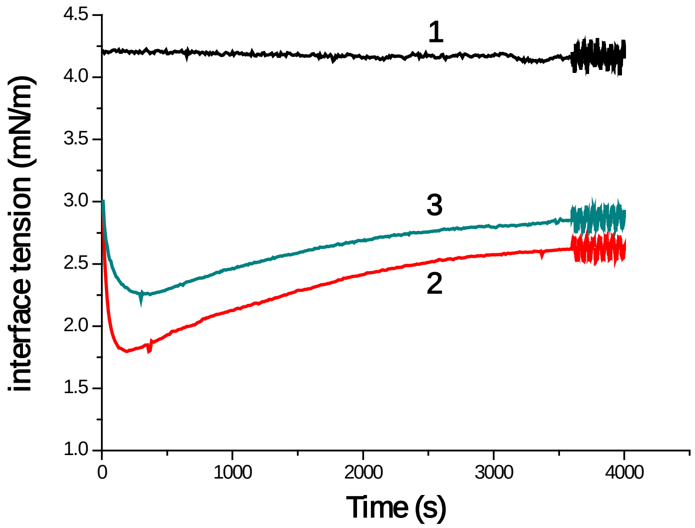
SI Figure 2 SEM image of PS sphere after toluene evaporation of PS emulsion droplets



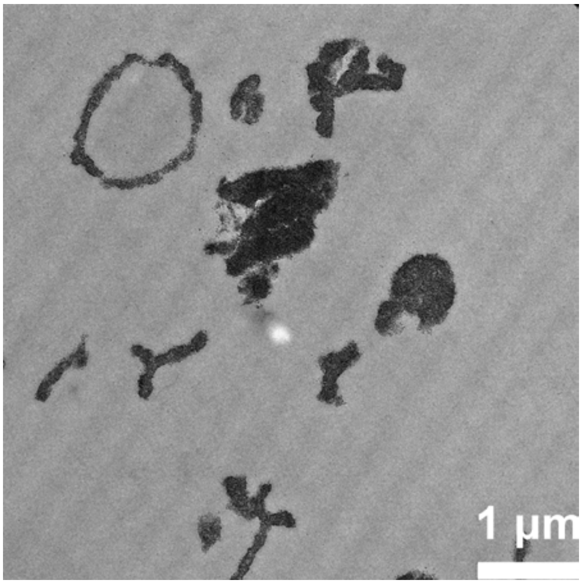
SI Figure 3 TEM image (ultrathin cross section) of the obtained NPs/PS composite particles (V_{NPs}/V_{PS}=1/17.7). The various NPs shapes show the collapsed state of the composite particles, and the positions of NPs suggest that they would prefer to stay at the interface.



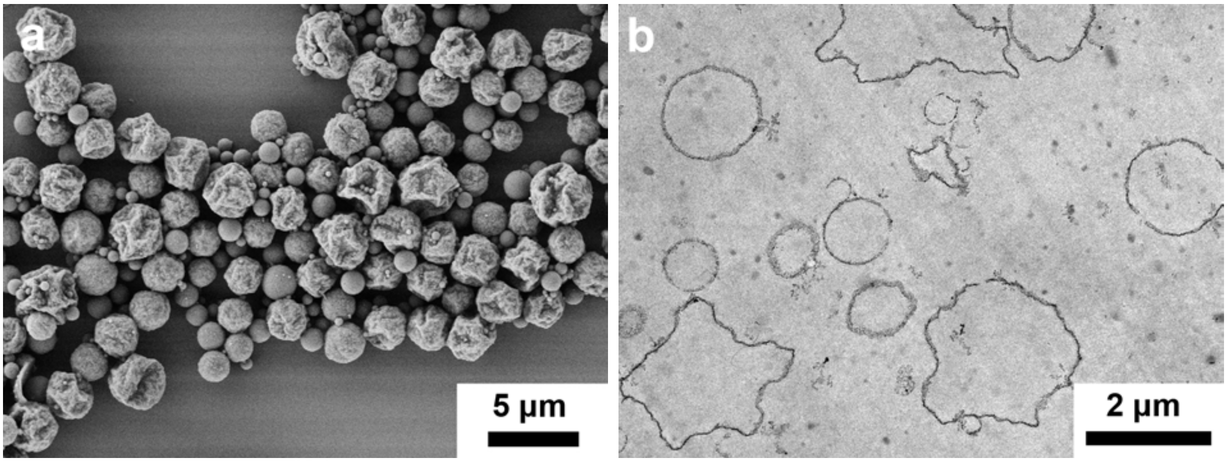
SI Figure 4 CLSM image sequence showing the shrinkage process of emulsion droplets in the buckling stage



5 SI Figure 5 The interfacial tension-time curves and oscillating drop experiments of three representative samples: 1) Toluene/Water(1 wt.-% of SDS); 2) Toluene (0.02 w/v.-% of LDNPs)/Water (1 wt.-% of SDS); 3) Toluene (0.02w/v.-% of LDNPs+1w/v.-% of PS)/Water (1wt.-% of SDS).



SI Figure 6 TEM image (ultrathin cross section) of the obtained NPs/PS composite particles (V_{NPs}/V_{PS}=1/0.74). The various NPs shapes show the collapsed state of the composite particles. In such a high ratio of NPs to PS, the positions of NPs suggest that the walls are mainly consisted in NPs, and PS situates in the interstices between NPs because no PS area can be seen inside a compeletly collapsed particles.



SI Figure 7 a) SEM image and b) TEM image (ultrathin cross section) of the obtained NPs/PS composite particles when the concentration of NPs and PS were diluted to 10% comparing with Fig. 7a in the main text.

SI Table 1 Comparison of six controlled experiments

polymer	Surfactant	T (℃)	NPs	Oleic acid	Oleylamine	1,2-hexadecanediol	Buckling or not
PS	CTAB	70	×				Yes
PS	SDS	70			×		No
PS	SDS	70		×			No
PS	SDS	70		×	×		No
PS	SDS	70				×	No
PS	SDS	R.T.	×				Yes

R.T.: Room Temperature

Reference

1) S. Sun, H.Zeng, D. B. Robinson, S. Raoux, P. M. Rice, S. X. Wang, and G. Li, *J. Am. Chem. Soc.*, 2004, **126**, 273.