Shaping the Assembly of Superparamagnetic Nanoparticles

Minghan Hu,† Hans-Jürgen Butt, † Katharina Landfester, † Markus B. Bannwarth, † Sanghyuk Wooh, ‡, * Héloïse Thérien-Aubin †, *

† Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, German
‡ School of Chemical Engineering & Materials Science, Chung-Ang University, Seoul 06974, Republic of Korea

The supporting information includes: (1) experimental section, (2) Figure S1 – Figure S17, and (3) video captions.

1. Experimental Section

Synthesis of oleate-coated iron oxide nanoparticles (Fe\textsubscript{3}O\textsubscript{4} NPs)

Oleate-coated iron oxide nanoparticles (Fe\textsubscript{3}O\textsubscript{4} NPs) were synthesized by co-precipitation.\textsuperscript{1, 2} Iron(III) chloride hexahydrate (24.36 g, 90 mmol) and Iron(II) chloride tetrahydrate (12.01 g, 60 mmol) were dissolved in 100 mL water. Then, an aqueous ammonia solution (40 mL, 28 wt.%) was added dropwise under vigorous stirring and oleic acid (4.00 g, 14 mmol) was added to the solution. Subsequently, the solution was heated in an oil bath to 70°C for one hour and then stirred at 110 °C for two hours. After the synthesis, the oleate-capped iron oxide nanoparticles were
precipitated and rinsed with distilled water five times and dried in an oven at 65 °C overnight. In order to remove the excess oleate, the oleate-capped iron oxide nanoparticles were dispersed in ethanol (technical grade), separated from the solvent with a permanent magnet (NdFeB, 30 × 30 × 15 mm) and redispersed in fresh ethanol, this procedure was repeated three times.

*Synthesis of hybrid Fe₃O₄/polystyrene nanoparticles (mgPS NPs)*

The Fe₃O₄ NPs (below 20 nm) were immobilized inside polystyrene nanoparticles by emulsion polymerization.³ Briefly, 1 g of Fe₃O₄ NPs was dispersed in 0.5 g of n-octane for 30 min in a sonication bath followed by the addition of 24 g of an aqueous solution containing 24 mg of sodium dodecyl sulfate (SDS). The two-phase suspension was sonicated with a tip (d (tip) = ½, Branson 450 Digital Sonifier, U.S.) for 3 min under ice cooling (70% amplitude, 5 s pulse, 5 s pause) and stirred using a mechanical stirrer (KPG) at room temperature. Separately, 1.2 g of styrene was mixed with 20 mg of n-hexadecane and 24 g of water containing 60 mg of SDS. An emulsion was prepared by the sonication of the water/styrene mixture with a tip (d (tip) = ½, Branson 450 Digital Sonifier, U.S.) for 1 min under ice cooling (10% amplitude, 5 s pulse, 5 s pause). The iron oxide-in-water dispersion and the styrene-in-water dispersion were mixed and then nitrogen was bubbled in the combined dispersions for 10 min. Then, 35 mg potassium persulfate (KPS) and 30 mg of sodium styrenesulfonate were added, and the reaction mixture was heated to 80°C under stirring for 14 h. Purification of the superparamagnetic polystyrene particles was carried out magnetically and by centrifugation. The final surface tension of the suspension was adjusted to 49 mN/m by controlling the SDS concentration.

*Synthesis of hybrid CoFe₂O₄/polyvinylpyridine ferromagnetic nanoparticles (mgPVP NPs)*
The CoFe$_2$O$_4$ NPs (20-30 nm) (Sigma Aldrich) were immobilized inside polyvinylpyridine nanoparticles by emulsion. Briefly, 0.5 g of CoFe$_2$O$_4$ NPs were dispersed under sonication in 5 g of a solution of 1% of PVP (1000 g/mol) in a 0.4 g/L solution of SDS. The clusters were purified from free PVP by 3 cycles of centrifugation followed by redispersion in a 0.4g/L solution of SDS. The final surface tension of the suspension was adjusted to 50 mN/m by controlling the SDS concentration.

*Fabrication of superparamagnetic supraparticles on superamphiphobic surfaces*

First, soot-templated superamphiphobic surfaces were prepared following the previously described method. Briefly, soot particles were deposited on the glass substrate by the candle-soot deposition method. Then 10-20 nm SiO$_2$ layer was coated on those particles by chemical vapor deposition of tetraethoxysilane catalyzed with ammonia. The soot particles were removed by heating at 550 °C, resulting in a fractal-like structure of SiO$_2$ with overhangs. The superamphiphobic surface was finally obtained by surface modification with trichloro(1H,1H,2H,2H-perfluoroctyl)silane which lowered the surface energy.

To fabricate the supraparticles, droplets (typically 5 µL) of an aqueous suspension of mgPS NPs (from 0.3wt% to 30wt%) were deposited using a micropipette on the superamphiphobic surface. To generate the magnetic field, a permanent magnet (NdFeB, 30 × 30 × 15 mm) was placed under the superamphiphobic surface. By controlling the distance between the magnet and the surface, it was possible to tune the strength of the magnetic field. The magnetic field was measured at the surface of the superamphiphobic substrate. Unless noted otherwise, the supraparticles were formed using 5 uL of suspension dried at a temperature of 23 °C under a humidity of 25%.
To obtain binary supraparticles, titanium dioxide nanoparticles (TiO$_2$ NPs, 25 nm, Aldrich, Germany) and polystyrene nanoparticles (PS NPs, 270 nm) were dispersed in distilled water to reach different concentrations and then mixed with a concentrated suspension of mgPS NPs in order to obtain a final nanoparticles concentration of 6wt%.

**Investigation of supraparticles magnetically-controlled movement**

The supraparticles were put in a petri dish with distilled water. The movement of those supraparticles was controlled by displacing a permanent ring magnet (NdFeB, Ø = 19.1/9.5 mm, height 6.4 mm) at different positions. The trajectory, moving speed, and orientation of the supraparticle over time in distilled water were analyzed with ImageJ.$^5$

**Characterizations**

The drying process of droplets was monitored with a goniometer equipped with a side-camera (OCA 35, DataPhysics, Germany). The movie of drying droplets was recorded at 12 frames/min and for ca. 1 hour. The movie was extracted and analyzed to obtain the contact angle and contact line over time using MATLAB. The morphologies of the supraparticles were obtained with a stereomicroscope (M80, Leica, Germany) equipped with a digital camera (IC80 HD, Leica, Germany). To observed the inner structures of supraparticles, they were first embedded in epoxy resin and then sliced (slice thickness of 500 nm) with an ultramicrotome (EM UC7, Leica, Germany). The magnetic properties of mgPS NPs and supraparticles were obtained with a vibrating-sample magnetometer (Cryogenic Ltd. UK). The morphologies of the nanoparticles and supraparticles were observed by transmission electron microscopy (TEM, JEOL JEM1400, Japan) and scanning electron microscopy (SEM, Hitachi SU8000, Japan). For the chemical analysis of
the supraparticles’ surface and interior, the SU8000 with an energy dispersive x-ray spectrometer (EDX) was used to measure the elemental composition.

2. Additional results (Figure S1 – Figure S17)

Building blocks characterizations

Characterizations of iron oxide nanoparticles (Fe₃O₄ NPs)

Figure S1a shows the morphology of synthesized Fe₃O₄ NPs, their average diameter was 13 ± 4 nm (Figure S1b). The crystal structure of synthesized Fe₃O₄ NPs was consistent with the structure of magnetite in X-ray diffraction (XRD) spectrum (Figure S1c).

![Figure S1](image)

Figure S1 a) TEM image of iron oxide nanoparticles (Fe₃O₄ NPs). b) Histogram of the size distribution of Fe₃O₄ NPs (>100 NPs). c) XRD spectrum of synthesized Fe₃O₄ NPs.

Characterizations of Fe₃O₄/polystyrene nanoparticles (mgPS NPs)

Figure S2 shows the morphology of the synthesized hybrid Fe₃O₄/polystyrene nanoparticles (mgPS NPs) obtained by TEM, the average diameter was 93 ± 16 nm. The hydrodynamic diameter
of the mgPS NPs measured by DLS (Nicomp, UK) was 110 ± 30 nm, and their Zeta potential (Zeta Nanosizer, Malvern Instruments, UK) was -67 ± 13 mV. The resulting hybrid mgPS NPs were supraparamagnetic has evidence by the variation of the magnetization in magnetic fields of different strength (Figure S2c).

**Figure S2** a) TEM image of Fe₃O₄/polystyrene nanoparticles (mgPS NPs). Insect is a single mgPS NP (scale bar is 50 nm). b) Histogram of the size distribution of mgPS NPs (> 100 NPs). c) Magnetization of mgPS NPs in a magnetic field of decreasing strength at room temperature.

Thermogravimetric analysis (TGA) of the mgPS NPs revealed that the hybrid material was composed of 63% of Fe₃O₄. Given the relative density of polystyrene (1.04 g/cm³) and iron oxide (5.17 g/cm³) and the average size of one mgPS NPs and one Fe₃O₄ NPs, every mgPS NPs contain on average ca. 150 Fe₃O₄ NPs.
Characterizations of CoFe$_2$O$_4$/polyvinylpyrrolidone ferromagnetic nanoparticles (mgPVP NPs)

CoFe$_2$O$_4$ nanoparticles (diameter below 50 nm, see **Figure S3a**) were used as building blocks to form the supraparticles. It is noted that the ferromagnetic nanoparticles have a magnetization even in the absence of a magnetic field. The hydrodynamic diameter of the resulting mgPVP colloidal suspension was 160 ± 16 nm (**Figure S3b**).
**Figure S4.** a) TEM image of CoFe₂O₄ NPs and b) TEM of the mgPVP hybrid clusters c) size distribution of mgPVP NPs determined by dynamic light scattering (DLS).

**Drying of ferrofluid droplets on hydrophobic fluorinated surfaces**

**Figure S5** a) Comparison between the drying kinetic of ferrofluid droplets (3 wt.%) on a hydrophobic fluorinated surface (blue) and a superamphiphobic (red) surfaces. Drying of a 3 wt.% droplet of ferrofluid on the hydrophobic fluorinated surfaces without (b) and with (c) a magnetic field of 160kA/m.

**Supraparticles characterizations**

**Inner structures of supraparticle**

**Figure S6** Inner structure of a supraparticles. The particle was obtained by drying a 21 wt.% suspension of ferrofluid. a) SEM images of the cross-section of the supraparticle, and zoomed-in SEM images of b) surface and c) interior of the supraparticle.
Table S1 Elemental composition of different areas of the cross-sections of supraparticle according to Figure S6

| Atom % | Surface | Interior |
|--------|---------|----------|
| C      | 61.47   | 53.07    |
| O      | 25.54   | 32.49    |
| Na     | 2.05    | 0        |
| S      | 3.63    | 0.4      |
| Fe     | 7.31    | 14.04    |

Figure S7. Cross-sections of supraparticles with varied concentrations and magnetic fields. The insets indicate the cutting place of the supraparticles. Scale bars are 500 µm.
**Figure S8.** Top view of the barrel-like supraparticle (prepared in a 16 kA/m magnetic field and $c_{\text{NP}} = 21 \text{ wt.\%}$). Scale bar is 0.5 mm.

Investigation of the splitting of droplets of concentrated ferrofluid suspensions

*Comparison of drying kinetics of ferrofluid droplets at different concentrations*

![Graph showing drying kinetics of ferrofluid droplets with different concentrations](image)

**Figure S9.** Drying kinetics of ferrofluid droplets with different initial concentrations (21 wt.%, 30 wt.%, and 60 wt.%) in a magnetic field of 160 kA/m. The arrows indicate the beginning of droplet splitting.

*Drying of ferrofluid droplets with different volumes*
Figure S10. Microscopic images of supraparticles fabricated from drying 21 wt.% of ferrofluid droplet with different volumes (from 1 µL to 5 µL) in a magnetic field of 160 kA/m. Scale bar is 0.5 mm.

Drying of ferrofluid droplets with intermediate magnetic field (80 kA/m)

Figure S11. Optical photos of supraparticles prepared with different initial cNP in the presence of 80 kA/m magnetic field. Scale bar is 0.5 mm.

Drying kinetics of ferrofluid droplets
Figure S12. Evolution of the contact line and the contact angle of the ferrofluid droplets during drying obtained with different initial nanoparticle concentrations (0.3 wt.%, 3 wt.%, and 30 wt.%) and magnetic fields (0 kA/m, 16 kA/m, and 160 kA/m).
Figure S13. Change in the aspect ratio of the droplet during evaporation without and with magnetic field ($H = 16 \text{ kA/m}$). The initial concentration is a) 3 wt.% and b) 12 wt.% The arrows indicate the beginning of droplet buckling.

**Drying of ferromagnetic nanoparticles**

*Drying and assembly of ferromagnetic mgPVP NPs*

With increasing the nanoparticle concentration, the final supraparticles can form the conical structure with high aspect ratio. A difference in magnetization and viscosity of the suspension, in comparison to mgPS, prevented the formation of more varied structures the low magnetic field used previously (16 kA/m) was not sufficient to induced the formation of anisotropic shapes.
Figure S14. Drying of a mgPVP NPs suspension on superamphiphobic surfaces. a) Effect of the strength of the magnetic field on the evaporation induced self-assembly of a 20% suspension of mgPVP; b) influence of the concentration on the structure formed in a magnetic field of 160 kA/m. c) Assembly and disassembly of the fabricated supraparticles by changing the separation distance.
Investigation of binary supraparticles

Triplicate of mgPS, PS/mgPS, and TiO$_2$/mgPS supraparticles dried in a 160 kA/m magnetic field

Figure S15. Reproducibility of the supraparticles structure obtained with the same drying conditions for 5μL droplets of a suspension containing 6wt% solid fraction. Scale bar = 0.5 mm.

Cross-section of binary supraparticles
Figure S16 shows the cross-section of PS/mgPS and TiO$_2$/mgPS supraparticles. In the case of coassembly between mgPS and PS NPs (Figure S16a), the PS NPs are clearly visible in the binary structure (white part). The gradient in the coloration of the supraparticle stemmed from the segregation of the mgPS and PS NPs. The same gradient of concentration was not obvious in the binary supraparticles made with TiO$_2$. The density of the TiO$_2$ NPs was much larger than the density of the PS NPs (respectively 4.23 and 1.04 g/cm$^3$) thus the volume fraction occupied by a constant loading of 9 wt% of non-magnetic nanoparticle was consequently 4 times smaller and more difficult to observe. However, using TiO$_2$ NPs with a smaller diameter than the mgPS NPs allowed to clearly observe the distribution of the different nanoparticles using SEM. Figure S16d shows that in addition to the macroscopic segregation that is clearly observable in the PS/mgPS binary supraparticles, the TiO$_2$ NPs also segregated into smaller microdomains dispersed in a mgPS-rich environment.

![Figure S16](image_url)

**Figure S16.** Cross-section of binary supraparticles. a) Cross-section of a mgPS/PS binary supraparticle prepared with a 10:1 weight ratio of NPs (91wt% of mgPS). b) Cross-section presented in (a) placed in a modeled magnetic field. c) Cross-section of a mgPS/TiO$_2$ binary supraparticle prepared with a 10:1 weight
ratio of NPs (91 wt% of mgPS) d) SEM image of cross-section in (c), the lighter regions correspond to TiO₂ rich-domains.

Reorientation of the superparamagnetic supraparticle in an inhomogeneous magnetic field

Figure S17. Lapse image of the reorientation of a cone-shaped supraparticle in distilled water under the influence of a magnet located on the right side
3. Video Captions

**Video S1.** Example video of drying ferrofluid droplet (5 µL) containing 3 wt.% nanoparticles on the superamphiphobic surface in the absence of a magnetic field.

**Video S2.** Example video of drying ferrofluid droplet (5 µL) containing 3 wt.% nanoparticles on the superamphiphobic surface in the presence of a magnetic field (M = 16 kA/m).

**Video S3.** Example video of drying ferrofluid droplet (5 µL) containing 21 wt.% nanoparticles on the superamphiphobic surface in the presence of a magnetic field (M = 16 kA/m).

**Video S4.** Example video of drying ferrofluid droplet (5 µL) containing 30 wt.% nanoparticles on the superamphiphobic surface in the presence of a magnetic field (M = 160 kA/m).

**Video S5.** Magnetically controlled movement of a cone-like supraparticle in distilled water with different directions of magnetic fields.

**Video S6.** Magnetically controlled movement of a cone-like supraparticle in distilled water with a rotational magnetic field.

References

1. Bannwarth, M. B.; Kazer, S. W.; Ulrich, S.; Glasser, G.; Crespy, D.; Landfester, K., Well-Defined Nanofibers with Tunable Morphology from Spherical Colloidal Building Blocks. *Angew. Chem. Int. Ed.* **2013**, *52*, 10107-10111.
2. Fischer, V.; Bannwarth, M. B.; Jakob, G.; Landfester, K.; Munoz-Espi, R., Luminescent and Magnetoresponsive Multifunctional Chalcogenide/Polymer Hybrid Nanoparticles. *J. Phys. Chem. C* **2013**, *117*, 5999-6005.
3. Bannwarth, M. B.; Utech, S.; Ebert, S.; Weitz, D. A.; Crespy, D.; Landfester, K., Colloidal Polymers with Controlled Sequence and Branching Constructed from Magnetic Field Assembled Nanoparticles. *ACS Nano*. 2015, 9, 2720-2728.

4. Deng, X.; Mammen, L.; Butt, H.-J.; Vollmer, D., Candle Soot as a Template for a Transparent Robust Superamphiphobic Coating. *Science*. 2012, 335, 67-70.

5. Schneider, C. A.; Rasband, W. S.; Eliceiri, K. W., NIH Image to Imagej: 25 Years of Image Analysis. *Nat. Methods* 2012, 9, 671-675.