The ISEN proposal “Imaging Carriers in Solar Cell Materials” was concerned with imaging electrostatic potential evolution through colloidal CdSe quantum dot films for applications in solar technology, and contributed to the findings discussed in our recent manuscript on nonlinear optical microscopy.\(^1\) Quantum dots (QDs) were chosen for their unique optical and physical properties such as the tunability of their light absorption characteristics, charge injection properties, and efficient use of sub bandgap photons through mid–bandgap states.\(^2\)-\(^5\) Previous studies concerning the properties of QD and other solar cell materials indicate that microscopic variations in topology and morphology are critically important in determining cell efficiency.\(^6\)-\(^9\) We therefore proposed to use nonlinear optical microscopy to obtain high resolution electrostatic potential maps of CdSe QD films deposited between gold electrodes on transparent substrates. By applying a potential difference between the electrodes, we expected to observe electron motion through the material and record the conditions conducive to charge transfer.

Because nonlinear optical imaging of surface potential is a third-order process, we first considered all equal- and lower-order contributions to the signal. As photons approach a sample surface subjected to a static electric field, an oscillating polarization is induced according to

\[
P^{(2)}_i = \chi^{(2)}_{ijk} E_j E_k + \chi^{(3)}_{ijkl} E_j E_k \phi,
\]

where \(P\) is the polarization of the sample, \(E\) is the incident electric field strength, \(\phi\) is the static electric field strength, and \(\chi\) is the susceptibility which describes how strongly the polarization in direction \(i\) responds to an electric field in direction \(j, k,\) or \(l\). Summation over the \(j, k,\) and \(l\) indices in Eq. 1 is assumed. Because the sample polarization is proportional to two electric fields, oscillations occur with a component at the sum of the incident frequencies. When the two incident photons oscillate at the same frequency, \(\omega\), the polarization oscillates with a component at the second harmonic, \(2\omega\), producing light that provides information regarding the properties of the sample. Importantly, the sample can undergo second harmonic generation (SHG) by two mechanisms, each described by a term in Eq. 1. It can be seen that the polarization may be produced by a second-order term that is only allowed in noncentrosymmetric environments, or a third-order term that can be used to track an electric field. CdSe QDs adopt a noncentrosymmetric wurtzite structure, and therefore undergo SHG by both mechanisms in the presence of a static electric field. We can characterize the signal obtained through the second-order term alone by taking an image with 0 V applied across the sample, which eradicates the third-order term in Eq. 1. Subtracting this signal intensity from the signal obtained with applied voltage isolates the intensity proportional to the electrostatic potential. We therefore begin with second-order nonlinear optics.

For CdSe QDs, the contribution from the first term in Eq. 1 should be constant over all voltages, whereas the contribution from the second term should vary as potential evolves through the material. In reality, the QDs coalesce into aggregates of various shapes, sizes and densities whose local environments and structures differ. Figure 1 shows optical and SHG images of CdSe QDs spin coated from \(\sim 10^{-6}\) M solutions in hexane onto clean glass slides. The optical image (A) taken with the 10x objective clearly shows heterogeneity in the structure adopted by the sample. Although we expect a homogeneous film and uniform signal intensity, we instead find that only a small fraction of the QDs appear to show SHG activity, as can be seen in (B). The SHG active spots appear to be locations where a number of QDs have gathered, establishing a unique environment and symmetry properties. That only the aggregated dots show SHG activity may be a result of the size or shape of the involved or resulting particles. We further investigate this phenomenon by zooming in to a local “hot spot” with more powerful objectives.
By comparing optical (C) and SHG (D) images, we observe that indeed only a sub-section of the particle aggregate undergoes SHG. This finding indicates that the local environment is important for optical properties, a characteristic that likely extends beyond nonlinear optics.

The chemical and physical properties of the QDs, as well as the local environment, are influenced on both the microscopic and macroscopic scale by the properties of the organic ligands coating each particle. For example, lengthening the carbon chain is expected to increase the inter-dot distance and thereby decrease the affinity for charge transfer. Similarly, the number and nature of electron pathways through the ligand governs the thermodynamics and kinetics of transport. Because optical properties are controlled by electron behavior, it is no surprise that the optical properties are also heavily influenced by the chemical identity of the ligand, the size of the QDs, and the local environment. These concerns are all relevant for the second-order contribution in Eq. 1.

The third-order term involves the electric field component important for solar cell material applications. We began with a simple sample that experienced no second-order contributions to the polarization. To this end, water was deposited between gold electrodes separated by a few microns. Because the oxygen in water is more electronegative than the attached hydrogens, the electron cloud is displaced and a permanent dipole is generated. If water is placed between two electrodes experiencing different potentials, the water will respond by aligning its dipole with the electric field. The combined dipoles constitute a macroscopic electric field available for participation in the third-order term of Eq. 1. The electric field produced by this process has been imaged and displayed as a false color representation in Figure 2, which
depicts the general phenomenon responsible for electric field induced SHG. Although the gold electrodes may also undergo SHG, Fig. 2 is background subtracted using the methods described above for QDs, and therefore shows no second-order contribution. The images demonstrate our ability to capture and display electrostatic potential. It is important to note that the mechanism previously described is not expected to contribute in systems involving QDs placed between electrodes. Because CdSe does not generate a permanent dipole, there is no alignment and subsequent participation in third-order SHG. Instead, the third-order contribution should arise only when electrons are excited and transported through the material, developing into an observable electric field. We have not yet imaged electrostatic potential on systems of QDs due to time constraints involving the understanding of the second-order contribution, calibration measurements performed on simple systems, construction in the laboratory, and instrument failures. Third-order nonlinear optical microscopy experiments involving CdSe QDs are the subject of current and future work.

The findings of this ongoing investigation advanced research in energy and sustainability by providing important information on the properties of QD films intended for use in solar energy applications. Our hypothesis was that microscopic variations in the materials could lead to enhanced or diminished efficiency, which we shown to be true for SHG. Our current goal is to extend our investigation from second- to third-order SHG, and understand the conditions under which charge transfer behavior may be enhanced.

References


