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## **Nano-Engineering by Optically Directed Self-Assembly**

Anne M. Grillet, Timothy P. Koehler, Christopher M. Brotherton, Nelson S. Bell, Allen D. Gorby, Matthew D. Reichert, Ryan A. Molecke, C. Jeffrey Brinker, Katherine H. A. Bogart, Eric Dufresne, Jason Merrill, Sunil Sainis, Jin-Gyu Park, Elissa Dunn, Eric Furst, Manish Mittal, Pushkar Lele, John Singh

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# Nano-Engineering by Optically Directed Self-Assembly

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## Abstract

Lack of robust manufacturing capabilities have limited our ability to make tailored materials with useful optical and thermal properties. For example, traditional methods such as spontaneous self-assembly of spheres cannot generate the complex structures required to produce a full bandgap photonic crystals. The goal of this work was to develop and demonstrate novel methods of directed self-assembly of nanomaterials using optical and electric fields. To achieve this aim, our work employed laser tweezers, a technology that enables non-invasive optical manipulation of particles, from glass microspheres to gold nanoparticles. Laser tweezers were used to create ordered materials with either complex crystal structures or using aspherical building blocks.

This project brought together a multidisciplinary team from Sandia, Yale University, and the University of Delaware. This partnership provided a unique educational opportunity for engineering graduate students and postdoctoral researchers, while enabling new nano-engineering manufacturing technologies.

## **ACKNOWLEDGMENTS**

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# CONTENTS

1. Introduction.....	9
2. Laser Tweezers System.....	11
3. Particle Interactions .....	13
4. Optical Assembly of Three Dimensional Structures .....	17
5. Optical Switching for Three Dimensional Assembly .....	19
5.1 Particle Preparation.....	20
5.2 Structure Assembly.....	20
5.3 Results.....	22
5.4 Conclusions and Discussion .....	22
6. Particle Assembly with Electric Fields.....	23
6.1 Field Driven Assembly of Zeolite Nanoparticles .....	25
6.2 Field Driven Assembly of Titania Nanoparticles .....	25
7. Ordered Three Dimensional Structures from Arrays.....	29
8. Educational Outreach and Scientific Impact.....	31
9. Conclusions.....	33
10. References.....	34
Appendix A: Sainis et al. Langmuir 2008 .....	35
Appendix B: Koehler et al. (Submitted 2009) .....	36
Appendix C: Grillet et al. AIChE Conference Paper (2008) .....	37
Appendix D: Merrill et al. Phys Rev Lett (2009) accepted .....	38
Appendix E: Merrill & Dufresne (2009) in preparation .....	39
Appendix F: Brotherton et al. AIChE Conference paper 2009.....	40
Appendix G: Singh et al. Phys. Rev. E (2009) .....	41
Appendix H: Mittal et al. Adv. Func. Mater. (2009) .....	42
Appendix I: Lele & Furst Langmuir 2009 .....	43
Distribution .....	44

## FIGURES

Figure 1: Laser tweezers optical trapping experimental design. [Appendix B] .....	11
Figure 2. Comparisons of interparticle forces acquired using the blinking laser tweezers (□) and direct force measurement (■) techniques for polystyrene particles in a hexadecane surfactant solution. [Appendix B].....	14
Figure 3: Interaction force acting on a pair of doublet particles as a function of initial separation. [Appendix E].....	15
Figure 4: Multi-body interaction measurements of the breathing mode for a 7 particle grouping (shown in inset). show the measured forces and the red line shows the expected force based on pair-wise addition of individual interactions: a) Measurement when the screening length is small relative to the particle diameter; b) Measurement where the screening length is large relative to the particle diameter. [Appendix E].....	15
Figure 5: Sandia thunderbird logo assembled from fourteen fluorescent particles using laser tweezers.....	17
Figure 6: Particle collected for A4 diamond structure. Numbers indicate which crystal lattice layer the particle will populate.....	17
Figure 7: Cross-section of the 4 layers of crystal lattice in assembled A4 diamond structure. ....	18
Figure 8: Spirobenzopyran/Zwitterionic merocyanins. [Appendix F].....	20
Figure 9: Directed assembly of three dimensional structures using laser tweezers and optically switchable particles: a-c) Assembly procedure; d-f) Demonstration using 2 micron particles. [Appendix F].....	21
Figure 10 : Ellipsoidal microparticle ordering in electric fields; a) electric field chamber coupled to a microscope and ellipsoidal microparticles of varying aspect ratios; b) dilute concentrations where particle align with the electric field; c,d) semi dilute concentrations where particles align into tilted chains; e,f) chains merge forming crystallites with open hexagonal structure; g) two dimensional crystal of ellipsoids with long range order and associated light scattering pattern. [Appendix G] .....	23
Figure 11: Coupled electric fields and optical trapping; a) Doublet particles aligned vertically by optical trapping; b) Doublet particles aligned horizontally in an electric field., but the 3 <sup>rd</sup> and 6 <sup>th</sup> particles are flipped into a vertical orientation using optical trapping; c) Doublet particles aligned horizontally in an electric field. ....	24
Figure 12: Aspherical nanoparticles: a) ZSM-5 zeolite nanoporous catalyst – disks 300nm diameter by 120nm thick; b) Titanium dioxide - ellipsoids 130nm by 30nm. ....	24
Figure 13: Electrically ordered zeolite nanoparticles: a) wide field view, b) ordered region and c) Fourier transform pattern showing hexagonal ordering of disks aligned parallel to the substrate. ....	25
Figure 14: Electric field assisted deposition of ordered titania nanoparticle films; a) experimental geometry; b) formation of oriented film as the liquid front recedes. Particles are drawn into the film by evaporation of the fluid at the liquid front. [Appendix H] .....	26
Figure 15: SEM images of deposited titania nanoparticle films: a) particles aligned perpendicular to the applied electric field, structure is also wavy; b) randomly oriented particles; c) particles aligned parallel to the applied electric field. Electric field orientation is shown by the blue arrow. [Appendix H] .....	27
Figure 16: Nanoparticle films with parallel orientation show unusual optical properties under crossed polarizers. The observed banded structure is also reflected in small angle light scattering	

Figure 17: Reflectivity spectrum for incident 325nm light showing the reflectivity of perpendicular sample is 4 times higher than parallel sample. .... 28

Figure 18: Demonstration of stretching of arrays of spherical particles to create controlled ellipsoidal particle crystal structure. [Appendix I] ..... 29

Figure 19: Three dimensional structures with parallel (a) or alternating (b) layer orientations. [Appendix I]..... 30

## NOMENCLATURE

<i>a</i>	particle radius
AOD	acousto-optic deflector
AOT	surfactant - sodium di-2-ethylhexylsulfosuccinate
ATRP	atom-transfer radical polymerization
BCC	body centered cubic crystal structure
<i>D</i>	diffusivity coefficient
<i>E</i>	electric field orientation
<i>F</i>	interparticle force
FCC	face centered cubic crystal structure
$k_B$	Boltzmann's constant
$\kappa$	inverse screening length [ $\mu\text{m}^{-1}$ ]
NA	numerical aperture
Nd-YAG	Neodymium Yttrium Aluminum Garnet
NSOM	near-field scanning optical microscopy
PVA	poly vinyl alcohol
SEM	scanning electron microscopy
<i>T</i>	temperature
<i>V</i>	relative velocity
ZSM	type of zeolite nanoparticle catalyst



# 1. INTRODUCTION

The lack of robust nanomanufacturing capabilities has limited industry's ability to make tailored materials with useful optical and thermal properties and harness the unique properties of nanomaterials. For example, traditional methods such as spontaneous self-assembly of spheres cannot generate the complex structures required to produce a full bandgap photonic crystals.<sup>1,2</sup> In order to achieve a full band gap, crystal structures need to break the symmetries of simple face-centered-cubic (FCC) and body centered cubic (BCC) lattices. Theoretical calculations have predicted wide photonic band gaps can be achieved by either building more complex crystal structures such as the A4 diamond lattice<sup>3</sup> or using aspherical particles.<sup>1</sup> However, current directed and self assembly techniques cannot create these types of structures. With aspherical particles, disorder in the orientation in the particle orientation prevents the formation of long range order during self-assembly. Complex crystal structures like the A4 diamond lattice are not the most energetically favorable state for particle assembly. The goal of this work is to develop and demonstrate novel methods of directed self-assembly of nanomaterials using optical and electric fields.

To achieve this aim, our work employed electric fields and laser tweezers, a technology that enables non-invasive optical manipulation of particles, from glass microspheres (diameter~3 $\mu$ m) to gold nanoparticles (diameter~20nm).<sup>4</sup> Our initial work focused on studying the interactions of both spherical and aspherical particles. In Section 3, we describe several techniques to study interactions of spherical particles and also new tensor-based methods to study interactions of aspherical particles and groups of many particles. During research into interactions of multiple particles, we discovered that under certain conditions, standard assumptions that particle interactions are pair-wise additive break down. When the screening length of the electrostatic interactions was large relative to the size of the particle, the measured electrostatic repulsions were much lower than expected. These multi-body effects have been confirmed for polymer microparticles in nonpolar solvent, but are expected to also be important for nanoparticles dispersions in both aqueous and organic solvents. The startling result is that dispersions with highly repulsive particles can be unstable due to multi-body effects on the particle interactions.

The main body of our work has focused on developing novel assembly methods to allow manufacture of novel structures and the capabilities to work with aspherical particles. Directed assembly using laser tweezers for particle-level construction of structures is described in Section 4. Using manual control, we have created smaller structures out of up to a dozen particles. Holographic optical trapping enables larger scale computer-controlled assembly of structures. Routines have been developed to recognize particles, gather them and build complex three dimensional structures. We have demonstrated automated assembly of the A4 diamond structure using this technique. Section 5 describes a new method developed at Sandia to preserve these particle structures using new functional coatings for microparticles with optical switching. Particles are stable in solution until exposed to ultraviolet (350nm) light at which point they bond together. We have demonstrated how these functional particles can be employed to build three dimensional structures.

Another method for assembly of particle structures using electrical fields is described in Section 6. Due to their dielectric properties most particles will be driven to assemble in electric fields. Large (several mm square) high quality two dimensional arrays of spherical microparticles have been demonstrated previously. We have, for the first time, applied this technique to study the assembly of aspherical particles and studied their interactions. Unlike spherical particles which assemble into straight chains aligned with the electric field, ellipsoidal polystyrene microparticles formed tilted chains oriented at a small angle to the electric field. At higher concentrations, these chains assembled into an open hexagonal structure. Finally we have demonstrated the ability to engineer defects into ordered crystalline structures using laser tweezers to locally reorient the aspherical particles.

These techniques are equally applicable to nanoparticle solutions. We have demonstrated electrical field driven assembly of two types of nanoparticles: ZSM-5 zeolite nanoparticles are used for catalytic conversion of hydrocarbons and titanium dioxide particles are commonly used in paints and consumer products such as sunscreen due to their light scattering properties. These two industrially relevant nanoparticles create novel ordered structures in electric fields due to their aspherical shapes. Zeolite ellipses are formed into ordered two dimensional arrays. For titania ellipses, the convective assembly was coupled to the electrical field method to create ordered nanoparticle films. Electric fields are employed during deposition to control the orientation of the deposited particles. Nanostructured titania films have been manufactured with several different orientation structures and are currently being investigated with their unusual optical, mechanical and thermal properties.

An alternate method has been developed specifically to harvest ordered structures created using electrical field assembly and build three dimensional structures (Section 7). Functionalized biotin coatings on the particles are used which covalently bind to each other on exposure to streptavidin. They can then be encased in a polymer matrix and two dimensional ordered films can be assembled into more complex three dimensional structures with controlled crystal orientation. With nanoparticles films, the convective assembly is coupled to the electrical field method to create ordered nanoparticle films. Electric fields are employed during deposition to control the orientation of the deposited particles. Using this technique, several ordered films with unique properties have been created.

This project brought together a multidisciplinary team from Sandia, Yale University, and the University of Delaware. This partnership has provided unique educational opportunities for several engineering undergraduate students, graduate students and postdoctoral researchers which will be discussed in Section 8 along with a summary of our impact in the scientific community and at Sandia.

## 2. LASER TWEEZERS SYSTEM

Optical trapping was used in these experiments to manipulate particles in solution using the systems described briefly here and in more detail in Appendices A&B. A 1064 nm beam (A) emitted from a Ventus Doubled Neodymium-Yttrium Aluminum Garnet (Nd-YAG) laser was attenuated by a neutral density filter (B) and expanded before being passed to the two-dimensional acousto-optic deflector (AOD). The AOD (D), A.A. Opto-Electronics DTSXY-400-1064, is powered by an Agilent E3640A DC supply and deflects the incident beam at an angle proportional to an input frequency supplied from a control program written in LabVIEW. The beam exited the AOD and was again expanded before entering a Nikon TE2000-S inverted microscope and passing through filtered beam splitters (E) to overfill the Nikon Plan Fluor 100x/1.3 N.A. oil immersion objective (F). Multiple time-shared optical traps were created by rapidly alternating the laser beam between two or more locations at a rate faster than the particle diffusion time scale.

Holographic optical trapping systems are similar except instead of using an acousto-optic deflector to control a single laser beam position, the laser is reflected off of a spatial light modulator to manipulate the phase of the light passing into the microscope (see Appendix A). Thus the laser light is projected into a three dimensional pattern of traps in the microscope field of view.

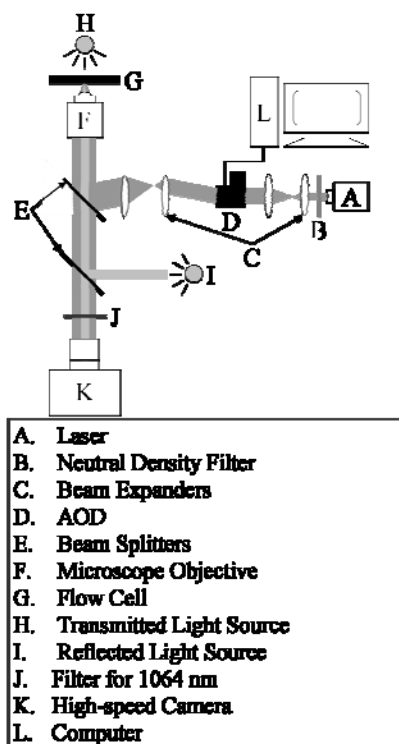


Figure 1: Laser tweezers optical trapping experimental design. [Appendix B]

A Harvard Apparatus RC-30 flow chamber (G) was used to contain the particle/solvent system, which consisted of carboxyl-modified polystyrene microspheres (Invitrogen 7-2400) dispersed in hexadecane (Sigma-Aldrich) with a surfactant. The microparticles have a manufacturer-specified radius  $a = 1.2 \mu\text{m} \pm 0.094 \mu\text{m}$ . In these tests, the AOT surfactant sodium di-2-ethylhexylsulfosuccinate (Sigma-Aldrich), was used at 1 mM concentration (above the critical micellar concentration) in hexadecane to initiate long range interactions between particles.<sup>5,6</sup> The viscosity of the solution was assumed to be unchanged from the literature value for pure hexadecane of 6.5 mPa·s.

The behavior of the optically trapped microparticles was monitored by utilizing a standard bright field white light source (H) and imaged in reflected light produced by a 120W EXFO X-Cite Series 120 Hg-Arc lamp. An optional 1064 nm filter (J) was placed before the high-speed 12 bit Vision Research Miro 4 camera (K) to eliminate most of the reflected laser light from reaching the camera. The filter was used primarily in the direct force experiments, when the particle is imaged while inside the optical trap. The particles were imaged at 500 Hz and exposure times up to 1997.5  $\mu\text{s}$ . The recorded images were then transferred to a computer for processing using a particle tracking code developed in MatLab.

### 3. PARTICLE INTERACTIONS

Understanding particle interactions is critical to directing assembly of many particles. Laser tweezers have been employed to measure interaction forces between colloidal particles because they have several advantages over other techniques. Optical trapping is non-invasive and has force resolution up to 10 femtoNewtons. Several variations of the optical trapping method have been proposed, but have never been validated against each other. We have implemented the two most common – blinking laser tweezers and direct force measurement on a model system. These experiments are described in detail in referred manuscripts attached as Appendices A, B & C.

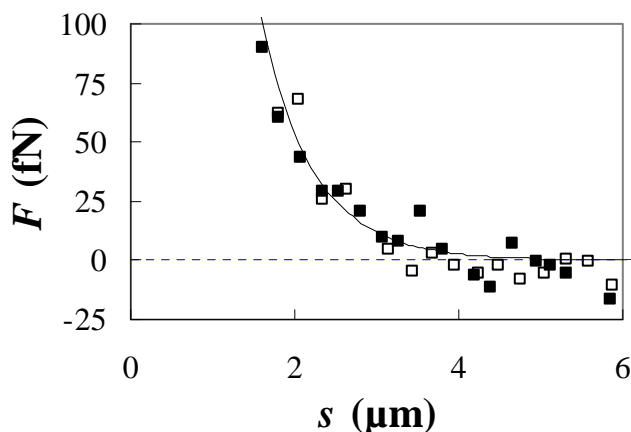
Three techniques are commonly employed to probe interactions between colloidal particles; direct force measurements,<sup>7-13</sup> blinking laser tweezers,<sup>14-18</sup> and scanning line optical tweezers.<sup>19-23</sup> We have chosen to focus on the first two as they are more widely accepted. Direct force measurements make use of linear correlation between the displacement of a particle held in an optical trap to the force exerted on that particle for small displacements. The proportionality constant, or optical trap stiffness, can be calibrated by either using a known viscous drag on the particle or measuring the diffusion of a particle held in the trap.<sup>5</sup> Typically, the particle position inside of the trap is determined using either a video camera or a quadrant photodiode, both of which offer similar position resolution, though the quadrant photodiode can operate at much faster speeds enabling feedback control for a “constant force” optical trap.<sup>5</sup> An advantage of the direct force measurement technique is the capability to measure attractive interactions.<sup>9</sup>

The second optical trapping method commonly used to measure particle interactions is blinking laser tweezers.<sup>14,17</sup> This technique uses a pair of particles held in separate optical traps which are repeatedly turned on and off. The two particles are free to diffuse when the optical traps are blinked off and by statistical analysis of their trajectories during this time, the force between the particles can be inferred. The optical traps in this method simply serve to position the particles in the field of view, away from walls and at close (potentially energetically unfavorable) separations. Crocker and Grier analyzed these data using Markovian Dynamics Extrapolation which identifies the equilibrium pair distribution from the experimentally sampled probability evolution operator.<sup>14</sup> More recently, Sainis *et al.* have proposed an alternative method which explicitly accounts for hydrodynamic coupling while calculating the forces between the particles.<sup>17,18</sup> The force between the particles is given by:

$$F = k_b T \frac{v}{D}$$

where  $F$  is the force between the particles,  $k_b$  is Boltzmann’s constant,  $T$  is the temperature,  $v$  is the relative velocity between the particles and  $D$  is the diffusion coefficient (see Appendix A for more detail on the derivation of this equation). Depending on the experimental operating parameters, particle interactions can be measured with a resolution of several femto-Newtons. The blinking laser tweezers method is attractive to use because the force measurements occur only when the laser is inactive, thus there is no concern about optical effects. However, close range attractive interactions are difficult to measure and the method is time and data intensive.

These two optical trapping methods of measuring interaction forces of spherical colloids were found to be in excellent agreement as shown in Figure 2.



**Figure 2. Comparisons of interparticle forces acquired using the blinking laser tweezers (□) and direct force measurement (■) techniques for polystyrene particles in a hexadecane surfactant solution. [Appendix B]**

The blinking method was then expanded for aspherical particles and groups of particles. For spherical particles, only one variable is required to capture the relative diffusion. For more complex interactions with multiple or complex shaped particles, there are multiple degrees of freedom which must be accounted for. Thus the simple scalar relationship was expanded to a tensor formulation as described in detail in Appendix D & E.

$$\vec{f} = k_B T \underline{\underline{D}}^{-1} \vec{v}_d$$

where  $\vec{f}$  is the vector containing all of the forces and torques between the particles,  $\vec{v}_d$  contains the linear and angular drift velocities,  $k_B$  is Boltzmann's constant,  $T$  is the temperature and  $\underline{\underline{D}}$  is the diffusion tensor. From experimental observation of the Brownian trajectories of groups of particles, the diffusion tensor and velocities can be measured. Application of this method to aspherical doublet particles is shown in Figure 3 for the normal mode of particles moving perpendicular to each other. No significant forces along the vertical direction or torques were measured.

This method can also be applied to study interactions among multiple particles. Figure 4 shows measurements performed on a grouping of seven particles under two solvent conditions. In the first case (c.f. Figure 4a), the screening length of the electrostatic repulsion is short relative to the size of the particle. The measured force for the breathing mode is the sum of the interactions between each pair. This confirms the traditional assumption of pair-wise additivity of colloidal forces. For the second solvent conditions shown in Figure 4b, the screening length of the electrostatic interactions is three times the particle diameter. In this case, the measured forces are significantly lower than predicted using the pair-wise assumption. While these measurements were performed on microparticles in a non-polar solvent, this result has significant implications for nanoparticles dispersions. Screening lengths typically observed in

aqueous solvents are only hundreds of nanometers. Thus multi-body effects should be especially important in concentrated nanoparticles dispersions and directed assembly of nanoparticles.

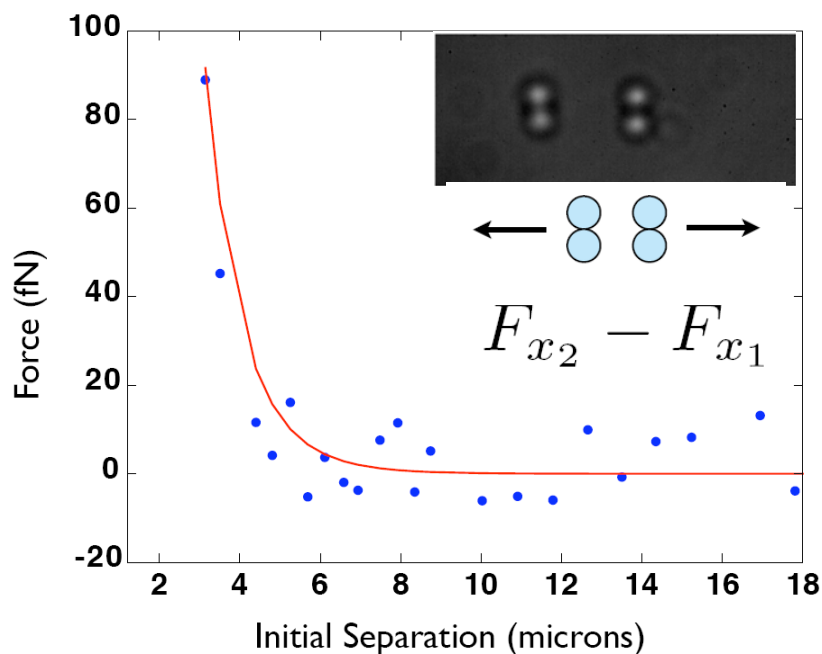


Figure 3: Interaction force acting on a pair of doublet particles as a function of initial separation. [Appendix E]

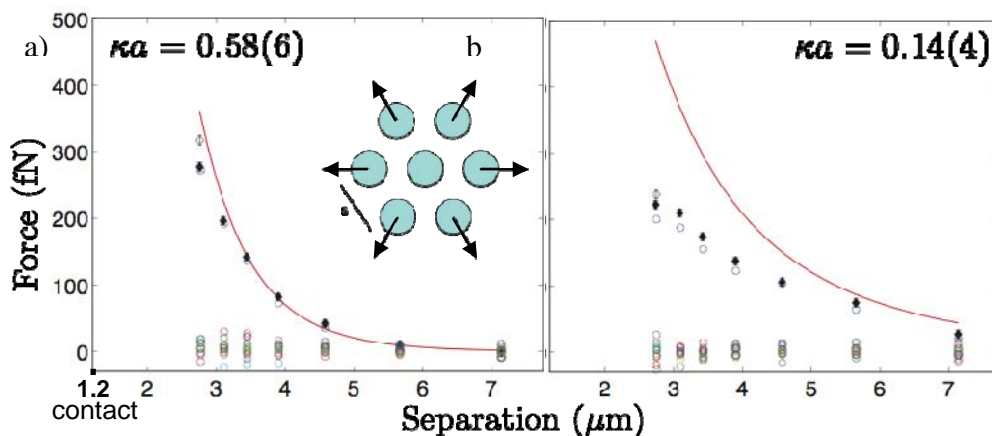


Figure 4: Multi-body interaction measurements of the breathing mode for a 7 particle grouping (shown in inset).  $\blacklozenge$   $\circ$  show the measured forces and the red line shows the expected force based on pair-wise addition of individual interactions: a) Measurement when the screening length is small relative to the particle diameter; b) Measurement where the screening length is large relative to the particle diameter. [Appendix E]





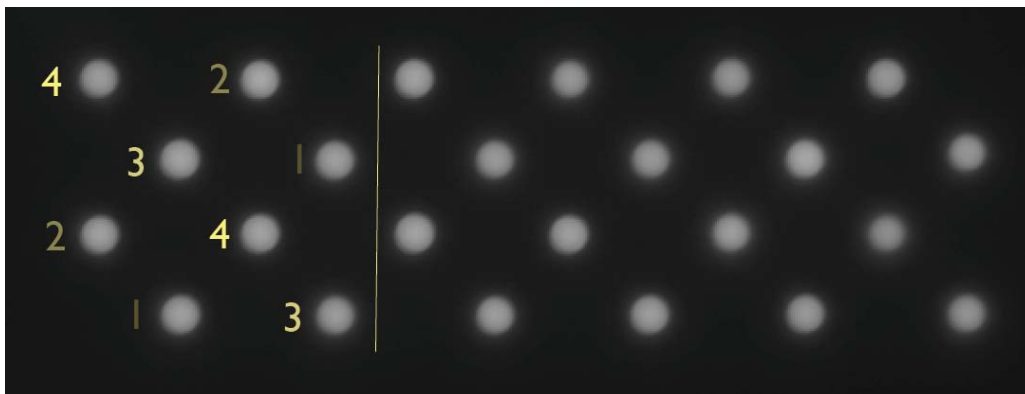
## 4. OPTICAL ASSEMBLY OF THREE DIMENSIONAL STRUCTURES

In addition to studying particle interactions, laser tweezers also have the capability to assemble structures from individual particles. Using an acousto-optic beam steering system, around a dozen simultaneous laser traps can be generated allowing the construction of simple structures as shown in Figure 5.

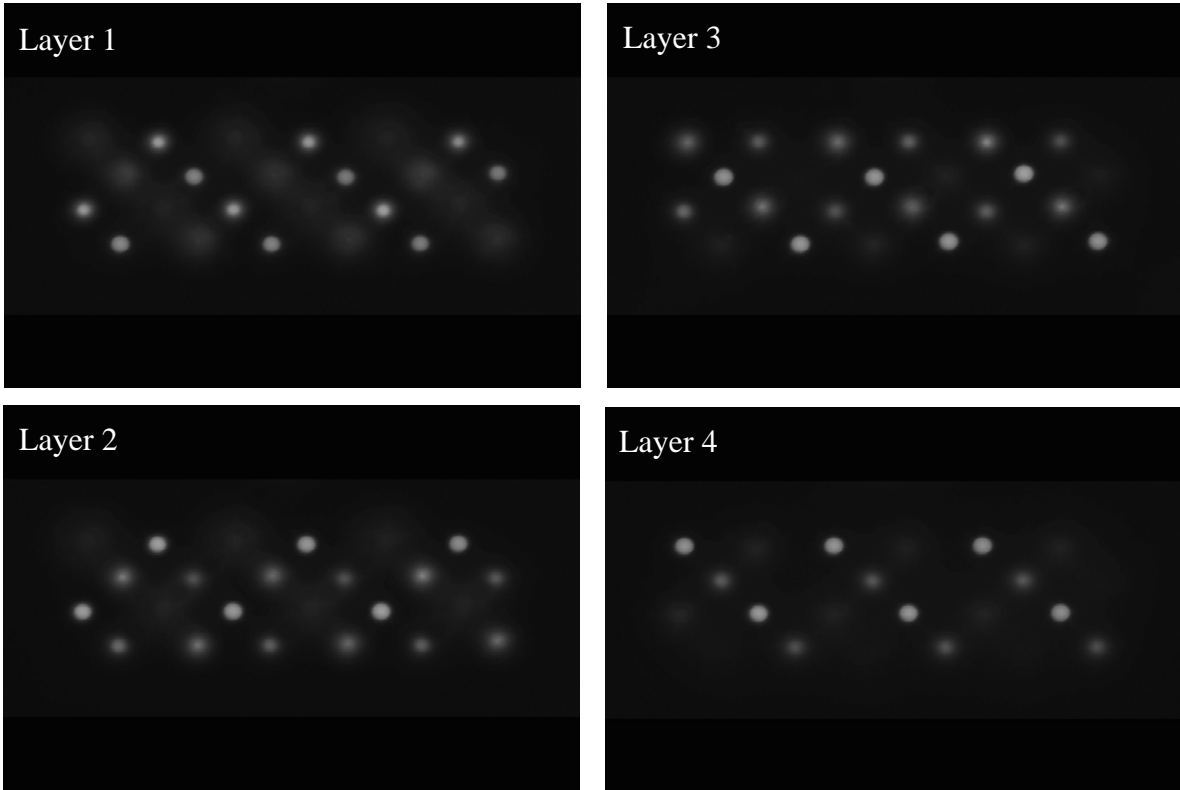


**Figure 5: Sandia thunderbird logo assembled from fourteen fluorescent particles using laser tweezers.**

For more complex structures of up to a hundred particles, holographic optical trapping offers a unique capability in micromanipulation. An automated computer algorithm was developed to automate assembly of complex three dimensional structures. First, particles were identified in the field of view,. The particle trajectories were determined and the required wavefront patterns for the spatial light modulator were calculated. Dynamic feedback corrections were performed for collision avoidance and updating of the assembly process. Using this process, complex two and three dimensional particle structures were assembled. Figure 6 shows the particles that have been collected which will be assembled into 3 unit cells of an A4 diamond crystal lattice. The crystal lattice layers that they will populate are shown on the left. The resulting three dimensional structure is read out layer by layer in Figure 7.



**Figure 6: Particle collected for A4 diamond structure. Numbers indicate which crystal lattice layer the particle will populate.**



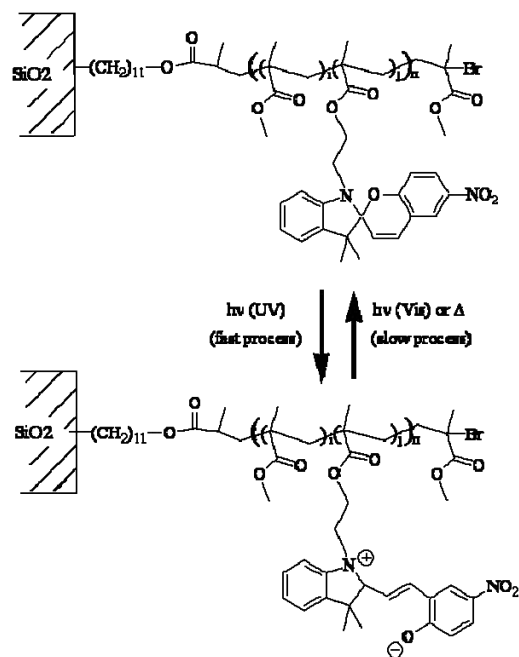
**Figure 7: Cross-section of the 4 layers of crystal lattice in assembled A4 diamond structure.**

## 5. OPTICAL SWITCHING FOR THREE DIMENSIONAL ASSEMBLY

Colloidal particles modified with photo-sensitive polymeric brushes exhibit reversible phase transformation properties allowing for the development of switchable particle aggregation and rheological response. By manipulating photo-sensitive particles using optical trapping, it is possible to assemble two and three dimensional microstructures as described in more detail in Appendix F. The system demonstrated here consists of 2 micron borosilicate particles, coated with poly methyl methacrylate/spirobenzopyran copolymer brushes, suspended in toluene. Particle structures are assembled in the solvent using time-shared optical traps and then exposed to ultraviolet light. The light induces a polarity change in the polymer brushes causing particle-particle adhesion. The resulting two dimensional structure is then attached to a substrate. The process is repeated with additional building blocks to assemble three dimensional microstructures with multiple particle layers. Research activities to develop this assembly capability are presented related to the material requirements needed in optical trapping systems, their application in this photo-sensitive system, and developments in particle assembly.

In this work, we demonstrate a technique using optical trapping to construct robust three dimensional microstructures using optically switchable functionalized microparticles. Borosilicate microparticles are coated with optically active polymethyl methacrylate / spirobenzopyran copolymer brushes. Spirobenzopyran is a nonpolar molecule that experiences a ring-opening isomerization, when exposed to UV ( $\lambda = 366\text{nm}$ ), resulting in a zwitterionic merocyanine with a higher dipole moment, as shown in Figure 8. The reverse reaction is caused by exposure to heat or visible light ( $\lambda = 533\text{nm}$ ), but is typically much slower than the forward reaction.<sup>24</sup> Using atom-transfer radical polymerization (ATRP), copolymer brushes of polymethyl methacrylate/spirobenzopyran can be attached to silica particles.<sup>25-28</sup> In a nonpolar solvent, such as toluene, the copolymer forms a stable solution. In the zwitterionic form, the copolymer solution phase separates due to the polarity difference between the polymer and the solvent. Likewise, micro particles coated with spirobenzopyran copolymer are stable in nonpolar solvents. When these suspensions are exposed to UV, the polarity change of the spirobenzopyran will cause the particles to develop a strong interparticle attraction and aggregate. In earlier work, this polarity change was used to moderate rheological properties of the suspension.<sup>29</sup> By controlling UV exposure, the particle-particle interactions can be manipulated and used for building microstructures.<sup>24,28</sup>

In this study, we describe a fabrication method that exploits the controlled interactions of particles coated with spirobenzopyran and the precise spatial manipulation of particles using optical trapping. For this method, layers of particles will be oriented using optical trapping and the isomerization of the copolymer brushes will cause the particles to adhere to one another, locking in the structure. Complex three dimensional structures can be constructed by combining multiple particle layers as described below.



**Figure 8: Spirobenzopyran/Zwitterionic merocyanins. [Appendix F]**

## 5.1 Particle Preparation

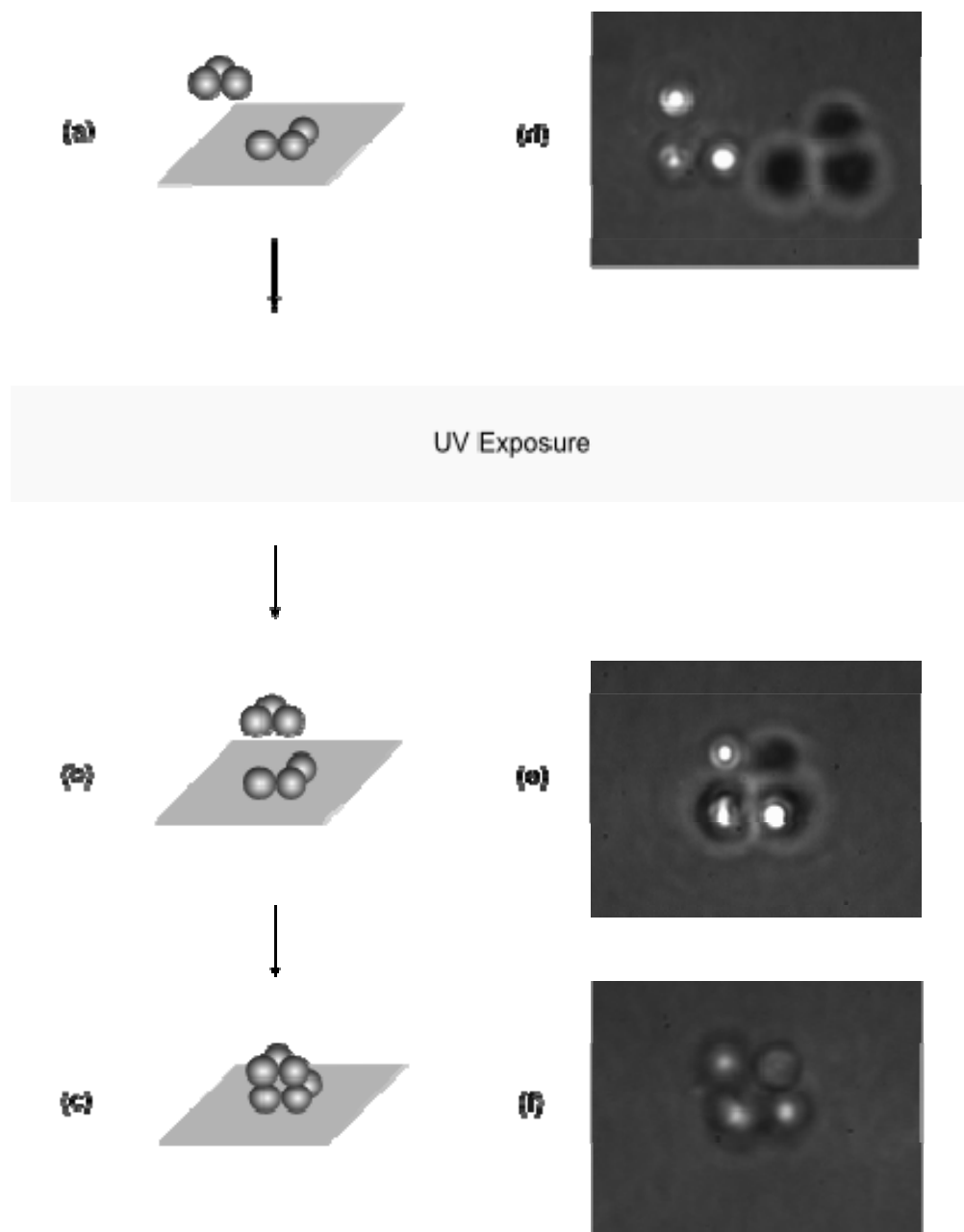
Polymethyl methacrylate/spirobenzopyran copolymer brushes were grafted to 2 micron spherical borosilicate particles (Duke Scientific) using ATRP. Borosilicate was chosen since it has a refractive index higher than that of toluene. The molar concentration of the spirobenzopyran in the copolymer brushes was kept constant at 20%. Following the synthesis, the modified particles were washed four times in toluene (Sigma-Aldrich) to remove any remaining catalysts or reactants. Finally, the particles were placed into toluene for the experiment.

## 5.2 Structure Assembly

Optical trapping was used in these experiments to spatially manipulate microparticles in solution and was accomplished using the apparatus described in Section 2. A custom flow chamber consisting of a 2 mm x 3 mm x 50 mm straight channel with a single inlet and outlet, was used to study the surface modified borosilicate particles dispersed in toluene. The top and bottom of the channel are glass coverslips affixed to the aluminum by two part epoxy to provide optical access to the sample.

Figures 3 (a-c) illustrates the layer-by-layer assembly procedure. Multiple optical traps are used to arrange a single plane of particles perpendicular to the optical axis of the microscope (Figure 9a). The polarity of the particle surface coating is manipulated by exposing the trapped particles to UV using a 120W EXFO X-Cite Series 120 Hg-Arc lamp (Figure 1 part I). After increasing the polarity, the particles adhere to one another and form a single particle layer. Figure 9b illustrates two particle groups. The first has been previously constructed and placed on the substrate. The second particle group remains suspended in the liquid and is moved into position with the optical tweezers. Once in position, the second particle group is lowered onto the

immobilized particle layer. Figure 9c shows the completed three-dimensional structure. The process can be repeated to include additional particle layers.



**Figure 9: Directed assembly of three dimensional structures using laser tweezers and optically switchable particles: a-c) Assembly procedure; d-f) Demonstration using 2 micron particles. [Appendix F]**

### 5.3 Results

Figure 9 (d-f) illustrates the assembly of a 2-layer structure made up of 6 borosilicate particles. In Figure 9d, two groups of particles are evident. The first group is immobilized on the substrate. The second group is controlled using three time-shared optical traps. The field of view is then illuminated using UV light causing a polarity change in the copolymer brushes. After exposure, the particles in the second group adhere to one another forming a particle layer. In Figure 9e, the second particle group is moved into position directly over the immobilized group. Finally Figure 9f shows the completed structure. The second particle group is in direct contact with the immobilized group. Since both layers contain particles with copolymer brushes and have been exposed to UV, adhesion between layers will occur. The resulting structure has dimensions of 4 micron cube.

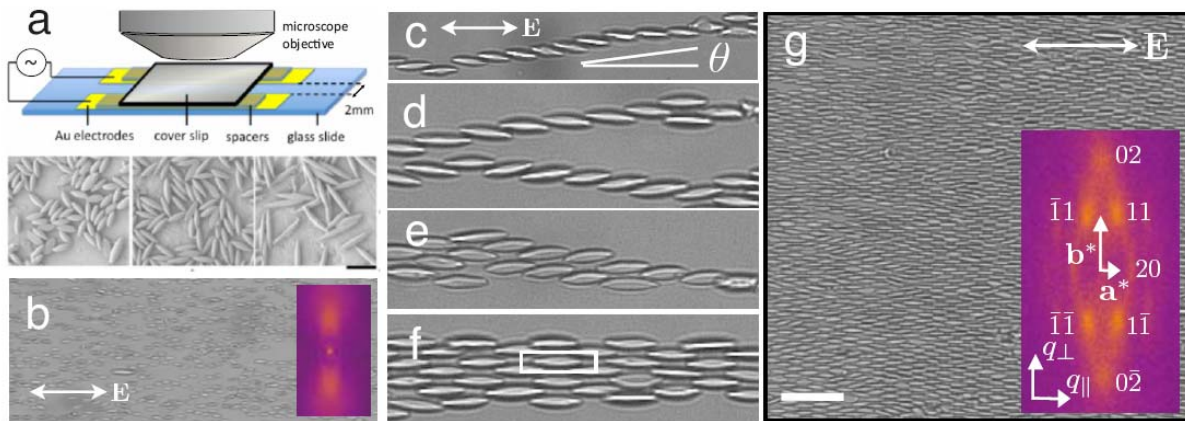
### 5.4 Conclusions and Discussion

A new microstructure fabrication method has been developed that is capable of constructing three-dimensional structures layer by layer using borosilicate particles in toluene. Potential applications for this technique are photonic crystal assembly or assembly of unique crystalline forms that have interesting macroscopic optical, thermal, or mechanical properties. The challenges of this technique are scalability and the required use of a hazardous solvent system. Scalability issues can be addressed by using holographic optical tweezers that allow the fabrication of complex three-dimensional structures directly instead of layer-by-layer. Alternatively, large crystal structures could be assembled via other techniques (*e.g.* convective or self assembly) and then optical tweezers could be used to create strategic defects within the large crystal. The large crystal, with engineered defects, could then be locked in using the photosensitive spirobenzopyran surface chemistry. Finally, the hazardous toluene system was chosen based on polarity and further investigation of other nonpolar solvents may allow for a less hazardous solvent.

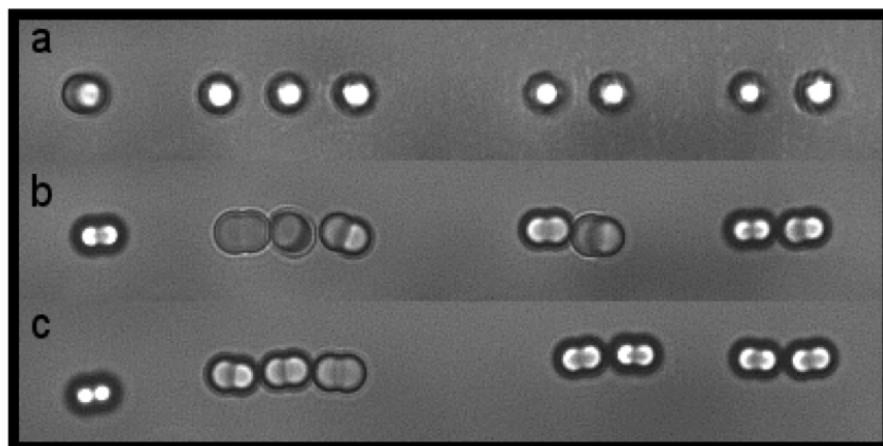
## 6. PARTICLE ASSEMBLY WITH ELECTRIC FIELDS

When working with aspherical particles, electric fields provide a useful tool to induce long range order in dilute solutions. For spherical particles as the concentration increases, the dipoles induced in the particles cause them to aggregate forming first long chains, then crystallites, and finally layers of highly ordered two dimensional crystal layers. We have extrapolated this technique to create ordered structures of aspherical particles. For aspherical polystyrene microparticles in dilute solution, they align with the long axis in the direction of the electric field. As the concentration increases, ellipsoids formed tilted chains oriented at a small angle to the electric field (c.f. Figure 10b,c). At higher concentrations, these chains assembled into an open hexagonal structure as shown in Figure 10f,g. These experiments are explained in greater detail in Appendix G along with a theory which explains the unusual ordering of the ellipsoids. Similar structures have also been observed with doublet or dimer particles.

We have additionally demonstrated the ability to include engineered defects into these ordered structures by coupling laser tweezers and electric field assembly. Separately, these two methods can each individually align the doublet particles. In this case, the particles are vertically aligned by laser tweezers and horizontally aligned by the electric field. In Figure 11b, we demonstrate the ability of laser tweezers to change the orientation of aspherical doublet particles in the presence of an electric field by flipping the third and sixth particles into a vertical orientation in the presence of an electric field. Thus optical tweezers can be employed to engineer defects within an ordered particle array generated with electric fields. We discuss methods to preserve particle structures in Sections 5 and 7.

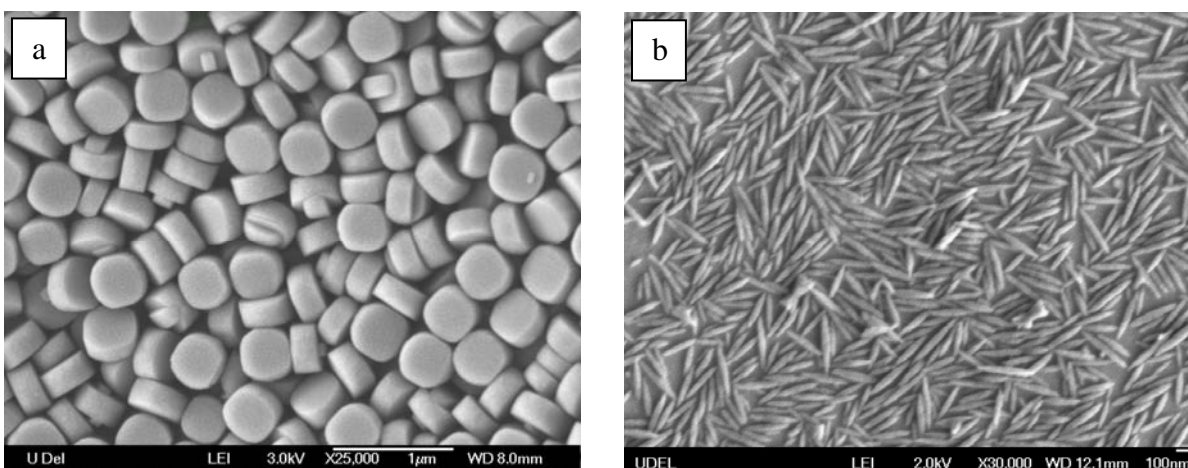


**Figure 10 : Ellipsoidal microparticle ordering in electric fields; a) electric field chamber coupled to a microscope and ellipsoidal microparticles of varying aspect ratios; b) dilute concentrations where particle align with the electric field; c,d) semi dilute concentrations where particles align into tilted chains; e,f) chains merge forming crystallites with open hexagonal structure; g) two dimensional crystal of ellipsoids with long range order and associated light scattering pattern. [Appendix G]**



**Figure 11: Coupled electric fields and optical trapping; a) Doublet particles aligned vertically by optical trapping; b) Doublet particles aligned horizontally in an electric field., but the 3<sup>rd</sup> and 6<sup>th</sup> particles are flipped into a vertical orientation using optical trapping; c) Doublet particles aligned horizontally in an electric field.**

Electrical field assembly has also been applied to several aspherical nanoparticles shown in Figure 12. ZSM-5 is an industrial catalyst used in the alkylation and isomerization of hydrocarbons. These nanoparticles were just large enough to visualize with visible light and were studied dynamically during assembly. The second nanomaterial studied was ellipsoidal titania. Titanium dioxide is prevalent in many applications from paint to sunscreens in part due to its high refractive index. These nanoparticles are too small to see optically so they were instead assembled convectively into a film which was deposited onto a glass slide. The particle orientation in the film was controlled with the electric field as the film was deposited. The films were 2 mm by 2 mm and generally several microns thick depending on the deposition speed. These nanostructured films appear to have interesting optical and thermal properties which are currently being investigated more completely.

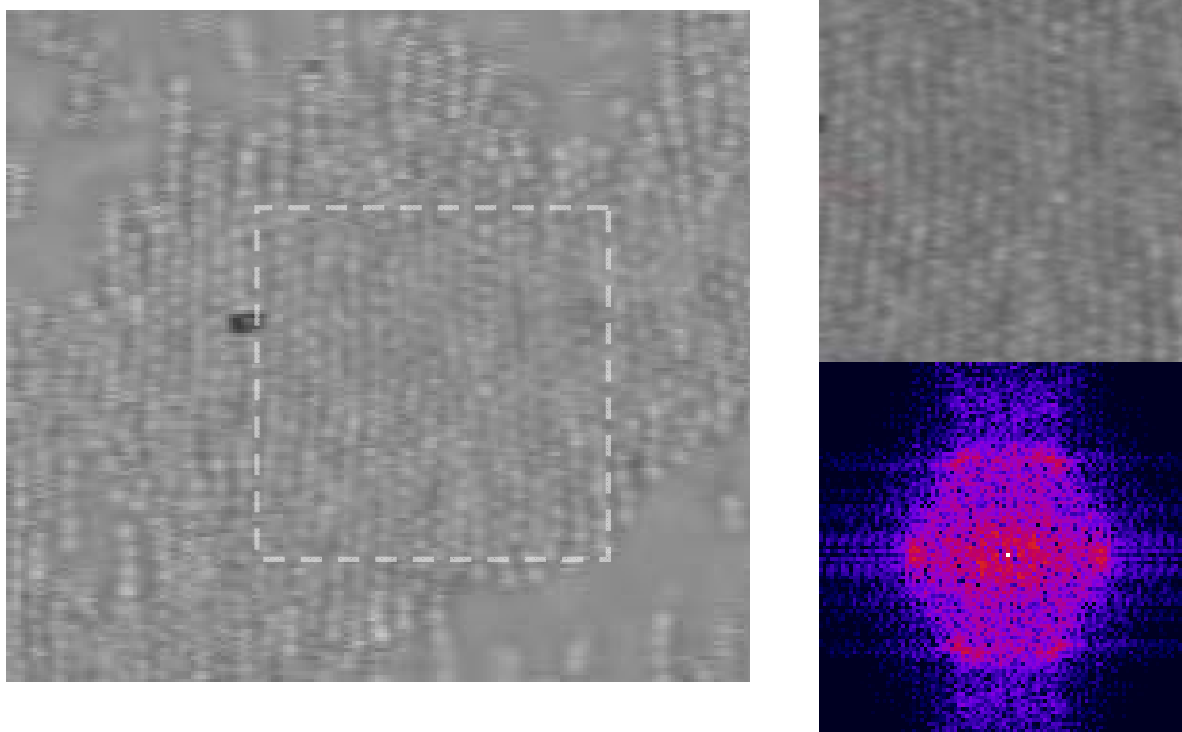


**Figure 12: Aspherical nanoparticles: a) ZSM-5 zeolite nanoporous catalyst – disks 300nm diameter by 120nm thick; b) Titanium dioxide - ellipsoids 130nm by 30nm.**



## 6.1 Field Driven Assembly of Zeolite Nanoparticles

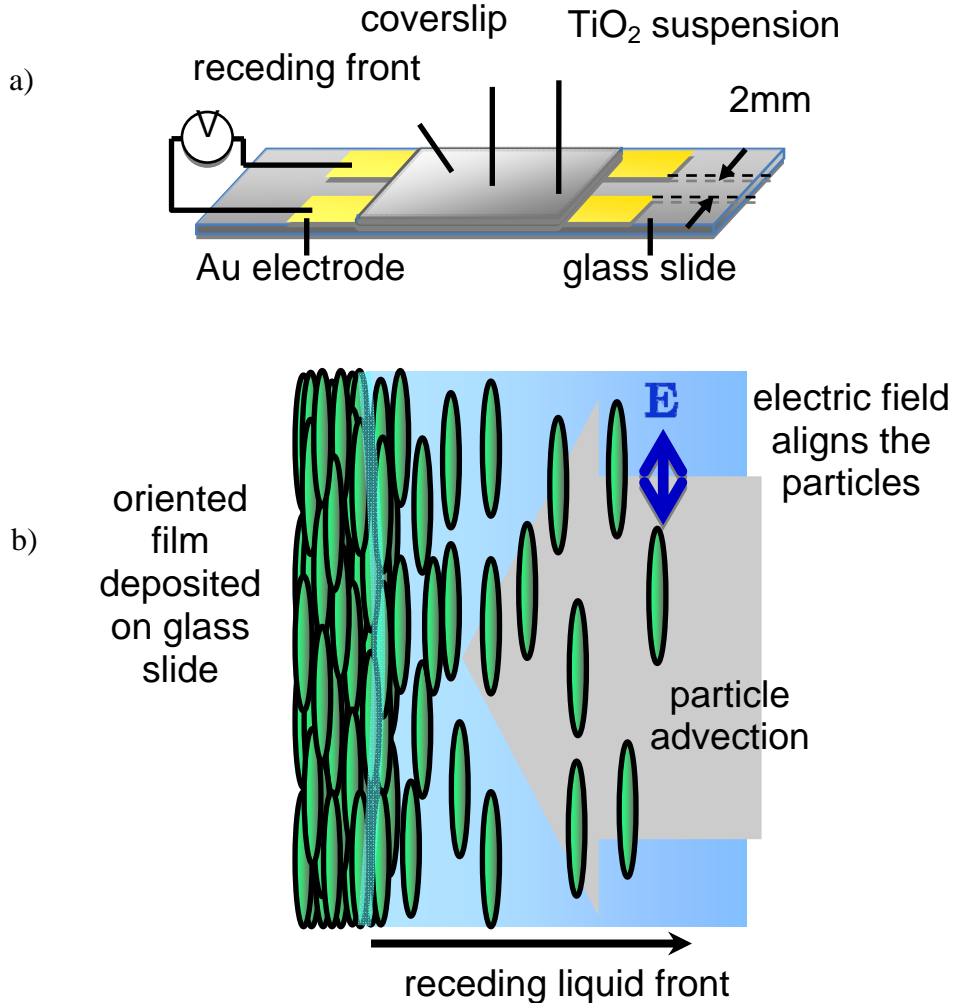
Figure 13 shows images of ordered two dimensional crystal regions of zeolite particles generated under an electric field. The disks tend to orient with their flat faces parallel to the field of view and then organize in a manner similar to spheres. First they form strings of disks aligned with the electric field direction. At higher concentrations, those strings combine to form hexagonally ordered two dimensional arrays. A more detailed explanation of the ordering dynamics and experimental conditions is in preparation for publication - M. Mittal and E. M. Furst, “Directed assembly of zeolites.”



**Figure 13: Electrically ordered zeolite nanoparticles: a) wide field view, b) ordered region and c) Fourier transform pattern showing hexagonal ordering of disks aligned parallel to the substrate.**

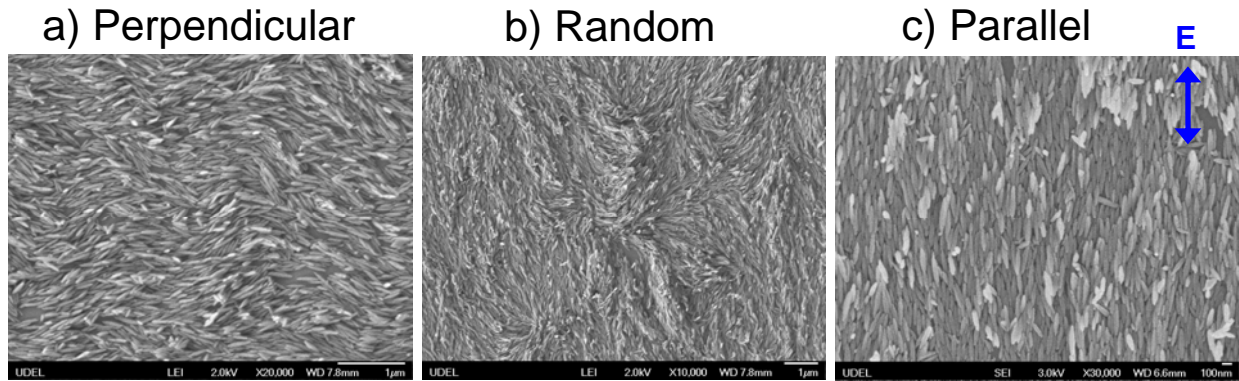
## 6.2 Field Driven Assembly of Titania Nanoparticles

Electric field driven assembly of titanium dioxide nanoparticles has been performed and is described in greater detail in Appendix H. Since these particles are too small to be observed through a microscope, nanoparticle films were deposited under the influence of the electric field as shown in Figure 14. By manipulating the electric field frequency and amplitude during the deposition process, various film nanostructures can be fixed into the film as shown in Figure 15. The resulting films can have particle volume fractions as high as 75%.

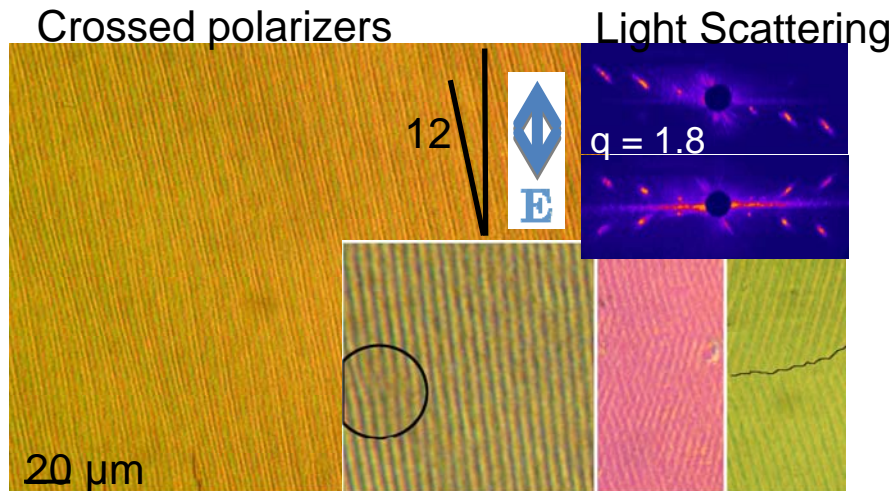


**Figure 14: Electric field assisted deposition of ordered titania nanoparticle films; a) experimental geometry; b) formation of oriented film as the liquid front recedes. Particles are drawn into the film by evaporation of the fluid at the liquid front. [Appendix H]**

We have begun analyzing the mechanical, optical and thermal properties of these nanostructured films. The anisotropic mechanical properties are discussed in Appendix H. The films of oriented particles are birefringent indicating anisotropic effective refractive index. Additionally when the films are viewed between crossed polarizers, a more complex structure appears (c.f. Figure 16). Alternating bright and dark bands with a length scale of  $\sim 3$  microns are observed. They are tilted at a small angle relative to the electric field. This microstructure was confirmed using small angle light scattering. The bands show typical crystal like defects including twinning and line defects (c.f. inset Figure 16). SEM imaging has confirmed that the particles are oriented in the direction of the electric field, not along the bands.



**Figure 15: SEM images of deposited titania nanoparticle films: a) particles aligned perpendicular to the applied electric field, structure is also wavy; b) randomly oriented particles; c) particles aligned parallel to the applied electric field. Electric field orientation is shown by the blue arrow. [Appendix H]**



**Figure 16: Nanoparticle films with parallel orientation show unusual optical properties under crossed polarizers. The observed banded structure is also reflected in small angle light scattering which also shows oriented microstructure at a slight tilt to the electric field. SEM confirms that particles are aligned directly with the electric field. [Appendix H]**

Further studies of the optical properties of the samples were performed using near field scanning optical microscopy (NSOM). The system used was a WITec alpha 250 Near-field Scanning Optical Microscope (NSOM). Confocal mode was employed using a 100x Nikon Ultrafluar objective (NA = 0.9, resolution at 325 nm ~0.92 μm) and a Kimmon Electric HeCd laser (325 nm, 20mW unpolarized). The spectrometer used was an Acton 2300 with a 300 blaze/300nm grating with a center wavelength of 450 nm. The detector was a 1300x100CCD chip thermoelectrically cooled to -41°C. Spectra were collected with Winspec software and images collected with ScanControl Spectroscopy Plus software. Reflectivity data was gathered using a 10x objective on the samples with the various particle nanostructures as demonstrated in Figure 15. The films with perpendicular orientation of the particles were found to have significantly higher reflectivity than the films with parallel particle orientation as demonstrated in Figure 17. There

was significant variability on each sample so the reflectivity behavior of these films needs to be studied in more detail.

The thermal properties of these novel materials are also of considerable interest. Because of their small scale structure, these films are expected to have very low thermal conductivity properties relative to their high density. Truman fellow Patrick Hopkins has started measuring their thermal properties using an advanced characterization technique available at Sandia called pump probe thermal reflectance.<sup>30,31</sup> Further study of these films has turned up many interesting properties and research in this area will continue at University of Delaware under a new DOE research grant and at Sandia.

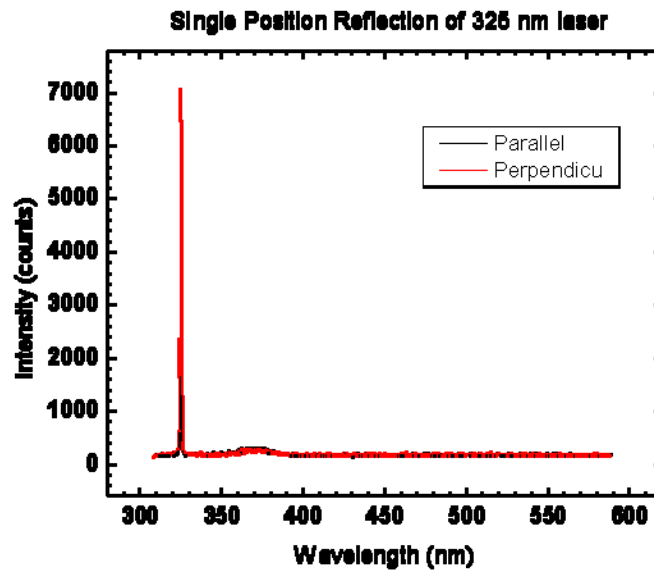
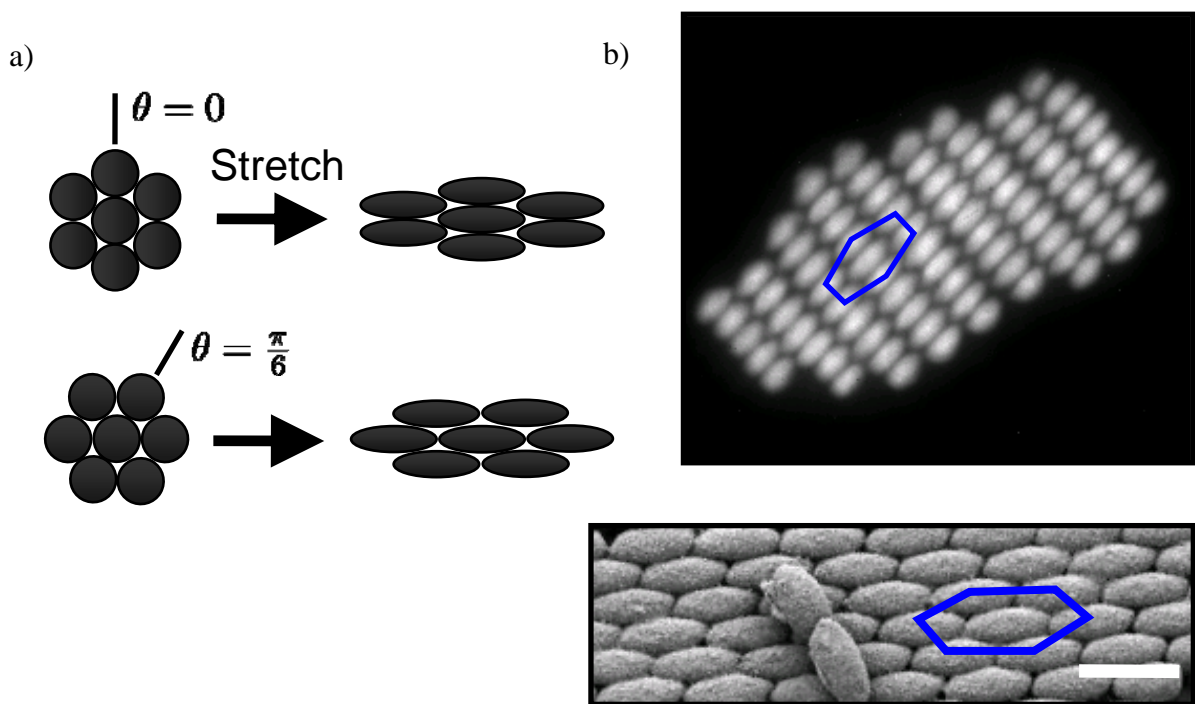


Figure 17: Reflectivity spectrum for incident 325nm light showing the reflectivity of perpendicular sample is 4 times higher than parallel sample.

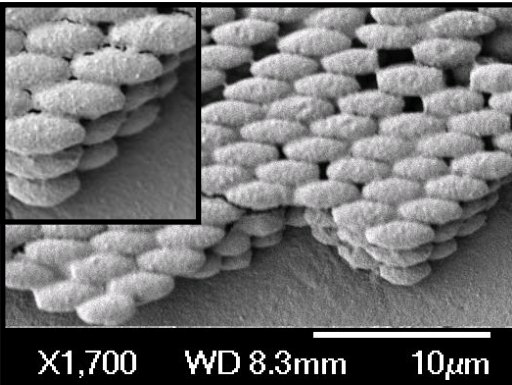
## 7. ORDERED THREE DIMENSIONAL STRUCTURES FROM ARRAYS

One challenge working with electrical field assembly is how to preserve and harvest the ordered structures. When the particles are in free solution, they will diffuse back to a random structure once the field is terminated. In Section 6.2, convective assembly process was discussed where particles are advected to the drying front and deposited as a film. Here we discuss an alternative which can preserve single layer ordered arrays such as those demonstrated in Figure 10. Standard electrical assembly is performed as discussed previously except with particles (in this case spherical) which have been surface functionalized with biotin antibodies. The crystal structure is locked in by adding a small quantity of the chemical streptavidin while the electric field is active. The electric field can then be deactivated without loss of the crystal order. The particle lattice is then encased in a poly vinyl alcohol (PVA) film and peeled from the glass substrate. Once encased in the flexible PVA film, the lattice can be stretched to create ordered arrays of ellipsoidal particles as shown in Figure 18. By stretching along different crystal planes of the original crystal, elliptical particle arrays of various crystal structures can be manufactured. Multiple layers can be assembled to create engineered three dimensional structures. The PVA matrix can then be dissolved leaving behind the free standing particle structure as demonstrated in Figure 19. Details of this crystal assembly method are explained in Appendix I.



**Figure 18: Demonstration of stretching of arrays of spherical particles to create controlled ellipsoidal particle crystal structure. [Appendix I]**

a)



b)

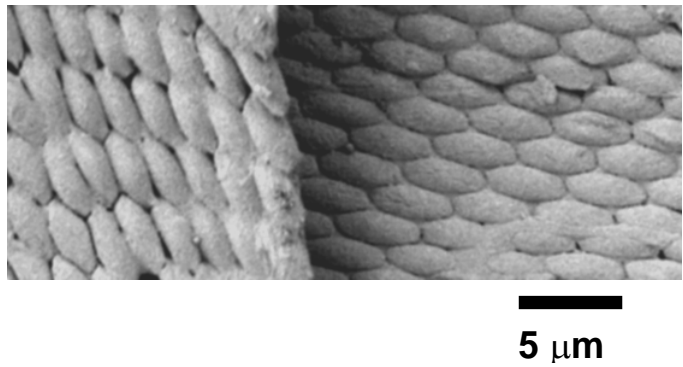


Figure 19: Three dimensional structures with parallel (a) or alternating (b) layer orientations. [Appendix I]

## 8. EDUCATIONAL OUTREACH AND SCIENTIFIC IMPACT

Over the course of the project, we have had a significant impact for many young and aspiring researchers, providing some unique opportunities for collaborative interactions not commonly available. Team building and semiannual project meetings have given students and postdocs at all three institutions opportunities to present their work and receive constructive feedback. Exposure to a large multidisciplinary team has provided valuable experience and interactions for all. Sandia has funded two postdoctoral researchers through this project: Timothy Koehler and Christopher Brotherton. Both have recently accepted permanent staff positions here at Sandia. Additionally undergraduate student Matthew Reichert has participated in the Sandia summer intern program and the National Institute for Nano-Engineering (NINE) summer program. He has decided to pursue a research career and started in the graduate chemical engineering program at Carnegie Mellon last fall. University of Delaware has two post-doctoral researchers, two graduate students who will be graduating this year and an undergraduate student. The work at Yale University as sponsored two post doctoral researchers, a graduate student and a talented undergraduate who is planning on continuing her technical career through graduate study.

Several new research efforts will continue the work which was begun here. Study of the nanostructured titania and zeolite films will be sponsored through a DOE grant to continue the strategic partnership between University of Delaware and Sandia. Sandia is actively involved in characterizing both optical (K. Bogart 1100) and thermal (P. Hopkins 1500) properties of these novel materials. Our fundamental understanding of particle interactions has resulted in two additional LDRD projects: one to study interfacial phenomena with application to foams and the other starting in FY10 to study effect of interactions between algae cells and their impact on harvesting of biofuels. Experiments have also been funded to measure colloidal particle interactions through the Nanoparticle Flow Consortium CRADA.

This work has generated a lot of technical impact in the scientific community. Journal and conference publications resulting from this work are listed below. There have been close to 50 conference and invited presentations stemming from this work.

1. S. K. Sainis, V. Germain, C. O. Mejean and E. R. Dufresne, "Electrostatic Interactions of Colloidal Particles in Nonpolar Solvents: Role of Surface Chemistry and Charge Control Agents," *Langmuir* 24, 1160-1164 (2008). DOI: 10.1021/la702432u
2. M. Mittal, P. P. Lele, E. W. Kaler and E. M. Furst, "Polarization and interactions of colloidal particles in ac electric fields," *J. Chem. Phys.* 129, 064513 (2008).
3. P. P. Lele, M. Mittal and E. M. Furst, "Anomalous particle rotation and resulting microstructure of colloids in ac electric fields," *Langmuir* 24, 12842–12848 (2008). DOI: 10.1021/la802225u
4. A. M. Grillet, T. P. Koehler, C. M. Brotherton, R. A. Molecke and C. J. Brinker, "Experimental Comparison of Particle Interaction Measurement Techniques Using Optical Trapping," Conference Proceedings of the Annual Meeting of American Institute of Chemical Engineers, 11/2008, Philadelphia, PA.
5. S.K. Sainis, J. Merrill, E.R. Dufresne "Electrostatic Interactions at Vanishing Ionic Strength", *Langmuir*, **24** (23), 13334 (2008).

6. J. P. Singh, P. P. Lele, F. Nettesheim, N. J. Wagner and E. M. Furst, "One- and two-dimensional assembly of colloidal ellipsoids in ac electric fields," *Phys. Rev. E* 79, 050401(R), (2009). DOI: 10.1103/PhysRevE.79.050401
7. P. P. Lele and E. M. Furst, "Assemble-and-stretch approach for creating two- and three-dimensional structures of anisotropic particles," *Langmuir*, ASAP Article (2009). DOI: 10.1021/la901743q
8. J.-G. Park, J. D. Forster, E. R. Dufresne, "Synthesis of Colloidal Particles with the Symmetry of Water Molecules" *Langmuir* 25(16) 8903-8906 (2009).
9. M. Mittal and E. M. Furst, "Electric field-directed convective assembly of ellipsoidal colloidal particles to create optically and mechanically anisotropic thin films," *Adv. Func. Mater.*, in press.
10. J. W. Merrill, S. K. Sainis and E. R. Dufresne, "Many-Body Electrostatic Forces Between Colloidal Particles at Vanishing Ionic Strength," *Phys Rev Lett*, accepted
11. T. P. Koehler, C. M. Brotherton and A. M. Grillet, "Comparison of Interparticle Force Measurement Techniques Using Optical Trapping," submitted in 2009.
12. C. M. Brotherton, T. P. Koehler, N. S. Bell and A. M. Grillet, "Directed Assembly of Non-Equilibrium Structures Utilizing Optical Trapping and Surface-Modified Colloids," submitted to Conference Proceedings of the Annual Meeting of American Institute of Chemical Engineers, 11/2009, Nashville, TN.
13. J. Merrill, S. K. Sainis, E. R. Dufresne "Many Body Force Measurements in Colloidal Systems," *in preparation*.
14. M. Mittal and E. M. Furst, "Directed assembly of zeolites," *in preparation*.
15. B. J. Park and E. M. Furst, "Two-dimensional self-assembled colloidal crystals by fluid interface templating," *in preparation*.
16. B. J. Park and E. M. Furst, "Quasi-two-dimensional colloidal interactions beneath an oil-water interface deformed by the disjoining pressure," *in preparation*.



## 9. CONCLUSIONS

During this LDRD project, we have explored several technologies for manufacturing particle structures. Using optical trapping, we can directly assemble particle structures into defined three dimensional configurations including the A4 diamond structure either manually or through automated computer control. Using electric field directed assembly, large area ordered arrays of spherical or aspherical particles covering several square millimeters can be created. These structures can be preserved either through deposition onto a glass slide or using functionalized particles that lock in structure when exposed to either light or a chemical stimulus. Our fundamental investigation of spherical and aspherical particle interactions resulted in the discovery of many body effects which can affect our ability to assemble these particles and the stability of concentrated nanoparticles dispersions.

We have achieved our initial project milestones. We have achieved our goal of constructing an A4 diamond structure. Additionally the nanostructured titania films manufactured using electric field directed assembly show unique optical and thermal properties. The impact of this work has been wide and varied both at the labs and within the technical community at large resulting in over a dozen research publications to date. Research activities in several new areas both here and with our university collaborators will continue in the future.

## 10. REFERENCES

1. Y Xia, B. Gates and Z.-Y. Li. *Adv. Mater.* **2001**, *13*(6), 409.
2. J. D. Joannopoulos, P. R. Villeneuve and S. Fan. *Nature* **1997**, *386*, 143.
3. M. Maldovan and E. L. Thomas. *Nature Materials* **2004**, *3*, 593-600.
4. Ashkin, A. *IEEE J. Selected Topics in Quantum Electronics* **2000**, *6*, 841-856.
5. Neuman, K. C.; Block, S. M. *Rev. Sci. Instrum.* **2004**, *75*, 2787-2809.
6. Hsu, M.F.; Dufresne, E. R.; Weitz D. A. *Langmuir* **2005**, *21*, 4881-4887.
7. Furst, E. M. *Soft Materials* **2003**, *1*, 167-185.
8. Simmons, R. M.; Finer, J. T.; Chu, S.; Spudich, J. A. *Biophys. J.* **1996**, *70*, 1813-1822.
9. Sugimoto, T.; Takahashi, T.; Itoh, H.; Sato, S., Muramatsu, A. *Langmuir* **1997**, *13*, 5528-5530.
10. Valentine, M.T.; Dewalt, L.E.; Ou-Yang, H.D.; *J. Phys.: Condens. Matter* **1996**, *8*, 9477-9482.
11. Meiners, J.-C.; Quake, S.R. *Phys. Rev. Lett.* **1999**, *82*, 2211-2214.
12. Gutsche, C.; Keyser, U.F.; Kegler, K.; Kremer, F. *Phys. Rev. E* **2007**, *76*.
13. Mellor, C. D.; Sharp, M. A.; Bain, C. D.; Ward, A. D. *J. Appl. Phys.* **2005**, *97*, 103114.
14. Crocker, J. C.; Grier, D.G. *Phys. Rev. Lett.* **1994**, *73*, 352-355.
15. Crocker, J. C. *J. Chem. Phys.* **1997**, *106*, 2837-2840.
16. Dufresne, E. R.; Squires, T. M.; Brenner, M. P.; Grier, D. G. *Phys. Rev. Lett.* **2000**, *85*, 3317-3320.
17. Sainis, S. K.; Germain, V.; Dufresne, E. R. *Phys. Rev. Lett.* **2007**, *99*, 018303.
18. Sainis, S. K.; Germain, V.; Mejean, C. O.; Dufresne, E. R. *Langmuir* **2008**, *24*, 1160-1164.
19. Verma, R.; Crocker, J.C.; Lubensky, T.C.; Yodh, A.G. *Macromolecules* **2000**, *33*, 177-186.
20. Owen, R. J.; Crocker, J.C.; Verma, R.; Yodh, A. G. *Phys. Rev. E* **2001**, *64*, 011401.
21. Crocker, J. C.; Matteo, J. A.; Dinsmore, A. D.; Yodh, A. G. *Phys. Rev. Lett.* **1999**, *82*, 4352-4355.
22. Nambiar, R.; Meiners, J.-C. *Optics Letters* **2002**, *27*, 836-838.
23. Biancaniello, P. L.; Crocker, J. C. *Rev. Sci. Instr.* **2006**, *77*, 113702.
24. Piech, M., et al., *Langmuir*. **2006**, *22*, 1379-1382.
25. Abbasian, M., et al. *Journal of Applied Polymer Science*. **2007**, *104*, 611-619.
26. Kamigaito, M., T. Ando, and M. Sawamoto. *Chemical Reviews*. **2001**, *101*, 3689-3745.
27. Matyjaszewski, M., et al. *Macromolecules* **1999**, *32*, 8716-8724.
28. Piech, M.; Bell, N.S. *Macromolecules* **2006**, *39*, 915-922.
29. Bell, N.S.; Piech, M. *Langmuir* **2006**, *22*, 1420-1427.
30. Hopkins, P.E., Serrano, J.R., Phinney, L.M., Kearney, S.P., Grasser, T.W., Harris, C.T., *Proceedings of 2009 ASME International Mechanical Engineering Congress & Exposition*, Lake Buena Vista, FL, November 13 – 19, 2009.
31. Hopkins, P.E., Serrano, J.R., Phinney, L.M., Kearney, S.P., Grasser, T.W., Harris, C.T., *currently under review ASME Journal of Heat Transfer*

# APPENDIX A: SAINIS ET AL. LANGMUIR 2008

1160

Langmuir 2008, 24, 1160–1164

## Electrostatic Interactions of Colloidal Particles in Nonpolar Solvents: Role of Surface Chemistry and Charge Control Agents<sup>†</sup>

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We study the electrostatic and hydrodynamic interactions of colloidal particles in nonpolar solvents. Using blinking optical tweezers, we can extract the screening length,  $\kappa^{-1}$ , the effective surface potential,  $|e\zeta^*|$ , and the hydrodynamic radius,  $a_h$ , in a single measurement. We apply this technique to suspensions of polystyrene and poly(methyl methacrylate) particles in hexadecane with soluble charge control agents, aerosol sodium di-2-ethylhexylsulfosuccinate (AOT) and polyisobutylene succinimide (OLOA-1200). We find that the electrostatic interactions of these particles depend sensitively on surface composition as well as on the concentration and chemistry of the charge control agent.

### 1. Introduction

Charge separation is energetically expensive in environments with low dielectric polarizabilities. This high energy cost inhibits ionization in nonpolar solvents ( $\epsilon \approx 2$ ). Nevertheless, charging of colloidal particles has been observed in nonpolar solvents under the influence of various charge control agents.<sup>1</sup> A number of interesting applications have been found for this surprising phenomena. Nonpolar colloids have been used as electrophoretic ink in flexible electronic displays.<sup>2</sup> OLOA, a commercial dispersant, has long been known to charge carbon black in oil,<sup>3</sup> but it is not clear whether electrostatic interactions significantly contribute to its efficacy. Similarly, aerosol-OT has been found to mediate charging in nonpolar environments.<sup>4–7</sup>

Charge control agents affect interparticle interactions and thus influence the stability and electrokinetic properties of nonpolar suspensions. In general, the electrostatic interaction between colloidal particles depends on  $\zeta$ , the surface potential, and  $\kappa^{-1}$ , the screening length of the solvent. The screening length depends on the concentration and valence of the ionic species in the solvent. When the ion sizes and valences are known, the screening length can be determined from the bulk conductivity. While this electrokinetic approach works well in aqueous systems where the ionic species are well characterized, it fails in many nonpolar environments because neither the valence of the bulk ions nor their hydrodynamic radii are known *a priori*. Thus, the screening length cannot be inferred from the conductivity alone. Alternatively, Prieve et al. have recently demonstrated that time-dependent current response to a stepwise increase in the voltage contains sufficient information to determine the screening length.<sup>8</sup> If the screening length is known, then the surface potential can be determined from the electrophoretic mobility.<sup>9</sup> However, this

is doubly challenging. Not only is the screening length difficult to determine, but the electrophoretic mobility of particles in nonpolar solvents is often too low to be measured accurately in conventional electrophoresis setups. Thus, new methods are required to characterize the electrostatic behavior of nonpolar suspensions.

At a deeper level, there is considerable debate on the nature of electrostatic interactions in nonpolar environments. Some observations suggest that the functional form of the interaction between these charged colloidal particles in nonpolar solvents<sup>6,7</sup> is identical to the predictions from the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory<sup>10,11</sup> developed for aqueous environments, while others suggest that a counterion-only double-layer theory is needed to describe observed forces.<sup>12</sup> While the surface forces apparatus and atomic force microscope are well suited to measuring forces between macroscopic surfaces or between a particle and a surface,<sup>4,5</sup> they are not appropriate for studying the interactions of free colloidal particles. In an earlier paper, we demonstrated that the equilibrium structure of a nonpolar dispersion can be used to determine interaction potentials.<sup>13,6</sup> Unfortunately, this elegant method is limited to relatively weak interactions of monodisperse particles with pairwise additive interactions.

In this paper, we extract interparticle forces from the statistics of trajectories of isolated particle-pairs driven out of equilibrium with blinking optical tweezers.<sup>14</sup> We examine the forces between polystyrene (PS) and poly(methyl methacrylate) (PMMA) particles suspended in hexadecane in the presence of charge control agents (aerosol-OT and OLOA-1200). Our recently described method of data analysis<sup>7</sup> self-consistently accounts for the hydrodynamic interactions and yields the solvent screening length, the apparent particle surface potential, and the particle hydrodynamic radius,  $a_h$ , in a single measurement. We find that the composition and concentration of the charge control agent have a significant impact on the apparent surface potential and screening length. Similarly, we observe significant differences in surface potential due to changes in surface functionalization.

<sup>†</sup> Part of the Molecular and Surface Forces special issue.

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(1) Morrison, I. D. *Colloids Surf.*, **A** 1993, *71*, 1.

(2) Comiskey, B.; Albert, J. D.; Yoshizawa, H.; Jacobson, J. *Nature* 1998, *394*, 253.

(3) Pugh, R. J.; Matsunaga, T.; Fowkes, F. M. *Colloids Surf.* 1983, *7*, 183.

(4) Briscoe, W. H.; Horn, R. G. *Langmuir* 2002, *18*, 3945.

(5) McNamee, C. E.; Tsujii, Y.; Matsumoto, M. *Langmuir* 2004, *20*, 1791.

(6) Hsu, M.; Dufresne, E. R.; Weitz, D. A. *Langmuir* 2005, *21*, 4881.

(7) Sainis, S. K.; Germain, V.; Dufresne, E. R. *Phys. Rev. Lett.* 2007, *99*, 018303.

(8) Prieve, D. C.; Fu, R. Unpublished data.

(9) O'Brien, R. W.; White, L. R. *J. Chem. Soc., Faraday Trans. 2* 1978, *74*, 1607.

(10) Derjaguin, B. V.; Landau, L. *Acta Physicochim. URSS* 1941, *14*, 633.

(11) Verwey, E. J. W.; Overbeek, J. T. G. *Theory of the Stability of Lyophobic Colloids: The Interactions of Sol Particles Having an Electric Double Layer*; Elsevier: New York, 1948.

(12) Briscoe, W. H.; Attard, P. *J. Chem. Phys.* 2002, *117*, 5452.

(13) Behrens, S. H.; Grier, D. G. *Phys. Rev. E* 2001, *64*, 050401(R).

(14) Crocker, J. C.; Grier, D. G. *Phys. Rev. Lett.* 1994, *73*, 352.

# Comparison of Interparticle Force Measurement Techniques Using Optical Trapping

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## Abstract

Optical tweezers has become a powerful and common tool for sensitive determination of electrostatic interactions between colloidal particles. Two optical trapping based techniques, blinking laser tweezers and direct force measurements, have become increasingly prevalent in investigations of interparticle potentials. The blinking laser tweezers method repeatedly catches and releases a pair of particles to gather physical statistics of particle trajectories. Statistical analysis is used to determine drift velocities, diffusion coefficients, and ultimately colloidal forces as a function of the center-center separation of the particles. Direct force measurements monitor the position of a particle relative to the center of an optical trap as the separation distance between two continuously trapped particles is gradually decreased. As the particles near each other, the displacement from the trap center for each particle increases proportional to the inter-particle force. Although these techniques are commonly employed in the investigation of interactions of colloidal particles, there exists no direct comparison of these experimental methods in the literature. In this study, we compare the interparticle forces using both methods using a model system of polystyrene particles in an aerosol-OT (AOT) hexadecane solution. We found that the interaction forces measured using the two techniques compare quantitatively with each other and Derjaguin-Landau-Verwey-Overbeek (DLVO) theory.

## Introduction

Since the discovery of optical trapping by Arthur Ashkin in 1970<sup>1</sup>, there have been numerous applications in the areas of soft matter, physics and biology.<sup>2</sup> Optical tweezers have

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## **APPENDIX C: GRILLET ET AL. AICHE CONFERENCE PAPER (2008)**

### **Experimental Comparison of Particle Interaction Measurement Techniques Using Optical Trapping**

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#### **Abstract**

Optical tweezers has become a powerful and common tool for sensitive determination of electrostatic interactions between colloidal particles. Two optical trapping based techniques, blinking tweezers and direct force measurements, have become increasingly prevalent in investigations of interparticle potentials. The blinking laser tweezers method repeatedly catches and releases a pair of particles to gather physical statistics of particle trajectories. Statistical analysis is used to determine drift velocities, diffusion coefficients, and ultimately colloidal forces as a function of the center-center separation of the particles. Direct force measurements monitor the position of a particle relative to the center of an optical trap as the separation distance between two continuously trapped particles is gradually decreased. As the particles near each other, the displacement from the trap center for each particle increases proportional to the inter-particle force. Although commonly employed in the investigation of interactions of colloidal particles, there exists no direct comparison of these experimental methods in the literature. In this study, an experimental apparatus was developed capable of performing both methods and is used to quantify electrostatic potentials between two sizes of polystyrene particles in an AOT hexadecane solution. Comparisons are drawn between the experiments conducted using the two measurement techniques, theory, and existing literature. Forces are quantified on the femtoNewton scale and results agree well with literature values.

#### **Introduction**

Since the discovery of optical trapping by Arthur Ashkin in 1970 [1], there have been numerous applications in the areas of soft matter, physics and biology.[2] In particular, optical trapping through the use of laser tweezers has become a primary tool for understanding the statics and dynamics of colloidal systems.[3] Using optical trapping researchers have been able to probe the microrheology of suspensions [4], microstructural mechanics of colloidal aggregates [5] and colloidal particle interactions.[6-15] Measurements of particle interactions in particular have been used to understand not only electrostatic forces between particles, but also the effects of polymer brushes and particle depletion effects.[15,16] Additionally, optical trapping techniques are now being used to validate longstanding models for colloidal interactions such as Derjaguin-Landau-Verwey-Overbeek (DLVO) theory.[17,18] However, there has never been a quantitative comparison between various implementations of optical trapping interaction methods to demonstrate that they make comparable measurements.

Interactions between colloidal particles can be probed using various implementations of optical trapping, but there are three main classes of techniques. Direct force measurement involves measuring

Many-Body Electrostatic Forces Between Colloidal Particles at Vanishing Ionic Strength

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(Dated: July 3, 2009)

Electrostatic forces between small groups of colloidal particles are measured using blinking optical tweezers. When the electrostatic screening length is significantly larger than the particle radius, forces are found to be non-pairwise additive. Both pair and multi-particle forces are well described by the linearized Poisson-Boltzmann equation with constant potential boundary conditions. These findings may play an important role in understanding the structure and stability of a wide variety of systems, from micron-sized particles in oil to aqueous nanocolloids.

Colloidal suspensions offer a unique opportunity to observe the relationship between microscopic interactions and macroscopic thermodynamic behavior because the component particles are both large enough to observe directly with light microscopy and small enough to come to thermodynamic equilibrium over experimental timescales. Colloids display a rich range of phase behavior including equilibrium gases, liquids, and crystals and nonequilibrium glasses and gels. Controlling and predicting this phase behavior has applications from ensuring the stability of paint to directing the self assembly of novel optical materials.

Predicting phase behavior requires an understanding of the interactions of the component particles. Forces between pairs of charged surfaces have been extensively characterized using direct force measurements [1]. Alternatively, observations of bulk correlations can be used to extract an “effective pair potential,” but this pair potential is found to vary with the density of the suspension [2, 3]. This suggests that charged colloidal particles do not, in fact, interact only through a pair potential. Many-body interactions evidently play an important role in determining macroscopic behavior.

To bridge the gap between pair interactions and bulk behavior, we explore the regime of few-body interactions by using blinking optical tweezers to directly measure electrostatic forces between sets of several isolated charged colloidal particles at low ionic strength. For screening lengths much shorter than the inter-particle separation, the measured forces are nearly pairwise additive; however, for screening lengths comparable to or longer than the inter-particle separation, there are significant deviations from pairwise additivity.

Our system consists of radius  $a = 600$  nm PMMA spheres suspended in hexadecane, a non-polar solvent. The spheres are coated in PHSA in order to stabilize them against aggregation [4]. Both the particle charge and screening length are adjusted by adding variable concentrations of a surfactant, NaAOT, as described in [5].

Forces are extracted from the trajectories of freely in-

teracting particles, which are trapped repeatedly in an initial configuration and then released using blinking optical tweezers created with a 1064 nm laser [6]. A detailed explanation of the apparatus is given in [7]. The physical ideas underlying the technique are developed in [8]. The central result of that paper is a relation between the force,  $f$ , and the two statistical parameters that describe ensembles of short-time Brownian trajectories, the drift velocity,  $v_d$ , and the diffusion coefficient,  $D$ :

$$f = k_B T D^{-1} v_d. \quad (1)$$

This relation holds for a single particle in one dimension, or separately for each of the hydrodynamic normal modes of a multi-particle system in several dimensions. The range of validity of this expression is explored in [8].

We measure forces between beads in pair, equilateral triangle, and hexagonal configurations, as depicted in Fig. 1. The first column of Fig. 1 shows the measured force as a function of separation between pairs of beads at two different surfactant concentrations:  $[AOT] = 10$  mM (top) and 0.5 mM (bottom). At each separation, three beads are chosen for pair measurements. The forces between each of the three possible pairs formed from this set are plotted with different colors. For a given concentration and separation, forces between each of the pairs are nearly identical, which suggests that each of the beads has nearly the same charge. The force at the smallest measured separation is roughly the same for both concentrations, but the interaction is screened much more rapidly at the higher surfactant concentration.

Next, the same three beads are formed into an equilateral triangle. The measured force projected onto the breathing mode of this configuration is plotted in column two of Fig. 1. The previously measured pair forces are used to make a pairwise prediction of the force on the equilateral triangle. Since the same beads are measured at the same separations for both the pair and equilateral geometry, this experiment provides a strong, model-independent test of pairwise additivity. At 10 mM, agreement with the pairwise prediction is very good, whereas

# APPENDIX E: MERRILL & DUFRESNE (2009) IN PREPARATION

## Many-Body Force Measurements in Colloidal Systems

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(Dated: September 3, 2009)

### Abstract

We demonstrate a technique for simultaneously measuring each component of the force on a small collection of colloidal particles.

In ref. [1], a flexible technique for measuring interactions between colloidal particles based on observations of free particle trajectories was presented. We have recently used this technique to investigate surfactant-controlled electrostatic interactions between pairs of colloidal particles in a non-polar solvent [2], and deviations from pairwise additivity for the forces between sets of several particles in the same system [3]. One of the great advantages of the technique presented in ref. [1] is that it extends simply to many-coordinate systems, allowing the simultaneous measurement of each component of the force on each of several particles interacting with one another. All of the above cited measurements have implicitly involved several coordinates—even a system of two spheres in two dimensions has a total of four coordinates—but for ease of presentation, we have previously projected the measured forces onto a single coordinate. Here, we provide additional detail on the extension of the technique to multiple coordinates, and exhibit the full force curves for each component of a multi-particle system.

Forces are extracted from the trajectories of freely interacting particles, which are repeatedly trapped and released using blinking optical tweezers [4] created with a 1064 nm laser. The central result of ref. [1] is a relation between the force,  $f$ , and the two statistical parameters that describe ensembles of short-time Brownian trajectories, the drift velocity,  $v_d$ , and the diffusion coefficient,  $D$ :

$$f = k_B T D^{-1} v_d. \quad (1)$$

## APPENDIX F: BROTHERTON ET AL. AICHE CONFERENCE PAPER 2009

### Directed Assembly of Non-Equilibrium Structures Utilizing Optical Trapping and Surface-Modified Colloids

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Colloidal particles modified with photo-sensitive polymeric brushes exhibit reversible phase transformation properties allowing for the development of switchable particle aggregation and rheological response. By manipulating photo-sensitive particles using optical trapping, it is possible to assemble 2D and 3D microstructures. The system of interest consists of 2 micron borosilicate particles, coated with polymethyl methacrylate/spirobenzopyran polymeric brushes, suspended in toluene. Particle structures are assembled in the solvent using time-shared optical traps and then exposed to ultraviolet light. The light induces a polarity change in the polymer brushes causing particle-particle adhesion. The resulting 2D structure is then attached to a substrate. The process is repeated to assemble three dimensional microstructures with multiple particle layers. Research activities to develop this assembly capability are presented related to the material requirements needed in optical trapping systems, their application in this photo-sensitive system, and developments in particle assembly.

#### Introduction

Since the discovery of optical trapping by Arthur Ashkin in 1970 [1], there have been numerous applications in the areas of soft matter, physics and biology [2]. Optical tweezers have become particularly useful in the study of colloidal systems where optical trapping enables the experimental investigation of the microrheology of suspensions [3-5], microstructural mechanics of colloidal aggregates [6, 7] and interactions of colloidal particles [8-10]. In this work, we demonstrate a technique using optical trapping to construct three dimensional microstructures in a borosilicate/toluene system. The structure assembly process requires controllable particle-particle interactions in order to fabricate robust microstructures. One potential solution utilizes polymethyl methacrylate/spirobenzopyran copolymer brushes attached to borosilicate particles.

Spirobenzopyran is a relatively nonpolar molecule that experiences a ring-opening isomerization, when exposed to UV ( $\lambda = 366\text{nm}$ ), resulting in a zwitterionic merocyanine with a higher dipole moment, as shown in figure 1. The reverse reaction is caused by exposure to heat or visible light ( $\lambda = 533\text{nm}$ ), but is typically much slower than the forward reaction [11]. Using atom-transfer radical polymerization (ATRP), copolymer brushes of polymethyl methacrylate/spirobenzopyran can be attached to silica particles



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## One- and two-dimensional assembly of colloidal ellipsoids in ac electric fields

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We investigate the assembly of colloidal ellipsoids in ac electric fields. Polystyrene latex ellipsoids with aspect ratios 3.0, 4.3, and 7.6 orient with the applied field and, at sufficient field strengths, interact to form particle chains at an angle with respect to the field. The characteristic chain angle decreases with increasing aspect ratio. The angled chains combine laterally to form an open centered rectangular two-dimensional structures belonging to the  $c2mm$  plane group. This chaining and assembly behavior is explained based on calculations of the particle pair interactions explicitly accounting for the electric field and shape of the ellipsoids.

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The solution phase assembly of colloidal particles using external fields is a powerful means for achieving structured and ordered phases, with potential applications in photonics [1,2], biosensors [3,4], electronic devices [5,6], and displays [7,8]. Suspensions of spherical colloidal particles exhibit rapid self-assembly in response to the application of an external ac electric field [2]. This disorder-to-order transition is driven by the interactions between particles, which polarize due to the contrast between their dielectric properties and that of the suspending medium [9]. The induced dipole-dipole interactions first lead to the formation of particle chains oriented in the field direction. These dipolar chains subsequently laterally combine to form hexagonal two-dimensional (2D) particle arrays.

The effect of particle shape on the disorder-to-order transition in electric fields remains unexplored, despite the fact that shape plays an important role in many applications, including the control of polarization modes of propagated light in photonic crystals [10,11]. Nonetheless, recent work recognizes that anisotropy in shape or properties is a key to forming complex higher-order structures from dispersions via self-assembly [12–14]. Excluded volume interactions alone lead to the expression of a rich equilibrium phase behavior in colloidal suspensions of anisotropic particles [15–18]. At dilute concentrations, where excluded volume effects are negligible, the shape dependence of the depletion interaction [19,20] and capillary forces [21,22] provide control over the interactions between particles and, ultimately, the self-assembled structures that form.

In this Rapid Communication, we report experiments investigating the assembly of ellipsoidal colloidal particles in ac electric fields. Similar to spherical particles, ellipsoids orient and form particle chains in the field direction. Surprisingly, however, chains of ellipsoids form at a distinct angle with respect to the applied field. Subsequent lateral coalescence of the angled chains leads to open particle arrays, in contrast to the hexagonal-close-packed arrays obtained for

spheres. Similar structures are observed for three different aspect ratios of the particles. We explain these observations using a simple model based on the polarization interactions between pairs of particles as the underlying mechanism of the assembly process. We find that the most stable configuration for two interacting ellipsoidal particles is to align at an angle with respect to the applied field. Before discussing these results in detail, we first briefly detail our materials and methods.

Anisotropic polystyrene particles are fabricated using the methods of Keville *et al.* [23] and Ho *et al.* [24]. Monodisperse spherical polystyrene latex particles with a diameter of 3  $\mu\text{m}$  are dispersed in a supersaturated solution of poly(vinyl alcohol) (PVA, Fluka 40-88, degree of hydrolysis 86.7–88.7,  $M_w = 2.05 \times 10^5$ , degree of polymerization  $\sim 4200$ ) in water, which is then cast and dried, resulting in a thin film. The film is heated above the glass transition temperature of polystyrene ( $T > T_g \approx 105^\circ\text{C}$ ) in a silicone oil bath and stretched uniaxially. After rapidly cooling the film, the PVA matrix is dissolved in a 7:3 water-isopropanol solution. The recovered anisotropic particles are redispersed in water and 2.5 mM sodium dodecyl sulfate (SDS). Three aspect ratios are investigated here,  $\alpha = b/a = 3.0, 4.3, \text{ and } 7.6$ , where  $a$  and  $b$  are the particle polar and equatorial radii, respectively.

A coplanar electrode geometry is used to generate the electric field [Fig. 1(a)]. The electrodes are fabricated on a clean glass slide ( $25 \times 75$  mm, Fischer Scientific) by first depositing a 10 nm chromium layer followed by 100 nm of gold using an electron-beam evaporator (Thermionics, VE series). A similar electrode geometry was used earlier to study the assembly and interactions of spherical particles [2,25,26]. The gap between the electrodes is 2 mm. The glass slide and electrodes are cleaned before each use using a freshly prepared cleaning solution (Nochromix, Godax Laboratories) and a plasma cleaner (Harrick Plasma, PDC-32G). Using an adhesive spacer and a coverslip, a chamber is built over the electrodes with a height of approximately 100  $\mu\text{m}$ . A particle solution with a volume fraction of  $10^{-3}$  is injected into the chamber using capillary action and the ends are sealed using a UV curing epoxy (NOA 81, Norland). We take care to avoid introducing air bubbles into the chamber. The ac electric field is generated using a function generator (Agilent technologies, 33220A) amplified 50 $\times$  (Tegam, 2340). A

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## Electric Field-Directed Convective Assembly of Ellipsoidal Colloidal Particles to Create Optically and Mechanically Anisotropic Thin Films

By Manish Mittal and Eric M. Furst\*

A method of simultaneous field- and flow-directed assembly of anisotropic titania (TiO<sub>2</sub>) nanoparticle films from a colloidal suspension is presented. Titania particles are oriented by an alternating (ac) electric field as they simultaneously advect towards a drying front due to evaporation of the solvent. At high field frequencies ( $\nu > \sim 25$  kHz) and field strengths ( $E > 300$  V cm<sup>-1</sup>), the particles orient with their major axis along the field direction. As the front recedes, a uniform film with thicknesses of 1–10  $\mu$ m is deposited on the substrate. The films exhibit a large birefringence ( $\Delta n \approx 0.15$ ) and high packing fraction ( $\phi = 0.75 \pm 0.08$ ), due to the orientation of the particles. When the frequency is lowered, the particle orientation undergoes a parallel–random–perpendicular transition with respect to the field direction. The orientation dependence on field frequency and strength is explained by the polarizability of ellipsoidal particles using an interfacial polarization model. Particle orientation in the films also leads to anisotropic mechanical properties, which are manifested in their cracking patterns. In all, it is demonstrated that the field-directed assembly of anisotropic particles provides a powerful means for tailoring nanoparticle film properties in situ during the deposition process.

Perhaps the most well-known example of colloidal self-assembly is the spontaneous formation of colloidal crystals, which arises from the entropically driven disorder-to-order transition of repulsive or hard-sphere particles.<sup>[21,22]</sup> Hydrodynamic forces, such as those that occur during drying<sup>[23]</sup> and low-amplitude oscillatory shear,<sup>[24,25]</sup> are typically strong enough to generate ordered structures. Convection-driven assembly has been used for deposition of coatings from spherical nano- and microparticles.<sup>[26]</sup> Colloidal self-assembly can also be effectively accomplished using external fields,<sup>[27]</sup> such as an electric field,<sup>[28,29]</sup> magnetic field,<sup>[30,31]</sup> or patterns of optical potentials.<sup>[8,32]</sup> Under electric (and magnetic) fields, induced polarization of the colloidal particles leads to self-assembly via dipolar interactions.<sup>[33]</sup> The resulting field-responsive order–disorder transition of spherical particles has been studied as a function of ac electric field strength and frequency.<sup>[28]</sup> The assembly and interactions of anisotropic particles due to capillary forces has also recently attracted considerable interest.<sup>[34–38]</sup>

### 1. Introduction

Colloidal particles are key building blocks in materials with nanometer- to micrometer-scale structure.<sup>[1–3]</sup> The use of colloidal particles as precursors for fabricating advanced materials in the fields of catalysis,<sup>[4]</sup> photonics,<sup>[5–8]</sup> phononics,<sup>[9–11]</sup> photovoltaics,<sup>[12–14]</sup> and electronics<sup>[15–17]</sup> has grown in the last decade. Due to their electronic, optical, and photocatalytic properties, structures assembled from colloidal suspensions of titania particles hold especially great promise for creating functional nanomaterials.<sup>[18–20]</sup> It is increasingly desirable to generate these materials via self-assembly by exploiting properties which arise from the size, shape, Brownian motion, response to external fields, and interparticle interactions of colloids.

tions of anisotropic particles due to capillary forces has also recently attracted considerable interest.<sup>[34–38]</sup>

In most approaches to colloidal self-assembly, however, the isotropic interactions of predominantly spherical colloidal particles limit the overall structures that can be formed to face-centered cubic crystals and related symmetries,<sup>[39,40]</sup> although more diverse assemblies can be created through the use of multiple particle sizes.<sup>[41,42]</sup> Building increasingly complex structures from colloids requires breaking the particle symmetry, either by their shape or through anisotropic interactions.<sup>[43–45]</sup> This has led to both numerical<sup>[46,47]</sup> and experimental<sup>[48–51]</sup> studies of the self-assembly of anisotropic particles. Furthermore, studies of anisotropic particles have yielded surprising fundamental discoveries. For instance, it was recently shown that the densest packing of ellipsoidal particles can exceed that of spheres, which was long believed to be the densest packing shape.<sup>[52,53,54]</sup> Thus, simple shape anisotropy has the potential to form structures that one cannot assemble from spherical particles.

Here, we report an assembly technique that uses an external electric field to direct the convective assembly of anisotropic titanium dioxide particles (see Fig. 1). The particles are oriented using an ac electrical field as they advect towards a drying front to create packed films. We demonstrate that the orientation of

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# APPENDIX I: LELE & FURST LANGMUIR 2009

## Langmuir Letter

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### Assemble-and-Stretch Method for Creating Two- and Three-Dimensional Structures of Anisotropic Particles

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We fabricate two-dimensional ordered arrays of anisotropic particles by embedding hexagonally close-packed monolayers of spherical latex particles in polymer films and subjecting them to an extensional strain. Furthermore, by stacking several films, we create three-dimensional structures. An important advantage of this approach is the ability to independently control the particle orientation in each layer of the structure. Additionally, the symmetry of a layer is controlled by the orientation of the original array of spherical particles versus the stretch direction. This technique may be readily used to generate structures for photonic applications, as well as to aid fundamental studies of packing of anisotropic particles.

#### 1. Introduction

Photonic crystals are materials with regular, repeating variations in refractive index that lead to a forbidden stop-band for a frequency range of electromagnetic radiation.<sup>1,2</sup> Photons in the stop-band will not propagate in any dimension inside the photonic band gap (PBG) crystal. The ability of PBGs to control, reflect, or redirect light has powerful applications in photonics and optoelectronics, including the fabrication of lossless waveguides to control the propagation of light along a desired direction in devices.<sup>3,4</sup> Since their initial conceptualization, many researchers have sought to create PBG crystals via the self-assembly of colloidal crystals, which is attractive because of its simplicity and scalability over a wide range of length scales.<sup>5–14</sup> However, a face-centered cubic (fcc) crystal, the favored packing structure of spheres, does not yield a complete band gap due to a symmetry-induced degeneracy of the spherical units in the lattice.<sup>15</sup> One possible route around this limitation is the substitution of spherical particles with *anisotropic* particles in the unit cell, which may result in complete band gaps.<sup>16–18</sup>

Creating ordered assemblies of anisotropic particles has remained a fundamental challenge,<sup>19</sup> although several methods have been successfully demonstrated.<sup>20–25</sup> A promising approach uses external fields to direct the self-assembly of asymmetric colloidal particles in a suspension.<sup>26–31</sup> For instance, recent work demonstrated the creation of ordered arrays of magnetic ellipsoids using a combination of magnetic fields and capillary driven flows.<sup>32</sup> However, field-induced particle interactions, and hence the resulting microstructures, are sensitive to the strength of the external field, as well as the size, aspect ratio, and polarizability (electric or magnetic) of the particles.<sup>12,31</sup> An alternative for creating large assemblies of ellipsoidal particles is the use of ion irradiation to deform assembled silica spheres.<sup>33</sup> Nonetheless, such approaches may be limited by the variability in the extent of deformation of particles over several layers in a three-dimensional (3D) crystal, thus resulting in changes in the aspect ratio and sizes of ellipsoids.

In this work, we demonstrate an elegant method to create large, ordered structures of anisotropic particles. Instead of directing the assembly of anisotropic particles, we first assemble two-dimensional (2D) arrays of spherical particles. By permanently locking in the 2D structure, heating it above the particle glass transition temperature, and subjecting it to an extensional strain, we create anisotropic particle arrays with high fidelity. Notably, by using a

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- (1) Yablonovitch, E. *Phys. Rev. Lett.* **1987**, *58*, 2059–2062.
- (2) John, S. *Phys. Rev. Lett.* **1987**, *58*, 2486–2489.
- (3) Vlasov, Y. A.; Bo, X. Z.; Sturm, J. C.; Norris, D. J. *Nature* **2001**, *414*, 289.
- (4) Joannopoulos, J. D.; Villeneuve, P. R.; Fan, S. *Nature* **1997**, *386*, 143.
- (5) Trau, M.; Saville, D. A.; Aksay, I. A. *Science* **1996**, *272*, 706–709.
- (6) Lu, Y.; Yin, Y.; Xia, Y. *Adv. Mater.* **2001**, *13*, 34.
- (7) van Blaaderen, A.; Ruel, R.; Wiltzius, P. *Nature* **1997**, *385*, 321.
- (8) Jiang, P.; Bertone, J. F.; Hwang, K. S.; Colvin, V. L. *Chem. Mater.* **1999**, *11*, 2132.
- (9) Lumsdon, S. O.; Kaler, E. W.; Velev, O. D. *Langmuir* **2004**, *20*, 2108–2116.
- (10) Wang, J.; Li, Q.; Knoll, W.; Jonas, U. *J. Am. Chem. Soc.* **2006**, *128*, 15606–15607.
- (11) Lele, P. P.; Mittal, M.; Furst, E. M. *Langmuir* **2008**, *24*, 12842.
- (12) Mittal, M.; Lele, P. P.; Kaler, E. W.; Furst, E. M. *J. Chem. Phys.* **2008**, *129*, 064513.
- (13) Min, W. L.; Jiang, P.; Jiang, B. *Nanotechnology* **2008**, *19*, 475604.
- (14) Erb, R. M.; Son, H. S.; Samanta, B.; Rotello, V. M.; Yellen, B. B. *Nature* **2009**, *457*, 999.
- (15) Ho, K. M.; Chan, C. T.; Soukoulis, C. M. *Phys. Rev. Lett.* **1990**, *65*, 3152.
- (16) Yablonovitch, E.; Gmitter, T. J.; Leung, K. M. *Phys. Rev. Lett.* **1991**, *67*, 2295.
- (17) Wang, R.; Wang, X.-H.; Gu, B. Y.; Yang, G. Z. *J. Appl. Phys.* **2001**, *90*, 4307.
- (18) Qiu, M.; He, S. *Phys. Rev. B: Condens. Matter* **1999**, *60*, 10610.

- (19) Glotzer, S. C.; Solomon, M. J. *Nat. Mater.* **2007**, *6*, 557.
- (20) Skjeltorp, A. T.; Ugelstad, J.; Ellingsen, T. *J. Colloid Interface Sci.* **1986**, *113*, 577–582.
- (21) Yin, Y.; Xia, Y. *Adv. Mater.* **2001**, *13*, 267–271.
- (22) Straub, M.; Gu, M. *Opt. Lett.* **2002**, *27*, 1824.
- (23) Lu, Y.; Yin, Y.; Li, Z.-Y.; Younan, X. *Langmuir* **2002**, *18*, 7772–7772.
- (24) Mock, E. B.; Zukoski, C. F. *Langmuir* **2007**, *23*, 8760–8771.
- (25) Xie, Z.-Y.; Sun, L.-G.; Han, G.-Z.; Gu, Z.-Z. *Adv. Mater.* **2008**, *20*, 3601–3604.
- (26) Míguez, H.; Meseguer, F.; López, C.; Blanco, A.; Moya, J. S.; Requena, J.; Mifsud, A.; Fornés, V. *Adv. Mater.* **1998**, *10*, 480.
- (27) Hwang, D. K.; Dendukuri, D.; Doyle, P. S. *Lab Chip* **2008**, *8*, 1640–1647.
- (28) Hosein, I. D.; Liddell, C. M. *Langmuir* **2007**, *23*, 8810–8814.
- (29) Hosein, I. D.; Liddell, C. M. *Langmuir* **2007**, *23*(21), 10479–10485.
- (30) Katz, E.; Yarin, A. L.; Salalha, W.; Zussman, E. *J. Appl. Phys.* **2006**, *100*, 034313.
- (31) Singh, J. P.; Lele, P. P.; Nettesheim, F.; Wagner, N. J.; Furst, E. M. *Phys. Rev. E* **2009**, *79*, 050401 (R).
- (32) Ding, T.; Song, K.; Clays, K.; Tung, C.-H. *Adv. Mater.* **2009**, *21*, 1–5.
- (33) Velikov, K. P.; van Dillen, T.; Polman, A.; van Blaaderen, A. *Appl. Phys. Lett.* **2002**, *81*, 838.

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