A. DOE Award Number: DOE DE-SC0006398, University of CA, San Diego

B. Rigid Biopolymer Nanocrystal Systems for Controlling Multicomponent Nanoparticle Assembly and Orientation in Thin Film Solar Cells. **PI: Jennifer N. Cha**

C. April 15, 2012 and Period 1 (year 1)

D. Accomplishments

The project seeks to direct the assembly of nanoparticles into three-dimensional crystals of any desired configuration and crystallographic orientation using tunable DNA interactions. Despite the wealth of nanoscale materials that may benefit many current and future solid state technologies, difficulties in controlling and directing their placement and orientation into desired architectures has led to significant impediments in their applicability. Biological systems can form such structures using their inherent molecular information as guides to assemble organic and inorganic materials into highly organized structures ordered at multiple length scales. Using bio-inspired strategies, the research will control the two- and three-dimensional arrangement of semiconductor nanocrystals into a seed layer that can nucleate successive layers of single nanocrystals with long-range order and tunable crystallographic orientations. The work will elucidate how particle-DNA interactions influence nanoparticle crystallographic orientation, how nanoparticles on patterned arrays of biomolecules can nucleate long-range order, and how to synthesize 2- and 3-D superlattice arrays of DNA conjugated semiconductor nanocrystals.

Prior to the start of this proposed research, we made significant discoveries toward obtaining body-centered-cubic (BCC) packed gold nanoparticle thin films on surfaces and, we published these findings in *SmalI.* A short description of this can be found below. The lessons gained from these studies are an integral part of the proposed DOE research, as they will enable engineering well-ordered binary semiconductor nanocrystal arrays on surfaces for heterojunction-based thin film solar cells. In order to apply the Au NP biomolecular assembly process toward semiconductor materials, however, methods are needed to synthesize DNA-conjugated semiconductor nanoparticles and nanorods. In addition, reversible conjugation chemistries were developed to remove the DNA ligands post-assembly to enable effective carrier mobility between the nanoparticles. *In the first year, we studied and created different methods to successfully conjugate semiconductor nanoparticles (CdSe, CdTe) with DNA. Methods were developed to coat the particles with multiple ligands and maintain their stability in the high magnesium concentrations required for DNA assembly. Finally these conjugation chemistries were all easily reversed through mild changes in pH.*

PRIOR RESULTS

In the past year, the PI has published work at the development of using surface adsorbed DNA to direct the assembly of DNA conjugated gold nanoparticles into either hexogonal or BCC packed arrays. Meso- and macroscale three-dimensional nanocrystal assemblies of arbitrary configuration and crystallographic orientation are highly desired for new solid-state optoelectronic and electromagnetic materials. However, the nanoscale precision and control required to engineer such devices in three dimensions over macroscopic areas site specifically has yet to be achieved. Early last year we demonstrated the generation of highly ordered 3-D body-centered-cubic (BCC) superlattices of differently modified gold nanocrystals at desired areas on a surface through specific DNA interactions. Through the combination of surface-bound printed

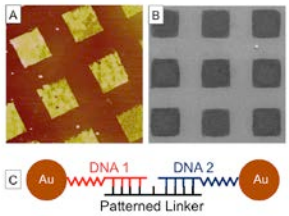

Figure 1. Micropatterns of ssDNA (A) and after Au NP adsorption (B). Schematic of DNA mediated assembly of BCC

DNA designed to capture the nanoparticles and two distinct DNA oligonucleotide sequences designed to arrange the particles in the confined space, 3-D BCC arrangements of nanoparticles were obtained through simple incubation of the surface with gold nanoparticles and subsequent thermal annealing. Furthermore, controlled film thicknesses from 20nm to 100nm were easily obtained through variation of initial gold nanoparticle concentration, and particles remained ordered in the z-direction as well.

In order to investigate substrate-adsorbed DNA for the generation of 3-D cubic nanoparticle arrangements, DNA sequences were designed that hybridize specifically to two different sets of DNA conjugated gold nanocrystals (Figure 1). By using two chemically distinct DNA conjugated gold nanoparticles and DNA linkers on the substrate that hybridize to both, BCC packing is thought to be favored because it maximizes the number of DNA hybridization events between the particles, resulting in non-close packed cubic structures with eight coordinated neighbors (CsCl-type superlattices). First, 3μm square arrays of DNA linkers were dual subtraction printed on UVO cleaned silicon (Figure 1a). Next, equimolar amounts of 10nm gold nanocrystals modified with different complementary sequences were adsorbed to the corresponding linker patterns in 125mM $MgCl_2$ for 1 h, followed with buffer and ethanol rinsing to remove excess particles and salts. This was followed by annealing the substrates at 70^{o}C in a humid environment to drive particle assembly toward a thermodynamically favored state (Figure 1b). After adsorbing 20 to 40 nM gold nanocrystal concentrations to the DNA arrays and annealing for 4 h, highly ordered, close-packed nanocrystal arrays were clearly observed from both sets of DNA conjugated gold and DNA linkers (Figure 2). In order to determine the crystallographic orientation of each superlattice, Fourier transform (FT) analyses of individual SEM images of representative arrays (Figures 2a,b and Figure 2c,d) were conducted, demonstrating BCC arrangement with the (110) plane, the most densely packed and lowest energy crystal plane, displayed at the surface. The relative degree of ordering and BCC packing through a single nanoparticle film was explored using cross-sectional SEM images of nanocrystal arrays generated from 40nM gold nanoparticle solutions. As shown in Figure 3, approximately 80nm thick film arrays were obtained with strong ordering both parallel and normal to the surface. While the top plane clearly showed a BCC (110) face, obtaining absolute vertical (220) facets along the z-axis of the cross section was difficult due to multiple grain boundaries within an array as well as issues of substrate cleaving. Finally, because there was no physical or chemical boundary in the z-direction, such as an air-liquid interface, that can limit the film thickness, highly-ordered nanocrystal films from 20 to 100 nm could be generated simply by controlling the gold nanoparticle concentrations from 10nM to 80nM. Although there was some variation in the exact DNA-conjugated gold nanocrystal concentrations, on average a linear correlation was observed between nanoparticle concentrations and the final array thicknesses obtained.

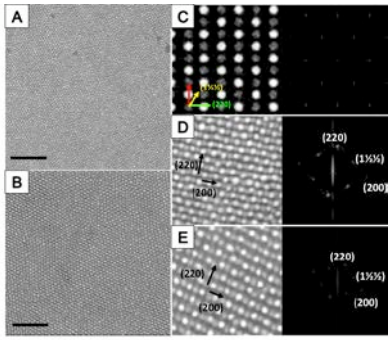

Figure 2. SEM and FT analysis of BCC arrays of gold nanoparticles.

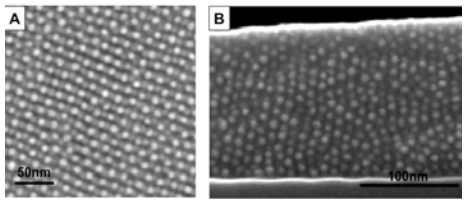

Figure 3. Top (A) and cross-sectional (B) view of BCC packed nanoparticle arrays.

ACCOMPLISHMENTS

In the past year, methods have been developed to apply the techniques developed for producing gold nanoparticle BCC arrays toward binary semiconductor arrays (CdSe, CdS, CdTe). One technical challenge for optoelectronic devices from nanocrystals has been orienting the layers of electron and hole

transport domains both normal with respect to the top and bottom electrodes and such that every donor is surrounded by an acceptor. To create this type of structure, multicomponent nanocrystals (e.g. CdSe, CdTe. CdS) need to be conjugated with DNA linkers such that only interactions between different types of nanoparticles will drive particle packing and assembly within the array. The DNA sequences used and the sizes of the nanoparticles will contribute to the crystallographic packing of the assembled particles in both 2- and 3-dimensions. After nanoparticle arrangement the exposed biomolecular ligands need to be removed, preferably through mild chemistries such as slight changes in pH.

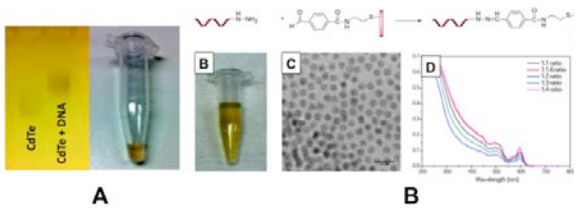

Figure 4. (A) DSPE-PEG-DNA conjugated CdTe nanoparticles. (B) DNA conjugated CdTe nanoparticles using hydrazone linkage chemistries.

As a first step, spherical CdSe, CdS, and CdTe nanocrystals, which have recently been shown as promising materials for thin film solar cells has been synthesized using published procedures. To create the DNA Cd(Se,Te,S) conjugates, the semiconductor nanoparticles must be well dispersed in water. In one method, CdSe and CdTe nanocrystals were dispersed in water by using maleimide terminated polyethylene glycol lipids and thioglycolic acid to make acid terminated nanoparticles. To remove excess organics, the dispersed nanoparticles in water were dialyzed followed by agaraose gel extraction, and centrifuge filtration. The water-soluble nanocrystals were characterized by UV-Vis and fluorescence measurements as well as TEM to ensure nanocrystal integrity during the transfer process. Preliminary studies with this method have produced highly stable solutions of dispersed nanocrystals in aqueous buffer, and TEM analyses showed the particles that the particles were well dispersed. The particles also appeared to remain stable in solution for at least 1-2 months. Next, amine-terminated DNA strands were reacted with the acid terminated nanoparticles by using standard EDC/sulfo-NHS chemistry and characterized by both UV Vis and gel electrophoresis. As shown in Figure 4a, successful DNA attachment to the nanoparticles caused an expect mobility shift in the CdTe nanoparticle band. Alternative strategies for attaching DNA to semiconductor nanoparticles were also studied, including the use of mercaptoundecanoic acid (MUA) and mercaptoethylcarboxyaldehyde to produce aldehyde terminated nanoparticles which were then reacted with hydrazine terminated DNA (Fig. 4b). Preliminary data suggests that such hydrazone chemistry can yield CdSe and CdTe nanoparticles that are conjugated with ~ 100 DNA per particle. The inherent beauty of using the aldehyde-hydrazine chemistry for DNA attachment is that the hydrazone groups that form are pH labile, meaning the at slightly acidic conditions the DNA de-attaches from the nanoparticle, lending to a potentially facile and benign way to remove DNA after nanoparticle assembly on surfaces. As organics including DNA will impede carrier mobility, coming up with methods to remove DNA easily is also necessary for the proposed research to succeed. Finally, a third method which has proved to be the easiest though less stable was to transfer the semiconductor nanoparticles directly into pH 10-12 thiolated DNA solutions. Although this easily yielded watersoluble quantum dots that were also DNA conjugated, the solutions are relatively unstable at neutral pH which could be attributed to the protonation of the S^- bond causing the DNA to dissociate from the CdSe or CdTe surface.

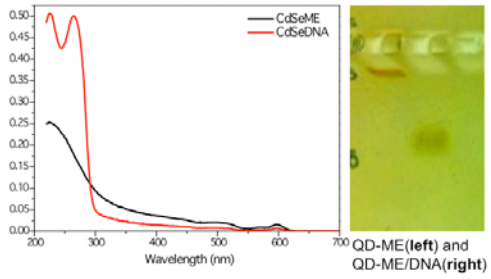

Figure 5. UV Vis spectra of mercaptoethanol (ME) (black) and ME+DNA (red) conjugated nanoparticles. Strong UV band at 260nm in the ME+DNA curve indicates DNA is successfully conjugated to the ME bound NPs. (Right) Gel electrophoresis showing different mobilities for ME vs ME+DNA QDs.

In all cases, the DNA conjugated quantum dots need to be stable at relatively high magnesium concenctraions as this was found to be critical to get large amounts of nanoparticle bound to any surface adsorbed DNA. Studies to improve the stability of the DNA conjugated nanparticles are underway. Preliminary data of conjugating a mixture of mercaptoethanol and thiol DNA to the nanoparticles show that the quantum dots are stable up to 50mM $MgCl_2$ (Figure 5).

E. No papers as of yet. It is expected that during the 2nd year of funding, 1-2 papers on this work will be published.

F. Graduate Students: Hyunwoo Noh, Sarah Chowdhury

G. At the end of year 1, ~30% of funds have not been used because a glove box has not been purchased. This is because the new building for Nanoengineering has not been completed but will be ready to move in August 2012. Once the entire lab is moved, a glove box will be purchased.

H. In the second year, the DNA conjugated nanoparticles (CdSe, CdTe) will be adsorbed to the DNA microarrays and characterized. Once thin films have been successfully fabricated, IV measurements will be run. In initial studies the DNA will not be removed after the particles have been assembled. Methods to remove the DNA post assembly will be studied including treatment with mildly acidic solutions (pH <5) and oxidation. As large cracks will most likely form when the DNA strands are removed, methods to fill the cracks with nanoparticles or inorganic chalcogenidometallate clusters will be studied.