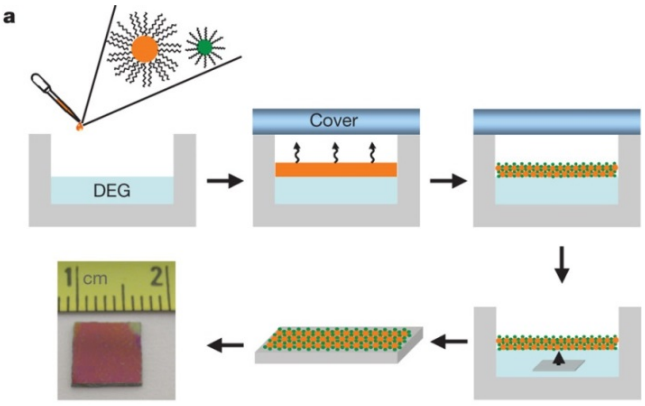
University of Pennsylvania, Dept. of Materials Science and Engineering
Senior Design 2013-2014

Artificial doping in self-assembled binary nanocrystal superlattices (of CdSe quantum dots and plasmonic Au nanocrystals)

Bianca Datta, Divij Damodhar
Dr. Chris Murray (Advisor)
Matteo Cargnello, Benjamin Diroll

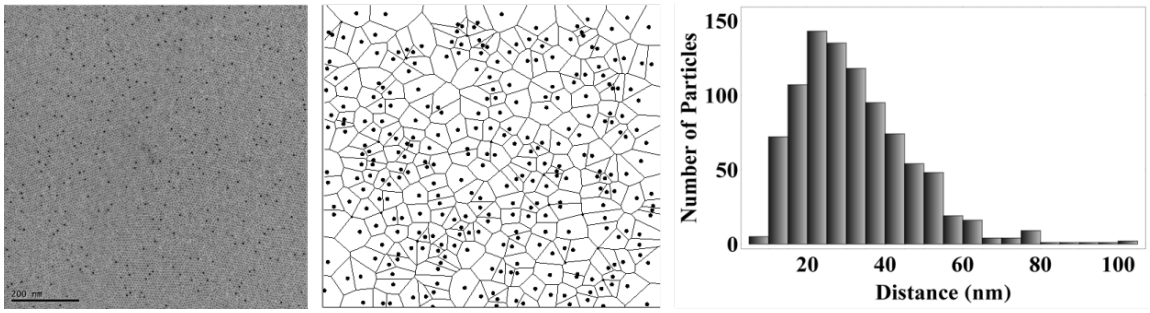
Quantum dots are fascinating materials with distinctive properties that make them appealing in several fields. In particular, they show optical properties that can be tuned by altering their size. The absorption and photoluminescence emission of cadmium selenide (CdSe), for example, can be tuned throughout a significant part of the visible range by changing its size in the range 10-100 Å (quantum size effect). The tunability of particles facilitates the matching of absorbance of materials to the solar spectrum. Additionally, they are solution-processible, so they can be functionalized and deposited onto surfaces in the form of thin films. Quantum dots have a broad range of potential applications based on post-synthesis manipulation: their surface chemistry can be altered to tailor the conductivity of the material and improve interparticle coupling, they can be assembled into binary nanocrystalline superlattices and multicomponent films, and processed through bottom-up fabrication techniques to produce electronic devices. The spontaneous organization of multicomponent nanocrystals into superlattices is being studied widely to understand the assembly process on the nanometer scale and has applications in the bottom-up fabrication of functional devices. In order to work towards the most efficient devices, we aimed to produce ideal systems. The focus of this study was the formation of binary superlattice structures of CdSe core-shell quantum dots with plasmonic gold(Au) particles. These coupled nanoparticles assemblies served as an observable model of atomic doping phenomena. They are fascinating for future studies on the effect of plasmonic particles on optically active layers in solar cells and energy conversion devices.

To properly model such systems, we prepared ordered, hexagonal close-packed monolayers of randomly dispersed mixtures of CdSe-based quantum dots and Au nanocrystals. The two building blocks were prepared with very similar average particle size (~6 nm) to study the presence of a nanoscopic dopant (Au nanocrystals) into ordered films of a nanoscopic host (CdSe). Monolayers are the ideal system to explore transport without scattering effects from the nanocrystal-substrate interface, and they serve as model systems for fundamental properties[2]. In contrast to prior assembly methods which took multiple hours due to high boiling point solvents, we utilized a liquid-air assembly process developed in our group, as shown in Figure 1. Hexane solutions of the mixture of the nanocrystals were used, allowing for controlled evaporation, and films were assembled on diethylene glycol subphase inside teflon



wells. This method allows for easy transfer of the films onto arbitrary substrates including TEM grids.

Transmission electron microscopy (TEM) was used to characterize and image the monolayer films (Figure 2, left). Due to the large difference in atomic number between Cd and Au, the Au nanocrystals are easily distinguishable in the TEM images because of their higher electron contrast that make them look darker compared to the lighter quantum dots. The position of the Au dopants can therefore be found. The films were studied using Voronoi Analysis, which allows us to examine how the particles are interspersed in the film by creating polygons based on distances between nearest neighbor distances (Figure 2, middle). The first objective of this analysis was to determine if dopant particle distribution was random. This was confirmed by demonstrating that nearest neighbor interactions followed a gamma distribution (Figure 2, right), indicating that particles were consistently spaced out. It also followed logically and was demonstrated experimentally that nearest neighbor distances decreased as the concentration of gold particles increased.



The formation mechanisms established in our study may be applicable to studies on the coupling of plasmonic materials with quantum dots for solar cell applications. Presently synthesized quantum dots have good absorption, but poor electron transport processes. Adding plasmonic materials such as gold improves the scattering cross section of the system and the transport properties, allowing for device fabrication with thinner active layers of quantum dot material. Ultimately this could lead to the fabrication of smaller, more efficient devices.

In future experiments, assemblies would be conducted using differently sized gold particles. Different sizes could be used to examine defect phenomena as compared to lattice mismatch on the atomic scale.

1. Dong, Angang, et al. "Binary nanocrystal superlattice membranes self-assembled at the liquid-air interface." *Nature* 466.7305 (2010): 474-477.
2. Dong, Angang, et al. "Two-dimensional binary and ternary nanocrystal superlattices: the case of monolayers and bilayers." *Nano letters* 11.4 (2011): 1804-1809.