

## CHAPTER I

### INTRODUCTION

Nanoparticles in an assortment of shapes (e.g., spherical, rod- and tube-like, sheet-like) have been the focus of far-reaching research pursuits due to their attractive material-dependent and size-dependent electronic, optical, and magnetic properties. Colloidal nanoparticles have been targeted for applications such as fluorescent tagging of cells, drug delivery, and magnetic imaging [1, 2]. Further applications may be accessed by forming dry casts of the nanoparticles. Multilayered thin films of nanoparticles have been featured in solid-state lighting, magnetic storage, and catalytic devices [3-6].

Of interest to us are techniques to create dry casts of nanoparticles. A wide variety of techniques can be used to deposit colloidal nanoparticles into a solid assembly, including spin casting, drop casting and evaporative assembly, electrophoretic deposition (EPD), Langmuir-Blodgett assembly, and layer-by-layer assembly [7]. The EPD technique is unique among these approaches in that it offers all of the following advantages:

- Applicable to a nearly endless list of materials, as long as they can be prepared as charged particles in suspension
- Control over quantity of material deposited (thickness of resulting deposit)
- Scalable over any deposition area, with the ability to pattern deposit using masks
- Extremely rapid, as most casts can be prepared in minutes, rather than hours
- Opportunity to tune the local ordering of particles or microstructure within the deposit.

In EPD, particles that are suspended in a liquid are driven by an electric field to aggregate at and deposit onto the field-emanating surface. Industrially, EPD has been used for tasks such as assembling ceramic materials and applying paint coatings to nonplanar surfaces [8]. In undertaking this dissertation, we believed that this particle assembly technique could be

drafted to tackle a question in the field of nanoscale materials science: Can nanoparticles be the sole building blocks of macroscopic solids?

The simplest architecture in which to deliver nanoparticles as a solid is to place them on a larger substrate to serve as a functional coating. All of the techniques mentioned above are capable of coating a surface with particles suspended in a liquid. The next step in the evolution of nanoparticle solids was to divorce them from the underlying substrate. This was accomplished initially by encasing the nanoparticles in a matrix such as a polymer [9-12]. When the polymer obstructed access to the nanoparticles, a new architectural concept arose: crosslinkers. The crosslinkers were molecules with two ends covalently bonded to two different nanoparticles [13]. Crosslinkers enabled the creation of robust, long-range assemblies of nanoparticles that could be studied without interference from an adjacent substrate or encasing matrix. Still, one limitation of crosslinkers is the need for specific crosslinker-to-nanoparticle-surface chemistry. We hypothesized that EPD could be utilized in a technique to produce macroscopic solids comprising nanoparticles only—no substrate, no polymer matrix, no crosslinkers.

Because EPD can produce tightly packed deposits of nanoparticles that are free of any additives, we surmised that the attractive van der Waals interaction between particles would be sufficient to hold the deposit together. Thus, we focused on the question of how to separate this deposit from the substrate on which it had been deposited. The concept we tested was adopted from MEMS fabrication: the use of a sacrificial layer [14]. If we could form a coherent deposit of nanoparticles atop a temporary material, the removal (sacrifice) of that material would liberate the nanoparticle deposit from the substrate. Done correctly, this “sacrificial layer electrophoretic deposition” (SLED) approach could yield a macroscopic solid consisting solely of nanoparticles (Figure 1-1).

Making the SLED approach work was a multifaceted problem, requiring attention to the nanoparticle suspension conditions, the selection of a sacrificial layer material, and the identification of deposition parameters for a given combination of substrate, sacrificial layer, nanoparticle, and solvent. In the subsequent chapters, we provide a map to analyze this problem. We begin by reviewing how to analyze a suspension of particles to determine the

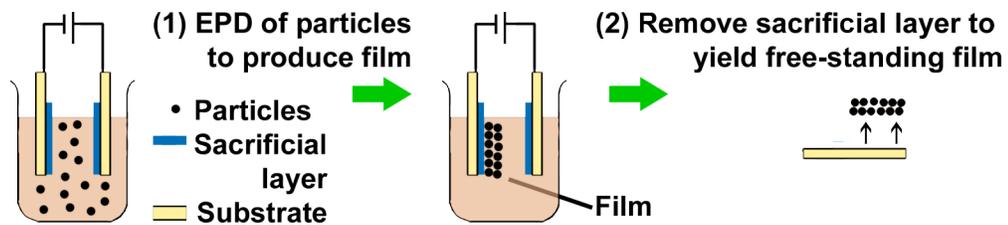


Figure 1-1. Schematic of proposed sacrificial layer electrophoretic deposition (SLED) method.

suspension's stability and predict how it will behave in the presence of an electric field (Chapter 2). A survey of EPD mechanisms follows, providing an understanding of how a suspension could be destabilized to produce the desired assembly of particles (Chapter 3). After covering the suspension and EPD concepts, we present the first set of experiments related to the sacrificial layer technique, in which we deposited spherical CdSe nanoparticles from a hexane suspension over a thin polystyrene layer to determine if nanoparticles would form a coherent deposit over a polymer (Chapter 4). Having ascertained the parameters for successful deposition of spherical nanoparticles atop a polymer layer, we explored the use of different polymers to identify which polymer attributes and dissolving conditions facilitated the production of macroscopic, nanoparticle-only assemblies (Chapter 5). Finally, we sought to test the applicability of the SLED technique to non-spherical nanoparticles. We chose to investigate sheets of exfoliated graphene oxide (eGO), suspended in water, because of their potential to constitute devices, coatings, and paper-like materials that exploit graphene's unique, enhanced electronic and mechanical properties [15, 16]. Colloidal forms of graphene are of high interest to the scientific community at present, with recent reports made on the electrophoretic deposition of substrate-bound films [17, 18], the preparation of free-standing films via filtration [19], and the tuning of wettability in drop cast eGO films [20]. In the investigation of colloidal graphene, we begin by reporting on the synthesis and characterization of eGO (Chapter 6). We then report the outcome of EPD experiments on different eGO suspensions, with the key finding that the microstructure of the resulting eGO films can be tuned by altering the deposition parameters (Chapter 7). We end by showing that the SLED technique could be applied to produce free-standing eGO films of both microstructure (Chapter 8).