FINAL REPORT

DOE Earlier Career Award (grant DE-SC0008446)

Modeling of Photoexcited Process at Interfaces of Functionalized Quantum Dots

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Funded by the DOE grant we achieved the following research results:

(i) We combined the time-domain density functional theory (TD-DFT) with the time-dependent density matrix technique (TD-DMT) and developed a new approach to non-adiabatic dynamics (NAMD) allowing us to get insights into various non-radiative relaxation pathways and simulate the time-resolved emission spectra of quantum dots (QDs) with complicated surface chemistry and interfaces.

(ii) Using the developed NAMD method, we determined which form – arrays or nanowires – maximizes the absorption and emission of nanostructures and how that efficiency is affected by the interactions between QDs and their structural disorder. In particular, we provided an exploitation of experimentally detected enhancement in blinking 'on' time corresponding to the system's state with the high quantum efficiency in closely packed Si QDs.

(iii) Using the NAMD method, we analyzed the fundamental process such as decoherence and Zeno effects in semiconductor nanostructures and established a direct connection between the phonon bottleneck (extremely slow energy dissipation to heat) and Zeno effect. This knowledge will be helpful in controlling dissipation process in QDs via synthetic manipulations of the QD's shells, dopants, ligands, packing, and interfaces.

(iv) Using the NAMD method, we elucidated the role of surface ligands in photoexcited dynamics of quantum dots (QDs), including slowing of elastic scattering in QDs by ligands providing favorable conditions for multiple excitons generation (MEG), controlling of which holds an important promise for improvement of the solar energy conversion.

(v) We have quantified the range of applicability of our DFT-based techniques in predicting both linear and non-linear optical properties of quantum dots (QDs) and confirmed highly efficient two-photon absorption in 1-2 nm CdSe QDs.

(vi) We identified mechanisms of the preferential binding of ionic ligands, such as carboxylates, thiolates, and halides, to various QDs. In particular, our calculations explained the mechanisms of formation of two-dimensional nanoplates (NPLs) of PbSe and the role that halide precursors play in controlling the surface direction and thickness of NPLs. This knowledge provides us insights into the nature of interactions between the QD and surface agents governing the efficiency of the optical response in QDs, which is important for their applications in optoelectronic and photovoltaic devices.

(vii) We conducted quantum chemistry calculations to model the morphology, the electronic structure, and optical spectra of QDs functionalized by organic dyes and metal-organic complexes, which led us to predictions of the prerequisite conditions that govern the direction and rates of the charge transfer from the QD to the dye. Thus, we obtained important insights into the charge transfer that is a key process in the realization of new nanomaterials for photovoltaic and photocatalytic applications.

(viii) Targeting design of metal-organic dyes with enhanced charge transfer and non-linear optical properties, we performed joined computational and experimental studies of optical properties of various Pt(II)-, Ru(II)-, and Ir(III)-complexes and demonstrated the practical realization of DFT-based predictions in rational structure-property design of molecular systems.

Overall, the results of the DOE funded research were summarized in **29 peer review scientific papers**, including high-impact journals, such as *Chemistry Review (54.3 impact factor), Accounts of Chemical Research (21.66 impact factor), the Journal of American Chemical Society (14.7 impact factor)*, *ACS Nano (13.9 impact factor), Physical Review Letters (9.2 impact factor), ACS Applied Materials & Interfaces (8.5 impact factor),* and *Journal of Physical Chemistry Letters (7.3 impact factor).* Additionally, **one** book chapter was just accepted. The research results were reported in **50** invited talks at conferences (35) and university seminars (15). **Nine** scientific symposia at national and international meetings were organized on topics closely related to the DOE funded project and **one** local conference was organized in Fargo, ND. **Two** postdocs, **five** graduate students and **six** undergraduate students were working on this project supported by this grant, with **three Ph.D. dissertations** defended in 2015 and 2016 and two are expected to be defended in December 2019 and May 2020.

More Insights to Achieved Scientific Results.

In many respects, colloidal QDs are near-ideal materials for solar energy conversion and lighting technologies. However, the electronic and optical properties of QDs are highly sensitive to their surface passivation and interfaces. As such, surface chemistry plays a crucial role in defining the functionality of QDs critical for technological applications. Our research was helpful in filling the gap in understanding the role played by surface chemistry in light-driven processes in QDs. In particular, here we report several cases, where our simulations based on density functional theory (DFT) and time dependent DFT (TDDFT) have succeeded in resolving this challenge, allowing for explanations of experimental trends and interpreting the light-driven observables sensitive to defects, passivating ligands, and interfaces in the QDs.

(i) Combining the time-domain density functional theory (TD-DFT) with the time-dependent density matrix technique (TD-DMT), we have advanced an approach to non-adiabatic dynamics (NAMD) allowing us to identify conditions affecting radiative and nonradiative pathways in nanostructures with complicated surface chemistry and interfaces. This approach is discussed in our two review papers.[1, 2] Applying this method to 1-1.5 nm Si QDs, we revealed ultrafast electron-phonon dynamics that is enhanced by a presence of a doping.[3] These simulations provide information on the nature and lifetime of emission states in doped Si QDs, which might be useful for interpretations of pump-probe spectroscopy measurements. Obtained computational insights into pathways and mechanisms of relaxation dynamics in silicon nanostructures is also useful in specifying ways of controlling both radiative and non-radiative process, which will help in rational design of Si-derived novel nanomaterials.

Using our NAMD method, we also obtained insights into cooperative effects of the quantum confinement and solvents onto femtosecond dynamics of photo-excited charge carriers in nanostructures. In particular, we found that TiO_2 nanowires surrounded by aqueous environment gain brighter but short-lived optical transitions, due to enhanced non-radiative relaxation channels.[4] Relaxation time of photoexcited carriers has been found of 2 to 4 times faster in water than in vacuum. Observed difference in relaxation time between electrons and holes, with much faster relaxation of holes, promises formation of long-lived charge-transfer state at the surface. This supports the vision of nanowires as material of choice for photo-electrochemical water splitting, compared to bulk structures and thin films. We anticipate that this feature can also be observed in nanostructures of other materials, experiencing same regime of quantum confinement i.e. similar ratio of the diameter to exciton Bohr radius, and with similar ratio

of effective mass of electron and hole, which is generally important for control of the charge transfer at the interface in nanomaterials.

(ii) We determined which form – QD arrays or nanowires – maximizes the absorption and emission of Si nanostructures and how that efficiency is affected by the *interaction between QDs* and their *structural disorder*.[5,6] Simulated current density induced by spatially non uniform time dependent electric field served as a characteristic of QD coupling in the arrays and, in particular, of the inter-QD-exciton transport. We observe rapid decay of the QD-QD coupling with the increase of the QD separation and its complete diminishing at the QD-QD distance comparable with the size of the QD.[6] Surprisingly, the structural disorder in the amorphous QD arrays resulted in better light absorption and inter-QD-exciton transport at the lowest energies, compared to crystalline-based nanowires.[5]

Additionally, our simulations of QD-QD interactions have provided an explanation of experimentally detected enhancement of 'on'-blinking times in closely packed Si QDs.[7] Calculated energy transfer rates from transition density matrixes obtained from TDDFT, suggest that ultrafast energy transfer from an excited QD to the nearest one provides an additional channel for occupation of long-living optically forbidden trap states in neighboring QDs, forcing the emission to happen from higher-energy optically active states. This pathway increases 'on' blinking time and photo-luminescent quantum yield in aggregates of strongly interacting Si QDs, as experimentally observed.

We also addressed the question how the p- and n-type impurities (doping) affect the interaction between QDs and their optical response.[8] For this, we analyzed the charge density distribution at p-n nano interface using model systems of dimers of doped Si QDs interacting through bonds (< 0.5 nm QD-QD distance) and through space (~ 1nm QD-QD distance). Spatial distributions of transition densities between the ground and excited states show a redistribution of electronic density from n-impurities to p-impurities. Although impurities contribute very few orbitals to the total density, changes in the ground state charge distribution and polarization both facilitate formation of a large number of the charge-transfer excitons (with hole localized on p-doped QD and electrons on n-doped QD) involving solely delocalized silicon orbitals, beyond doping sites. As such, our calculations confirm that the interface between p- and n-doped QDs governs formation of charge-transfer states, even in QDs separated from each other at distances of ~1nm. Formation of such charge-transfer states is critical for enhancing photovoltaic efficiency in QD-based devices.

(iii) We adapted our TDDFT-based NAMD method to phonon-mediated dynamics in QDs with the surface passivated by organic ligands and/or covered by another type of the semiconductor, the core/shell QDs. Our NAMD approach treats phonons semi-classically, which allows us to explicitly incorporate quantum decoherence effects within the electronic subsystem. Using this approach, we elucidated the role of surface defects on decoherence and the ultrafast loss of photoexcitation to heat in CdSe QDs. Thus we established a connection between the slow energy relaxation – the phonon bottleneck – and Zeno effect. Quantum confinement can significantly slow down electron-phonon relaxation in QDs; known as the phonon-bottleneck, the effect remains elusive. Our simulations confirm that the bottleneck in CdSe QDs occurs under quantum Zeno conditions: To achieve the bottleneck, elastic electron-phonon scattering (decoherence) must be faster than the coherent electronic transition.[9] The calculated electron-phonon relaxation time shows excellent agreement with the experimental data. Our studies also show that defects on the surface in the CdSe/ZnS core/shell QDs can destroy the electron-hole decoupling allowing for faster relaxation. The established relationship between the phonon-bottleneck and the quantum Zeno effect together with the atomistic

details obtained from our simulations, provide the understanding of the conditions necessary to achieve and control rates of energy dissipation via synthetic manipulations of the QD's shells, dopants, ligands, and packing.

(iv) Our NAMD simulations also provided fundamental insights into the origin of the pure-dephasing process in the bare and ligand passivated QDs. We have shown that *elastic and inelastic scattering respond in the opposite manner* to CdSe QD surface passivation by ligands. Thus, phonon-induced pure-dephasing processes determined by elastic electron-phonon scattering in CdSe QD capped with ligands are much longer than that in the bare CdSe QDs.[10] The difference is rationalized by the fact that ligands have no direct contributions to the electronic densities of the lower-energy states involved in the superpositions, while they indirectly reduce mobility and fluctuations of the surface atoms. In contrast, the higher-energy electronic states involved in the relaxation are delocalized over ligands and the QD, and therefore, ligands increase the electron-phonon coupling in the case of inelastic processes. Increase in the pure-dephasing time results in decreasing of the homogeneous luminescence linewidth in the ligated QDs, as detected experimentally. The lifetime of quantum superpositions of single and multiple excitons created upon photo-excitation increases as well, providing favorable conditions for multiple excitons generation (MEG), which is expected to significantly increase the efficiency of photovoltaic devices. Overall, both elastic and inelastic electron-phonon interactions play the key roles in solar energy harvesting, since quantum transitions can occur only through buildup of coherence.

(v) We have quantified the range of applicability of our TDDFT-based techniques in predicting both linear and non-linear optical properties of CdSe QDs.[11] Comparison of the experimental results with effective-mass and TDDFT calculations allows us to quantify the ranges of applicability of these commonly used simulation techniques and facilitate the physical interpretation of experimental results. We found that linear (1PA) and nonlinear (2PA) optical properties of the large-size (>3.5 nm) regime QDs are described rather well by a simple single-band effective mass model. This allows one to use the simple and physically transparent simulation methods to gain an insight into complex optical nonlinear processes. However, in the intermediate-size regime (2-3.5 nm), comparison of the spectra measured experimentally and calculated using the effective-mass model suggests deviation. The effective-mass models become inaccurate as the optical properties are affected by structural atomistic details. For the small nanoclusters (<2.5 nm), were surface to volume ratio is the largest, significant deviations between the effective-mass and quantum-chemical calculations suggest that detailed description of QD surfaces chemistry is important for proper determination of their optical properties. For small-size QD's regimes, 1PA and 2PA cross sections are found to be comparable and even higher to that of the best organic molecules, enables them to be potential competitors with organic dyes in the endeavor for photonic applications.

(vi) We identified mechanisms of the preferential binding of ionic ligands to the QD surface and its effect on their optical properties. Our calculations have revealed conditions for the binding of carboxylate and thiolate groups and their derivatives to the CdSe QDs. We found that the most stable ligated conformations are those where a carboxylate group is attached to extra Cd^{2+} forming a $[Cd^{2+}(CH_3COO^-)]$ cation at the surface, while also accompanied by an carboxylate anion attached nearby at the surface balancing the overall neutral charge of the system.[12] This results in 2:1 ratio between carboxylate and extra Cd ions agreeing with experimental findings, while also exhibiting the strongest optical response. Also our calculations reveal much more complicated exchange mechanism of the native surface ligands of CdSe QDs with phenyl-dithiocarbamates (PTCs) as it was though before.[13] PTCs decompose during exchange

with native ligands, while only a small portion of deprotonated PTCs covalently bounds to the Cd-enriched QD's surface. These predictions well agree with NMR measurements of PTC-ligated QDs. Overall, we found that ionic ligands are mainly bound to non-stoichiometric $Cd_{n\neq m}Se_m$ QDs, eliminating surface-driven optically inactive midgap states. This explains enhanced emission in metal-enriched compared to nonmetal-enriched QDs in a presence of ionic ligands that is observed experimentally. These results are essential in understanding the role of acidic ligands during synthesis and ligand exchange, as well as in manipulating the QD's photophysical properties.

We also elucidated the role of halides on the formation of two-dimensional (2D) (100) face-oriented PbSe nanoplates (NPLs).[14] PbSe QDs show efficient absorption and emission in near IR range, which is beneficial for solar cells. Additionally, engineering of interfaces in PbSe-based QDs via 2D confinement, allows for altering unique carrier cooling dynamics, reduce Auger recombination rates, raise carrier multiplication, and low amplified spontaneous emission thresholds; such behavior is valuable for opto-electronics and photovoltaics. Our studies show that halide passivation of PbSe QDs is critical to the growth of the (100) face-dominated NPLs. DFT predicts that $PbCl_2$ precursors are attached to the Pb-enriched (111) and (110) facets blocking these surfaces from interactions, while creating Pb-Cl-Pb bridging network with neighboring QDs along (100) facet. We found that a 2D bridging network is energetically favored over a 3D network, driving the formation of NPLs with 2 nm thickness. Due to much longer Pb-I compared to Pb-Se bond length, iodides do not contribute to bridging, while they destabilize the amine ligated (100) faces of NPLs, providing means for tuning NPL thickness. These results perfectly agree with experimental observables.

(vii) We got atomistic insights into charge transfer mechanisms in QDs functionalized by metal-organic dyes. New photovoltaic and photocatalysis applications have been proposed based on these hybrid systems. The charge transfer from the photoexcited QD to the dye or backward is the key process in these applications. However, the exact mechanism and ways of controlling the charge transfer rates in QD-dye composites are still unclear. Our DFT simulations of the morphology, electronic structure, and optical response of chemically functionalized QDs led us to predictions of the thermo-dynamic conditions that govern the direction of charge transfer in these systems. We found that independent on the attachment and the QD type (CdSe, PbSe, or ZnO), dyes with neutral ligands (e.g., bipyridines) introduce additional states at the edge of the QD conduction band, governing the direction of electron transfer from the dye to the QD, while making the hole transfer from the QD to the dye unfavorable.[15] In contrast, negatively charged ligands and less polar solvents significantly destabilize the dye's occupied orbitals shifting them toward the very edge of the valence band, thus, providing favorite conditions for the hole transfer.[16] Compared to the energy offsets of the isolated QD and the dye, QD-dye interactions strongly stabilize dye orbitals with respect to the QD states, while the surface chemistry of the QD has a minor effect on the energy offsets. As such, the energy offsets in the QD/dye composites does not represent a simple difference of the isolated Ru(II) complexes and the QDs, which should be accounted for in experimental studies.

We also elucidated a degree of sensitivity of the electronic level alignment and related electronic couplings to binding conformations of Ru(II) dyes at the surface of CdSe QD. Our calculations reveal a lack of direct correlations between the strength of the QD-dye interaction in terms of their binding conformations and the donor-acceptor electronic couplings.[17] In fact, while the QD-dye binding conformations are the most stable when the N719 dye is attached to the QD via two carboxylate groups, the strongest electronic coupling between the QD as an electron donor and the dye as an

electron acceptor is observed in structures bonded via the iso-cyanate ligands. Analysis of frontier orbitals rationalizes this trend by increased amount of interfacial states with a charge transfer character, when iso-cyanates are involved in coordinated bonding between the dye and the QD surface. Interfacial states increase donor-acceptor electronic couplings but have insignificant effect on the QD-dye binding energy. Our calculations predict that the most stable binding conformations are those occurring via two carboxylate linkages, which also provide the most favorable thermodynamic conditions for the hole transfer from the photoexcited CdSe QD to the N719 dye. Overall, our calculations demonstrate that variations in the dye's ligands, specifically in their charge and anchoring groups, are instrumental in adjustments of the electronic structure of QD/dye assemblies that govern conditions for the charge transfer in these systems.

Applying our NAMD method to the CdSe QD functionalized by the tris-thiocyanato-ruthenium (II) terpyridine complex (a black dye), we revealed ultrafast hole transfer from the photoexcited QD to the dye during first 10-30 fs, followed by slower hole cooling of ~100 fs resulting from the redistribution of population between the sub-band of the QD states.[18] The mechanism of such ultrafast QD-to-dye hole transfer, despite significant energy splitting between the dye and QD states, is rationalized by strong non-adiabatic couplings between the delocalized surface orbitals of the QD and the high-frequency vibrations of isothiocyanate ligands of the black dye. This mechanism is also confirmed by a very rapid loss of coherency of the excitation due to strong electronic couplings with vibrational modes of the dye. Our calculations prove the realization of the ultrafast interfacial hole transfer from the photoexcited CdSe QD to the black dye, which is instrumental for improving photovoltaic and photocatalytic performance of these materials.

(viii) We conducted a number of DFT-based simulations to reveal the relationship between molecular structure and photophysics of various Pt(II)[19,20] and Ir(III),[21-30] complexes with the goal to enable a systematic design procedure for this important class of energy materials, focusing on structures that provide conditions for destabilizing the highest occupied molecular orbital (HOMO) of the complex in order to facilitate the hole or electron transfer from the QD. In addition, these studies helped to identify how the ligand modification changes the lowest energy absorption band, including triplet states, with respect to the absorption band of the QD. This information is important because the accuracy of charge/energy transfer measurements depends on the overlaps of optical transitions of each species in the hybrid QD/dye composites. The small overlap between optical transitions of the QD and the dye ensures better resolution and control in experiments. In contrast, for large overlaps, photoexcitation to the QD's absorption maxima can be uniquely assigned neither to the QD nor to the complex, and determination of the charge transfer process is challenging. Our calculations complemented experiments by providing insights on characters of optical transitions and their changes upon ligand modification in metal-organic complexes.

In particular, electron donor/acceptor substituents have been shown instrumental in red-shifting lowest energy optical bands both in Pt(II)[19,20] and Ir(III)[22, 27,28] complexes. Increasing the electron donating character of substitute groups at the C^N ligands[21] of Ir(III) complex results in extending the ground-state absorption to the near-IR region, while retaining the long-lived and broadly absorbing triplet excited state.[27] We also found that Ir(III) complexes mainly possessed intraligand charge transfer (^{1}ILCT) mixed with metal-to-ligand charge transfer (^{1}MLCT) dominated transitions in their low-energy absorption bands, which red-shifted with the increased electron-releasing strength of the substituent. With a stronger electron-releasing substituent, the degree of charge-transfer contribution increases both in singlet and triplet transitions, leading to a decrease of the

emission quantum yield of Ir(III) dyes.[28] In contrast, the nature of the terminal substituent does not influence the parentage and energies of the lowest singlet and triplet excited states of Pt(II) complexes. However, the triplet excited-state lifetimes of the complexes with the electron-donating diphenylamino (NPh_2) terminal substituent on the bis(ethynylfluorenyl) or tris(ethynylfluorenyl) ligands are much longer than that of their counterpart with monofluorenylacetylide ligands; while the triplet lifetimes of the complexes containing the electron-withdrawing benzothiazolyl (BTZ) terminal substituent are similar to their counterpart with monofluorenylacetylide ligands.[20]

Our calculations confirmed that variation of the conjugation length of N^N ligands[24] versus C^N ligands[21,23,25] in Ir(III) complexes allows for tuning transition energies and transition strength for both linear and nonlinear absorption. Increasing the π-conjugation of the N^N ligand causes enhanced molar extinction coefficients of the absorption bands and a bathochromic shift of the lowest energy band, while induces a pronounced red-shift of the emission band and decreases the emission lifetime and quantum yield. [24] Gradually increasing the π-conjugation along the pyridine or pyrazine ring of the C^N ligands, the energies of the lowest singlet (S_1) and triplet (T_1) excited states are significantly reduced.[26] Additionally, our TDDFT calculations confirm that the natures of the S_1 and T_1 states vary with the increased π-conjugation of the C^N ligands, with the S_1 state changing from the exclusive ^{1}LLCT (ligand-to-ligand charge transfer)/^{1}MLCT transitions to the predominant highly mixed ^{1}ILCT/^{1}π,π*/^{1}MLCT/^{1}LLCT transitions. In addition to enhancement of non-linear absorption,[23,25] we also found that the naphthalimidyl substitution at the C^N ligand of Ir(III) complexes dramatically increases the triplet excited-state lifetimes and broadens the triplet excited-state absorption to the NIR region,[29] which is an important property for photovoltaic, applications.

We also studied new class of N_6-coordinated $[Ir(N^N)_3]^{3+}$ complexes, which are analogous to well-known $[Ru(N^N)_3]^{2+}$ dyes, but more challenging to synthesize, while benefiting from their water solubility. In comparison to their Ru(II) analogs, these Ir(III) complexes show blue-shifted UV-vis absorption and emission spectra with predominantly, ligand-localized π,π* character, in contrast to the dominant MLCT characters in the Ru(II) complexes. This leads to dramatically increased triplet lifetimes with much broader and stronger triplet excited-state absorption of $[Ir(N^N)_3]^{3+}$ dyes.[30]

Overall our calculations of optical properties of metal-organic complexes performed in the close collaboration with experimentalists have demonstrated practical realization of DFT predictions. It also helped us to understand which modifications of the Ir(III) dyes make them an optimal hole acceptor (or donor) in QD/dye composites, which are promising materials in photovoltaic and photocatalytic applications.

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Conference Presentations (supported by DE-SC008446)

Invited Talks at Conferences

08/2019 **ACS National Meeting,** COLL Division, Symposium on Nanoscience, San Diego, CA; *Effect of the Heterostructure on Charge Transfer Processes in PbSe/CdSe Janus Quantum Dots Functionalized by Ru(II) Dyes*.

07/2019 **TSRC Conference,** Symposium on Nanomaterials: Computations, Theory, and Experiment, Telluride, CO; *Controlling Charge Transfer in Nanostructures and their Interfaces* (a session chair).

10/2018 **Midwest Regional Meeting,** COMP and PHYS Division, Ames, IA; *Role of Surface Shell in Photoexcited Dynamics of PbSe and PbS Quantum Dots.*

08/2018 **ACS National Meeting,** COMP Division, Symposium on Photoexcited Processes, Boston, NY; *Impact of Binding Conformations on Charge Transfer in CdSe Quantum Dots Capped by N719 Dyes* (a session chair).

06/2018 **Excited State Properties (ESP) Conference,** Santa Fe, NM; *Charge Transfer in Nanocrystals Functionalized by Ru(II) Dyes* (a session chair).

05/2018 **Computational & Theoretical Chemistry Research PI Meeting,** Annapolis, MD; *Effect of Anionic Ligands and Functional Groups on Optical Transitions and Charge Transfer in Quantum Dots.*

04/2018 **Nano-World Conference,** San Francisco, CA; *Role of Anionic Surface Ligands in Photophysics of Quantum Dots* (a session chair).

10/2017 **NDSU-KU Joint Symposium** on Biotechnology, Nanomaterials, and Polymers, Fargo, ND; *Restricted Exciton Extent around Defect Governs Emission in Aryl Functionalized Carbon Nanotubes.*

07/2017 **TSRC Conference,** Symposium on Nonequilibrium Phenomena, Non-adiabatic Dynamics and Spectroscopy, Telluride, CO; *Comparing Contribution of Organic and Inorganic Surface Shells into Light-Driven Processes in Nanostructures.*

07/2017 **TSRC Conference,** Symposium on Nanomaterials: Computations, Theory, and Experiment. Telluride, CO; *Controlling Phonon-Mediated Photoexcited Processes via Shell Composition in IR-Emitting Quantum Dots* (a session chair).

06/2017 **ACS Grate Lake Regional Meeting,** Fargo, ND, *Exciton Dissipation in Core/Shell Nanocrystals* (a session chair).

05/2017 **Computational & Theoretical Chemistry Research PI Meeting,** Annapolis, MD; *Effect of Interactions between Quantum Dots and Their Passivating Shells on Radiative and Non-Radiative Processes.*

10/2016 **ACS Midwest Regional Meeting**, Manhattan, KS; *Role of Organic-Inorganic Interfaces in Photophysics of Nanostructures.*

07/2016 **4th International Conference on Chemical Bonding,** Kauai, Hawaii; *Bond Analysis and Electronic Properties of Functionalized Cyclosilanes* (a session chair).

07/2016 **TSRC Conference,** Symposium on Charge and Energy Transfer in Photoreactions and Photodynamics, Telluride, CO; *Charge Transfer and Phonon-Mediated Dynamics in Ru(II) Dye-Nanocrystal Composites* (a session chair).

07/2016 **TSRC Conference,** Symposium on *Non-Equilibrium Statistical Physics: from molecular materials to theoretical engineering,* Telluride, CO; *Light-Driven Processes in Semiconductor Nanostructures: Effect of their Surface Chemistry.*

06/2016 **Excited State (ES) Conference,** Albuquerque, NM; *Theoretical Insights into the Surface Chemistry and its Effect on the energy relaxation and dephasing processes in Nanomaterials.*

06/2016 **Excited State Properties (ESP) Conference,** Santa Fe, NM; *Surface Chemistry of Semiconductor Nanostructures: Theoretical Perspectives".*

03/2016 **ACS National Meeting**, PHYS Division, Symposium on Frontiers in Solar Light Harvesting Processes, San Diego, CA; *Role of Surface Ligands in Formation of PbSe Nanoplates and Their Photophysics.*

10/2015 **NDSU-KU Joint Symposium** on Biotechnology, Nanomaterials, and Polymers, Fargo, ND; *Quantum Dot to Quantum Dot Interactions: Ordered Self-Assembling and its Effect on Blinking and Energy Dissipation.*

07/2015 **TSRC Conference**, Symposium on Nanomaterials: Computations, Theory, and Experiment, Telluride, CO; *Contribution of Surface States to Energy Transfer and Energy Dissipation in Quantum Dots: Computational Insights* (a session chair).

04/2015 **Computational & Theoretical Chemistry Research PI Meeting,** Annapolis, MD; *Role of Surface in Photodynamics of Quantum Dots.*

04/2015 **MRS Spring Meeting**, Symposium on Interplay of Structure and Carrier Dynamics in Energy-Relevant Nanomaterials, San Francisco, CA; *Oxidation and Halide Passivation of PbSe Quantum Dots: Theoretical Insights.*

03/2015 **ACS National Meeting**, PHYS Division, Symposium on Modeling Excited States of Complex Systems, Denver, CO; *Energy Transfer in Closely Packed Si Quantum Dots: The Role of Surface Defects* (a session chair).

01/2015 **Energy Materials Nanotechnology (EMN) Annual Meeting** on Photovoltaics, Orlando, FL; *Role of Surface Ligands in Directed Assembly and Photophysics of Quantum Dots as Energy Materials*" (a session chair).

07/2014 **TSRC Conference**, Conference on Excited States and Time-Dependent Electronic Structure Theory, Telluride, CO; *First-Principles Simulations of Dissipation and Time-Resolved Emission in Nanosystems*" (a session chair and discussion leader)

06/2014 **Excited State Phenomena (ESP) Conference,** Santa Fe, NM; *Theoretical Insights into Oxidation of Quantum Dots.*

11/2013 **Russian American Scientific Association Annual Conference,** Tampa, FL; *Theoretical Insights into Surface Chemistry of Quantum Dots.*

02/2013 **International Conference on Electro/Information Technology,** Rapid City, SD; *First Principle Computations of Electronic Properties of Nanomaterials.*

04/2012 **ACS National Meeting,** COMP Division, Symposium on "Solar Energy and Solar Fuels", New Orleans, LA; *Theoretical Insights into Optoelectronic Properties of Quantum Dots Functionalized by Ru(II) Complexes.*

02/2013 **Sanibel Symposium,** St. Simon Island, GA; *Modeling of Phonon-mediated Dynamics in Semiconductor Nanosystems.*

11/2012 **Nanoporous Materials Genome Center Kick Off Meeting,** Minneapolis, MN; *DFT for Describing Electronic and Magnetic Properties of Organic-Based Magnets.*

11/2012 **21st Conference on Current Trends on Computational Chemistry,** Jackson, MS; *Non-Adiabatic Dynamics of Quantum Dots: The Role of Surface in Energy Dissipation.*

08/2012 **ACS National Meeting**, PHYS Division, Philadelphia, PA; *Electronic Structure and Absorption Spectra of CdSe Quantum Dots Functionalized by Ru(II)-polybipyridine Complexes.*

07/2012 **TSRC Conference,** Symposium on Nanomaterials: Theory and Computation, Telluride, CO; *Modeling of Photoexcitation in Ligated Quantum Dots.*

Invited Talks Research Institutions

11/2017 **University of North Dakota:** Seminar at Physics Department, Grant Forks, ND; *Role of Surface Chemistry an Interface in Photophysics of Quantum Dots.*

09/2017 **Pacific Lutheran University:** Seminar at Chemistry Department, Takoma, WA; *Focus on Sustainable and Nanoscale Materials and Materials Modeling.*

03/2017 **North Dakota State University:** Colloquium at Civil and Environmental Engineering, Fargo, ND; *Impact of Surface Chemistry on Energy Relaxation and Elastic and Inelastic Dephasing in Nanocrystals.*

02/2016 **University of Florida:** Colloquium at Chemistry Department, Quantum Theory Program (QTP), Gainesville, FL; *Brightening Nanostructures via Chemical Functionalization*.

03/2015 **Saint Louis University:** Colloquium at Physics Department, St. Louis, MO; *Chemical Functionalization of Nanomaterials for Improving their Dispersion and Optical Properties.*

11/2014 **North Dakota State University:** Presentation at Science Café, Fargo, ND; *Nanomaterials: History, Technological Potentials and Concerns.*

04/2014 **Concordia College**, Moorhead, MS; Invited lecture: *Nanomaterials for Solar Cells.*

01/2014 **University of Rochester,** Colloquium at Chemistry Department, Rochester, NY. *Charge versus Energy Transfer in Functionalized Quantum Dots*.

01/2014 **Argon National Lab,** Seminar at Center for Nanoscale Materials, Chicago, IL; *Simulations of Photoexcited Dynamics in Quantum Dots: Surface Effects.*

10/2013 **University of Rochester,** Colloquium at Chemistry Department, Rochester, NY; *Charge versus Energy Transfer in Functionalized Quantum Dots*.

11/2012 **University of Florida,** Colloquium at Chemistry Department, Gainesville, FL; *Role of Surface in Photoexcited Dynamics in Quantum Dots*.

10/2012 **University of Oregon,** Colloquium at Chemistry Department, Eugene, OR; *Morphology and Optical Response of Covalently and Non-covalently Functionalized Nanomaterials*.

09/2012 **Iowa State University,** Colloquium at Chemistry Department, Ames, IA; *Chemical Functionalization of Quantum Dots: Effects of Surface Ligands on Photoexcitation and Dissipation in Nanomaterials*.

09/2012 **Augustana College,** Seminar at Chemistry Department, Sioux Falls, SD; *Spectroscopic & Electronic Properties of Coordinated & Functionalized Cyclosilanes for formation Si-Nanostructures*.

08/2012 **Stepanov Institute of Physics, National Academy of Sciences of Belarus, and National Technical University of Belarus,** Joint seminar organized by Laboratory of Nanooptics, Minsk, Belarus; *Electronic Structure, Absorption Spectra, and Relaxation Dynamics of Functionalized Semiconductor Quantum Dots.*

Contributed Presentations from Students & Postdocs Distinguished by Awards

7/18/2019 **TSRC Conference**, Symposium on Nanomaterials: Computations, Theory, and Experiment. Telluride, CO

- Jabed Mohammed and Svetlana Kilina, *Conditions for Charge Transfer in CdSe Quantum Dots Functionalized by Metal-Organic Complexes* (contributed talk; Peter Salamon Award for Outstanding Young Scientists and NDSU College of Science and Mathematics Travel Award).

8/24/2019 **ACS National Meeting,** COMP Division, Symposium on Photoexcited Processes, Boston, NY;

- Levi Lystrom and Svetlana Kilina, *Influence of Chemical Composition on Relaxation rates of Electron/Hole Pair in* $(PbX)_{16}/(CdX)_{52}$*, (X = S, Se) Core/Shell Quantum Dots (NDSU College of Science and Mathematics Travel Award).*

2/18/2017 **Sanibel Symposium,** St. Simon Island, GA;

- Levi Lystrom and Svetlana Kilina, *DFT Insights into Mechanisms of Brightening of CdSe Quantum Dots by Hydrides* (poster, IBM Zerner Graduate Student Award).

6/12/2016 **Excited State Properties (ESP) Conference,** Santa Fe, NM;

- Levi Lystrom and Svetlana Kilina; *Brightening of CdSe Quantum Dots by Hydrides: Computational Insights* (poster, LANL Travel Award)

- Whitney Ong, Naveen Dandu, and Svetlana Kilina; *Oxidation of PbSe Quantum Dots: Insights from First-Principle Calculations* (poster, LANL Travel Award)
- Naveen Dandu and Svetlana Kilina; *Effect of Charge And Surface Defects on the Electronic Structure and optical Properties of CdSe and Silicon Quantum Dots* (poster, LANL Travel Award)

3/15/2016 **ACS National Meeting**, COMP Division, San Diego, CA;

- Naveen Dandu and Svetlana Kilina, *Deeper Understanding of Surface Chemistry of Particles Interactions in the Formation of Nanoplates and Nanocrystal Aggregate* (poster, NDSU College of Science and Mathematics Travel Award)
- Peng Cui and Svetlana Kilina, *Effect of Electronic Couplings on Charge Transfer Rates in $Cd_{33}Se_{33}$ Quantum Dots Functionalized by Ru(II) Complexes* (poster, NDSU College of Science and Mathematics Travel Award)
- Levi Lystrom and Svetlana Kilina, *DFT Insights into Mechanisms of Brightening of CdSe Quantum Dots by Hydride* (poster, NDSU College of Science and Mathematics Travel Award)
- Patrick Tamukong and Svetlana Kilina, *Ground State Properties and Nonadiabatic Dynamical Studies of $Pb_{16}X_{16}/Cd_{52}Y_{52}$ (X, Y = S, Se, Te) Core/Shell Quantum Dots* (poster, Red River Valley ACS Travel Award for Outstanding Yung Investigators)

7/4/2015 **TSRC Conference**, Nanomaterials: Computations, Theory, and Experiment. Telluride, CO

- Peng Cui and Svetlana Kilina, *Conditions for Charge Transfer in CdSe Quantum Dots Functionalized by Metal-Organic Complexes* (contributed talk; Peter Salamon Award for Outstanding Young Scientists and NDSU College of Science and Mathematics Travel Award).

8/10/2014 **ACS National Meeting,** COMP, San Francisco, CA;

- Naveen Dandu and Svetlana Kilina, *Role of Surface Defects in Electronic and Optical Properties of Silicon Quantum Dots* (poster, NDSU College of Science and Mathematics Travel Award).

3/16/2014 **ACS National Meeting,** COMP, Dallas, TX;

- Mary Hedrick and Svetlana Kilina, *Computational Study of Effect of Ligands on Photophysics of PbSe and ZnO Quantum Dots* (poster; ACS Red River Valley Travel Award for the Best Poster Presentation).

2/15/2013 **Sanibel Symposium,** St. Simon Island, GA;

- Mary Hedrick and Svetlana Kilina, *Computational Study of the Optoelectronic Properties of Quantum Dots Functionalized by Ru(II) Complexes* (poster; Dell-Intel-O'Brien Undergraduate Student Award and The Best Poster Presentation Award).

2/15/2013 **Los Alamos National Lab Student Symposium,** Los Alamos, NM;

- Christopher Olson and Svetlana Kilina, *DFT Modeling of the Nonlinear Optical Properties of Semiconductor Nanocrystals* (poster; The Best Poster Presentation Award).

ORGANIZED SCIENTIFIC SYMPOSIA

July 16-20, 2019	National Workshop at Telluride Science Research Center (TSRC), *"Nanomaterials: Computation, Theory, & Experiment"*, Telluride, CO.
Aug. 20-24, 2018	Symposium at National Meeting of American Chemical Society, COMP Division, "*Computational Photocatalysis: Photophysics and photochemistry at interfaces*", Boston, MA.
July 11-18, 2017	National Workshop at Telluride Science Research Center (TSRC), *"Nanomaterials: Computation, Theory, & Experiment"*, Telluride, CO.
June 27-30, 2017	Symposium at the ACS Great Lake Regional Meeting (GLRM) *"Photophysics and Photochemistry of Interfaces"*, Fargo, ND.
Dec. 15-20, 2015	Symposium at American Chemical Society PASIFICHEM, Physical, Theoretical & Computational Chemistry: *"Photocatalysis and Charge Transfer at Interfaces and Nanomaterials" (#344)*, Honolulu, HI.
June 29-30, 2015	National Workshop at Telluride Science Research Center (TSRC) on "*Nanomaterials: Theory, Computation, and Experiment".* Telluride Summer Research Center, Telluride, CO.
July 14-18, 2014	National Workshop at Telluride Science Research Center (TSRC) on *"Excited States and Time-Dependent Electronic Structure Theory"*, Telluride, CO.
Sept. 8-12, 2013	Symposium at National Meeting of American Chemical Society, COMP Division, "*Symposium on Computational Photocatalysis*", Indianapolis, IN.
June 26-29, 2013	National Workshop at Telluride Science Research Center (TSRC) on "*Advances in Photo-Reactions: When Spin-Orbit Coupling, Optical Excitation, and Nuclei Motion are of Equal Importance"*, Telluride, CO.
April 26-27, 2013	NDSU Symposium on "Excellence in Nurturing Undergraduate Research in Chemistry", NDSU, Fargo, ND.