Magnetic Polymer-Grafted Nanoparticles

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Abstract:

In this project, polymer-grafted nanoparticles with various magnetic cores (Fe_3O_4, $CoFe_2O_4$, etc.) and different polymer canopies are synthesized. The magnetic interactions among cores and the chemical forces (hydrogen bond, ionic interactions, etc.) among polymer brushes are assumed to affect the self-assembly property of the nanoparticles. The self-assembly structures (monolayers, superlattices, etc.) of the particles are made on silicon wafers and other substrates for further study. The polymer canopies would not only modify the surface properties of the metal oxide nanocores to prevent them from aggregating, but also introducing tunable chemical forces into the polymer-graft nanoparticles self-assembly structures.
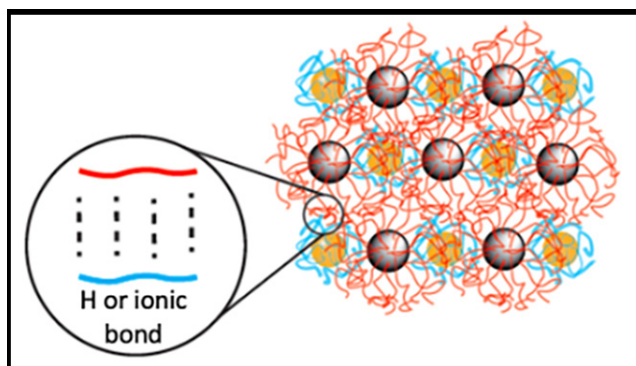
Figure 1: Demonstration of the inter-particle hydrogen bonding or ionic interactions.

Summary of Research:

Polymer-grafted nanoparticles (PGNs) have received increasing attention because they possess the advantages of both the grafted polymer and inorganic cores, and thus demonstrate superior optical, magnetic, electronic, and catalytic properties. One potential application for PGNs is the formation of self-assembly structures and as a building block for the development of photonic/optical/magnetic devices. Thus, PGNs with tailorable interparticle interactions, via either inorganic magnetic cores (magnetic interactions) or polymer brush chemistry (hydrogen bonds, ionic interactions, etc.) (Figure 1), are indispensable for the formation of a superlattice with a defined and ordered structure.

A combined approach of mini-emulsion polymerization and surface-initiated Atom Transfer Radical Polymerization will be used to make the PGNs [1]. To couple the initiator molecules and the metal oxide surface, a silane-based coupling agent is used. The surface-initiated Atom Transfer Radical Polymerization is carried out by adding appropriate combination of ligand, copper, monomer, reducing agent, and shuttling agent. The emulsion is prepared by Pluronic F-127, a non-ionic surfactant. The PGN self-assembly structures are fabricated using multiple techniques, including Langmuir-Blodgett method and simply drop-casting. The morphology of PGNs and order of the self-assembly structure are characterized by scanning electron microscope (SEM), transmitting electron microscope (TEM), scanning transmission electron microscopy (STEM), and atomic force microscope (AFM), and the magnetic properties are characterized using Physical Property Measurement System (PPMS). Besides these, many facilities in CNF would help this research project.

For example, the Malvern Nano ZS Zetasizer will be helpful for characterizing the size of synthesized particles. To study the magnetic properties of the particle self-assembly, we need to cut silicon wafers into 2 mm × 2 mm square pieces precisely, and the DISCO Dicing Saw can help us doing this. The polymer-grafted nanoparticles with different polymer canopies are mixed in the self-assembly structure, and the Energy-dispersive X-ray Spectrometer will help us see which polymer corona is around the particles. Also, we may

MATERIALS

characterize the surface modified by those particles, so facilities like contact angle would be very helpful.

An example HAADF-STEM image of polymethyl methacrylate-grafted Fe3O4 nanoparticles is shown in Figure 2. The polymer chains are entangled together and form a thick shell around the particle cores. Because of the low electron scatter ability of the polymers, the polymer shell is transparent than the inorganic crystal cores.

In conclusion, polymer-grafted nanoparticles with various polymer chemistries and different magnetic core materials are synthesized using a grafting-from approach. The self-assembly structures of these PGNs are made using several techniques. While we are getting some promising initial results that are showing the potential of these magnetic PGNs for fabricating self-assembled structures, further research is still needed to optimize the inter-particle interactions and tune the self-assembling behaviors. In future, the effect of the size, the polymer composition, and graft density, etc., will be studied.
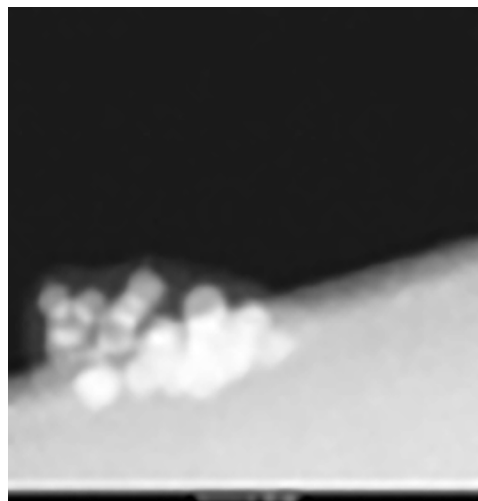

Figure 2: An example HAADF-STEM image of PMMA-grafted Fe_3O_4 cores.

References:

[1]   Yuan, C., Käfer, F., and Ober, C. K. (2021). Polymer-Grafted Nanoparticles (PGNs) with Adjustable Graft-Density and Interparticle Hydrogen Bonding Interaction. Macromolecular Rapid Communications, 43(12), 2100629. https://doi.org/10.1002/marc.202100629.

[2]   Oh, J. K., and Park, J. M. (2011). Iron oxide-based superparamagnetic polymeric nanomaterials: Design, preparation, and biomedical application. Progress in Polymer Science, 36(1), 168-189. https://doi.org/10.1016/j.progpolymsci.2010.08.005.