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Perspective

Perspective: altering structure in a hierarchically assembled magnetic nanocomposite to rapidly tune optical reflection

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Work in this issue by Lu and coworkers [1] exemplifies one of the more exciting areas in the field of materials science, the controlled hierarchical assembly of functional materials. This work assembles nanoparticles and polymers into micron-scale particles, which then assemble into macroscopic assemblies whose spacing can be actively tuned in real time to control interactions with light. While this kind of hierarchical assembly has been ongoing for a number of years, it represents a growing trend where multiple levels of precise control are used to develop new materials with properties that are impossible in a single-component material [2]. The challenge and opportunity presented to materials scientists is to understand and control the various components and length scales to produce structures with unique functions. Examining the details of this work makes it clear that what enables this function is the detailed understanding and careful control of each level in this hierarchy.

At the smallest scale, magnetic nanoparticles have been the subject of intense study for decades due to their intriguing properties, in particular their high susceptibility. Susceptibility, the magnetization per unit applied field, is probably the most important magnetic property in a magnetizable material as it defines the ease with which a material can be magnetized. This magnetized material can then be harnessed to do useful work. Magnetic nanoparticles can be superparamagnetic, where they lack magnetic hysteresis and can have susceptibilities that are higher than are possible in bulk materials [3]. Saturation magnetization, the other commonly reported metric of magnetic strength, is often lower in nanoparticles than in their bulk counterparts. While this is certainly undesirable, it is of less practical concern as saturation is only achieved at very high fields, and most of the applications of these materials occur well below a saturation field. Simply stated, superparamagnetic nanoparticles can respond more

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strongly to commonly applied magnetic fields than any other material. Therefore, a mass of magnetic nanoparticles will generally respond more strongly to an applied magnetic field than a similar mass of micron-scale or larger particles. Magnetic nanoparticles can be used individually or assembled into larger structures to perform a function more efficiently than a bulk material, whether that function is to do move, bend, absorb energy, or some other process. This has led to applications in fields as widely varied areas as electronic components [4], biomedical applications [5, 6], and magnetically recoverable catalysts [7].

At a larger length scale, artificial, regularly assembled spheres that have optical properties reminiscent of natural opals have also been a fixture of the literature for several decades. Both natural and artificial opals have coloration that is defined by the spacing between self-assembled spheres. The uniformly sized spheres and regular spacing act as a photonic crystal, yielding constructive interference at specific wavelengths of reflected light. Artificial opals predate the explosion of work on optical metamaterials and plasmonic structures we are currently seeing but are representative of similar physics where periodic structures generate new material properties. Just like responsiveness and tunability are highly desirable in metamaterials and plasmonic materials, they have long been highly desirable in opalescent materials.

What makes tunability in photonic crystals such a difficult problem is that it requires not only carefully balancing of forces, but systematic altering of one or more of the forces. Specifically, to tune the spacing of a particulate system requires two forces, an attractive force and a repulsive force, with one of those forces being tunable. In a magnetic system, the obvious choice is to tune this attractive force through the application of an eternal magnetic field, and there is a long history of doing just that. The problem becomes that the magnetic forces can be so overwhelming that returning to the premagnetized state can be difficult or impossible [5, 8]. In this issue, Lu et al. have overcome this obstacle by using highly charged particles to provide a strong repulsion that very quickly restores the premagnetized state.

The overall approach taken by Lu et al. is shown in Fig. 1. In summary, they have synthesized a sample of polystyrene spheres with very low size dispersity, which are heavily loaded with magnetic nanoparticles and possess a very strong surface charge. The result is particles whose behavior is dominated by two powerful forces, magnetic attraction and electronic repulsion. In these experiments, the electronic repulsion is held constant, while the magnetic attraction is systematically varied. A magnetic field is applied, which in turn magnetizes the nanoparticles within the larger polymer spheres. Since these nanoparticles are dispersed in polymer, they act as individual superparamagnets and retain their high magnetic susceptibilities. The magnetic moments of the individual nanoparticles within a single polymer sphere sum and drive a magnetic attraction between the polymer spheres. This attraction increases with an increase in applied field, resulting in a systematic change in the uniform interparticle spacing as a function of applied field. Since the interparticle spacing determines the optical properties of the composite, the frequency of light preferentially reflected can be systematically varied. Additionally, since the nanoparticles are superparamagnetic, they lack magnetic hysteresis. When the magnetic field is lowered or removed, the particles promptly demagnetize allowing the electrostatic charge to push them back apart. This allows full reversibility of the process.

To be clear, there is precedent for many of these features, and elegant demonstrations of the systematic variation of interparticle spacing have been shown in magnetic photonic crystals [9]. Still, the work highlighted here includes improvements on nearly every aspect of the assembled structure. The polymer spheres are more magnetic than previously reported materials, allowing for greater forces between the particles for a given magnetic field. Critically, the particles also have a higher surface charge than previous efforts, allowing for rapid and complete restoration of the unmagnetized structure. There is also an addition of an organic dye, acid black, that absorbs stray light scattering to enhance the relative intensity of the desired wavelength.

What this work amply demonstrates is the importance of tuning the properties of each level of structure in a hierarchy to create a material with maximum performance. The general principles involved in this study can be applied to many problems. The same materials can obviously be scaled up or down to change the relevant wavelengths of light. Moving farther afield and shifting from dielectric to conducting particles moves us into the arena of tunable plasmonics. Thinking expansively, the assembly

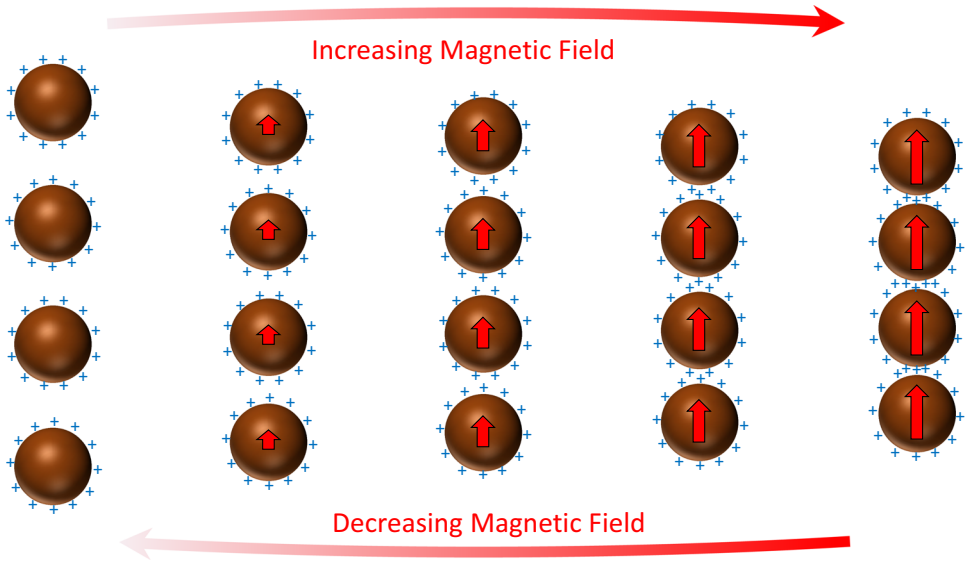

Figure 1 Schematic of the approach to control spacing between magnetic nanoparticle-loaded polymer spheres. Application of a magnetic field leads to the generation of a magnetic moment in the particles, which attracts neighboring particles, decreasing the distance in the particle spacing as field increases. Decreasing the field leads to the particle spacing increasing as the positive surface charge on the particles drives them back apart. The end result is that an increasing applied magnetic field smoothly blueshifts the wavelength of light that is preferentially reflected, while a decreasing magnetic field leads to a redshift.

of hierarchical structures that can do work in response to external stimuli is an enormously interesting topic that will continue to allow imaginative researchers to apply fundamental physical properties to develop intricate responsive systems. Work of this kind really emphasizes the exciting place that materials science occupies at the intersection of chemistry, physics, and engineering.

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References

[1] Lu X, Chen C, Wen X, Han P, Jiang W, Liang G (2019) Highly charged, magnetically sensitive magnetite/polystyrene colloids: synthesis and tunable optical properties. J Mater Sci. https://doi.org/10.1007/s10853-019-03445-4

[2] Firestone MA, Hayden SC, Huber DL (2015) Greater than the sum: synergy and emergent properties in nanoparticle–polymer composites. MRS Bull 40(09):760–767. https://doi.org/10.1557/mrs.2015.202

[3] Huber DL (2005) Synthesis, properties, and applications of iron nanoparticles. Small 1(5):482–501. https://doi.org/10.1002/smll.200500006

[4] Silveyra JM, Ferrara E, Huber DL, Monson TC (2018) Soft magnetic materials for a sustainable and electrified world. Science 362(6413):eaao0195. https://doi.org/10.1126/science.aao0195

[5] Saville SL, Woodward RC, House MJ, Tokarev A, Hammers J, Qi B, Shaw J, Saunders M, Varsani RR, St Pierre TG, Mefford OT (2013) The effect of magnetically induced linear aggregates on proton transverse relaxation rates of aqueous suspensions of polymer coated magnetic nanoparticles. Nanoscale 5(5):2152–2163. https://doi.org/10.1039/c3nr32979h

[6] Linh PH, Chien NV, Dung DD, Nam PH, Hoa DT, Anh NTN, Hong LV, Phuc NX, Phong PT (2018) Biocompatible nanoclusters of *O*-carboxymethyl chitosan-coated Fe_3O_4 nanoparticles: synthesis, characterization and magnetic

heating efficiency. J Mater Sci 53(12):8887–8900. https://doi.org/10.1007/s10853-018-2180-0

[7] Singh H, Rajput JK (2017) Chelation and calcination promoted preparation of perovskite-structured $BiFeO_3$ nanoparticles: a novel magnetic catalyst for the synthesis of dihydro-2-oxypyrroles. J Mater Sci 53(5):3163–3188. https://doi.org/10.1007/s10853-017-1790-2

[8] Martin JE, Venturini EL, Huber DL (2008) Giant magnetic susceptibility enhancement in field-structured nanocomposites. J Magn Magn Mater 320(18):2221–2227. https://doi.org/10.1016/j.jmmm.2008.04.111

[9] Xu X, Friedman G, Humfeld KD, Majetich SA, Asher SA (2002) Synthesis and utilization of monodisperse superparamagnetic colloidal particles for magnetically controllable photonic crystals. Chem Mat 14(3):1249–1256. https://doi.org/10.1021/cm010811h