Nanoparticle Monolayers of Iron Oxide Fabricated using Electrophoretic Deposition: A New Path to Superlattices?

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Abstract

Nanoparticles (NPs) are known to display properties that differ distinctly from their bulk counterparts. Also, *ensembles* of NPs are known to exhibit collective properties, which differ from the characteristics of an *individual* NP. A few examples demonstrate this fact quite clearly. In one example, CdSe NP arrays were created. Ordered arrays, unordered arrays, and a system of isolated particles were studied for their optical properties. Measurements of the optical properties exposed a pronounced enhancement in the sharpness of the photoluminescence peak for in the ordered array of NPs[1]. In another example, the electrical properties of Ag NPs were measured for two-dimensional arrays that were hexagonally packed NPs and cubically packed NPs and compared to the electrical properties of individual NPs. The electrical properties measured in all three cases were dramatically different simply due to the change in geometry of the NP system[2]. In a final example, arrays of Ag NPs were created and then sintered. By sintering ordered arrays, the researchers were able to create large monocrystals of silver, which were not created with unordered arrays[3]. These are just three examples that elucidate the power that can be achieved by obtaining control of order within NP ensembles.

In this presentation, we will begin by discussing a new technique we have developed for making two-dimensional assemblies of NPs, or nanoparticle monolayers (NPMs) (Figure 1a). The NPMs are fabricated using electrophoretic deposition (EPD) (Figure 2). EPD is a rapid, safe, and facile process for depositing suspended nanomaterials onto large substrates. In the discussed work, for example, we fabricated homogeneous NPMs on 1 cm X 4 cm silicon wafers with only one minute of deposition[4]. Beyond this, the substrate could be easily scaled to make even larger films if desired. EPD is also very versatile in the materials that can be used. To date, we have fabricated NPMs composed of monodisperse iron oxide, titania, and CdSE NPs. However, we expect other materials can easily be assembled into NPMs with little change in the current technique.

Next, because we know that order is so important in these films, we will discuss statistical methods by which we have been able to measure and enhance ordering within iron oxide NPMs. We created Voronoi tessellations based on scanning electron microscope images of the NPMs[5] (Figure 1b). Using the tessellations and particle locations, we quantified order using three previously developed statistical quantities. Additionally, we developed a fourth measure of order, which is designed to detect anisotropy in particle-particle bond orientations. With these measures of order we detected changes as small as 5% in the ordering. With these tools, we intend to understand the mechanisms that create ordering within the NPMs as well as the variables that affect ordering. Then, given the precision by which we can analyze the films and the knowledge of how to vary the ordering, we can attempt to fine tune the ordering and potentially fine tune the properties of the NPMs.

Inspired by work done on block copolymer ordering, we choose to first study the changes in order that can be controlled by varying the geometry of the substrate on which the NPs are deposited[6]. Substrate geometry is manipulated by using electron beam lithography to create rectangular elements arranged in hexagonal arrays (a framework)[7]. We studied multiple frameworks with various scales and orientation of rectangular elements. By using the statistical tools discussed above, we have analyzed the ordering from the various framework designs and observed that the framework of certain sizes and orientations can indeed affect ordering within the NPMs.

To date, substrate geometry has been our major focus, however many other variables such as NP surfactant, solvent, deposition rate, etc., can just as well be studied using the statistical tools we assembled. Additionally, the tools can be applied to other monolayer fabrication processes such as Langmuir-Blodgett, evaporative self-assembly, spin coating, etc. The main limitation of these statistical measurement tools is that one must be able to locate each particle within the film. However, given the ability of current imaging techniques (TEM, SEM, AFM, etc), this is easily overcome for most two-dimensional samples. Thus, we will discuss a highly versatile technique for fabricating NPMs and additionally introduce a set of tools that can precisely measure order in NPMs fabricated using virtually any process.

References

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Figures

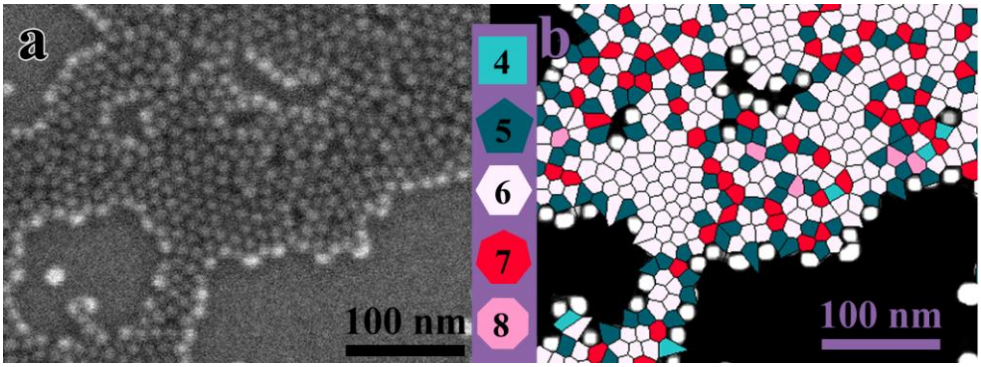

Figure 1: (a) SEM image of an NPM composed of 9.6 nm diameter, spherical, iron oxide NPs. The monolayer is not completely filled in, thus regions of substrate are visible (b) Voronoi tessellation plotted over SEM image of NPs. The neighbors for each particle share a Voronoi edge. The number of neighbors of each particle is indicated by the color of the cell. (Regions of substrate are excluded from the tessellation and shown in black.)

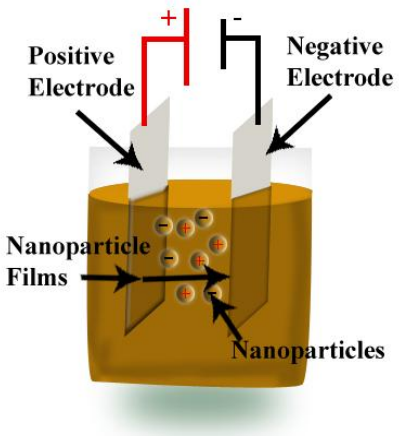

Figure 2: Schematic of electrophoretic deposition. Two electrodes are inserted into a suspension of particles. An electric field applied between the two electrodes draws the charged particles toward the electrodes.