

Magnetic Nanocomposites

Magnetic nanocomposites, comprising a diblock copolymer (DBC) template and incorporated magnetic nanoparticles (NPs), have attracted increasing research interest because the magnetic nanocomposites have shown potential applications in areas like magnetic sensors and information storage devices. In some areas, such as magnetic sensors and switches, the arrangement of the magnetic NPs exhibit a strong influence on the magnetic properties of the resulting nanocomposites. DBCs have proven to be suitable templates for hosting magnetic NPs because of their ability to form various periodic nanostructures (spheres, cylinders, and lamellae). As shown in Figure 1, the idea is to utilize the DBC templates with various nanostructures for the arrangement of the NPs. To ensure the selectivity of the NPs to a specified block of the DBC template, surface modification of the NPs is required. The arrangement of the magnetic NPs can be achieved by reproducing the template structure offered by the self-organization of DBCs.

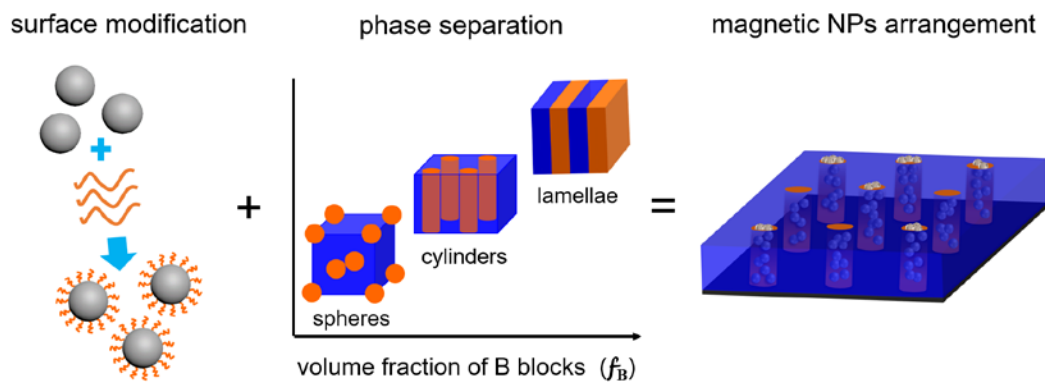


Figure 1. Schematic of combining diblock copolymer templated matrix and surface-modified magnetic nanoparticles.

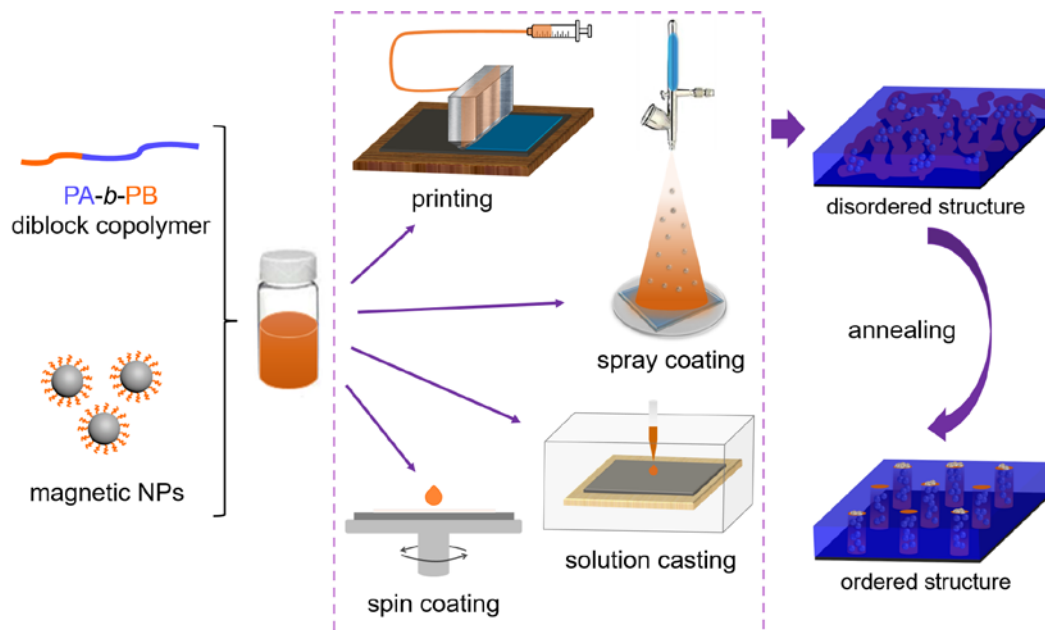


Figure 2. Schematic of sample fabrication with various approaches.

The reported magnetic nanocomposites are prepared by various approaches (small and large-scale productions), such as spin coating, solution casting, spray coating, and printing as shown in Figure 2. To improve the order of the obtained nanostructures and achieve an expected arrangement of the magnetic NPs, post-treatment techniques (thermal annealing and solvent vapor annealing) are applied.

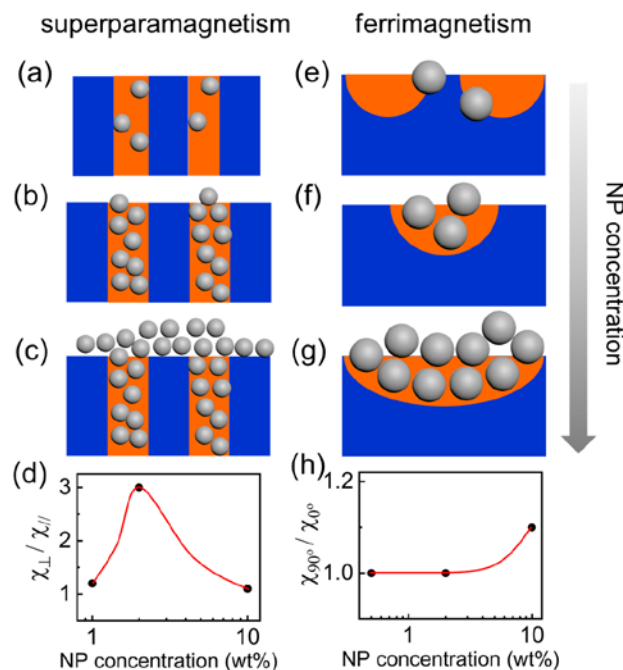


Figure 3. Cross sectional sketch showing the influence of NP concentration on the morphology and corresponding magnetic properties (susceptibility ratio between two orthogonal orientations). Left column: small iron oxide NPs in common DBC (superparamagnetic nanocomposite), right column: large iron oxide NPs in ultra high molecular weight DBC (ferrimagnetic nanocomposite).

Magnetic nanocomposites with multiple and controllable magnetic properties can be achieved by using different sizes of magnetic NPs. Small iron oxide NPs (below 20 nm) exhibit superparamagnetic behavior while large iron oxide NPs (above 20 nm) show ferrimagnetic or ferromagnetic behavior at room temperature. For a better illustration of the structural evolution, a simplified cross sectional sketch of the common DBC films with different small iron oxide NP concentrations is shown in Figure 3a-c. At low NP concentrations (Figure 3a), the NPs are preferentially dispersed inside the specified domains (orange areas). As the NP concentration increases (Figure 3b), more NPs appear and start to locate on the top of the specified domains (orange areas). At high NP concentrations (Figure 3c), the initially formed column-like NP aggregates are perturbed due to an oversaturation of the NPs loading. As a result, excess NPs are located on the top of another domains (blue areas), resulting in the formation of network-like NP aggregates. To analyze the orientation-dependent responsive behavior to external magnetic field, susceptibility ratio between two orthogonal orientations (magnetic field parallel and vertical to the film surface are marked by χ_{\parallel} and χ_{\perp} , respectively) is obtained and plotted as a function of NP concentration at temperature of 2K. In Figure 3d, a maximum susceptibility ratio can be seen at NP concentration of 2 wt% due to the strongest magnetic anisotropy (column-like NP aggregates) as shown in Figure 3b.

For the large iron oxide NPs with ferrimagnetic behavior, ultra high molecular weight (UHMW)

DBC template with large-sized domains is required. The common DBC template is no longer suitable for large NPs because they are too small to accommodate the big NPs. As shown in Figure 3e-g, a localization change of the NPs inside the UHMW DBC films depending on the NP concentration is observed. At low NP concentrations (Figure 3e), the NPs are located at the interfaces between two blocks due to the strong segregation strength of the UHMW DBC. As the NP concentration increases (Figure 3f), the decrease in polymer elastic penalty becomes dominant. The NPs are preferentially located inside the specified domain (orange area). At high NP concentrations (Figure 3g), a chain-like NP aggregate appears due to strong dipoles among large iron oxide NPs, resulting in a change of the DBC's morphology from sphere to ellipsoid for the specified domain (orange area). Such chain-like NP aggregates lead to a weak magnetic anisotropy as shown in Figure 3h (susceptibility ratio is around 1.1 at an NP concentration of 10 wt%). The applied external magnetic field is rotated by 90° in the film plane to obtain χ_{0° and χ_{90° .

Selected Publications:

- 1. Y.Yao, E.Metwalli, B.Su, V.Körstgens, D.Moseguí González, A.Miasnikova, A.Laschewsky, M.Opel, G.Santoro, S.V.Roth, P.Müller-Buschbaum**
Arrangement of maghemite nanoparticles via wet chemical self-assembly in PS-*b*-PNIPAM diblock copolymer films
ACS Appl. Mater. Interfaces **7**, 13080-13091 (2015)
- 2. Y.Yao, E.Metwalli, M.Opel, M.Haese, J.-F.Moulin, K.Rodewald, B.Rieger, P.Müller-Buschbaum**
Lamellar diblock copolymer films with embedded maghemite nanoparticles
Adv. Mater. Interfaces **3**, 1500712 (2016)
- 3. S.Xia, L.Song, V.Körstgens, M.Opel, M.Schwartzkopf, S.V.Roth, P.Müller-Buschbaum**
Magnetic nanoparticles containing soft-hard diblock copolymer films with high order
Nanoscale **10**, 11930-11941 (2018)
- 4. S.Xia, L.Song, N.Hohn, K.Wang, S.Grott, M.Opel, M.Schwartzkopf, S.V.Roth, P.Müller-Buschbaum**
Spray-coating magnetic thin hybrid films of PS-*b*-PNIPAM and magnetite nanoparticles
Adv. Funct. Mater. **29**, 1808427 (2019)
- 5. W.Cao, S.Xia, X.Jiang, M.Appold, M.Opel, M.Plank, R.Schaffrinna, L.P.Kreuzer, S.Yin, M.Gallei, M.Schwartzkopf, S.V.Roth, P.Müller-Buschbaum**
Self-assembly of large magnetic nanoparticles in ultrahigh molecular weight linear diblock copolymer films
ACS Appl. Mater. Interfaces **12**, 7557-7564 (2020)