

## Autobiography and Scientific History of Arthur J. Nozik

### 1936–1953

I was born on January 10, 1936, in Springfield, Massachusetts, the last of six children and separated in age from my youngest sibling by 8 years and from my oldest by 21 years. During the Russian Civil War of 1917–1922, my mother had made a sudden and dangerous departure in 1921, with only one night's preparation, from a small village named Glusk (now spelled Hlusk) in the southeastern part of what soon thereafter became the Soviet Union (now Belarus) to escape an impending pogrom by Cossacks loyal to the Russian Czar (the Whites) and engaged in the counter-revolutionary battle with the Bolsheviks (the Reds). Such pogroms against Jews were common in that period, as it was during the reign of the Russian Czars in previous centuries. My mother was warned of the impending pogrom by kind and compassionate neighbors; she left with her three young children on a 2 year's journey across Europe to emigrate to the safety of America and to meet up with my father who had departed Russia earlier and whose own father had already emigrated to Springfield in 1919 to earn money to bring his family to the United States.

The period of my birth was still one of national economic depression following the 1929 economic collapse and our family was quite poor; this situation was severely aggravated by the premature death of my father from tuberculosis in 1938 at age 46. Hearing about all these events as a young boy had a major early influence on my perspective of life, which is basically—be thankful today for what you have now; you never know what is around the corner, and it may be the Cossacks.

Our family situation resulted, in part for the practical reason that this allowed my mother some free time to work in the local war industry since the male work force was depleted, in my being enrolled in Hebrew school (called Chaydar) even before I was enrolled in kindergarten in public school. For nearly 10 years, attendance at public school was followed daily (and also on Saturdays and Sundays) by several hours of Hebrew school or prayer studying the Hebrew texts of the Torah (the Old Testament) and the Talmud (Jewish law and wisdom). But as a young boy I also developed an inherent and spontaneous interest in science and in questions about the nature of the universe; I distinctly remember being totally awed and fascinated by the dramatic news accounts in 1945 of the splitting of the atom and its application to the development of atomic energy but also disturbed by its initial use to destroy in singular events the cities of Hiroshima and Nagasaki, even though this brought a rapid end to World War II. In the ensuing years I came to doubt and ultimately turn away from the doctrines and dogma of “organized” religion. But I am grateful to my stern Hebrew school teachers (rebbe) who conveyed the passion, joy, and value of learning, of disciplined and difficult study, of asking and answering complicated questions, and for the psychological and emotional rewards and recognition one receives for achievement in intellectual pursuits. This is a Jewish tradition that in my opinion transcends religious faith.

I graduated from Classical High School in Springfield in 1953, and had already decided years prior to pursue the best possible higher education, not knowing or even worrying about how to finance this objective. Since age 14, I had worked in the summers in the tobacco fields of nearby Connecticut, at

various other jobs after high school classes, and during my final high school year had earned money driving and selling ice cream from an ice-cream truck; I also received several scholarships so that by the Fall of 1953 I had sufficient funds to at least begin college. Thus, I entered Cornell University in 1953 (it is amazing to recall that tuition was \$400 per semester)—in the chemical engineering program—then a 5 year course leading to a Bachelor's degree in chemical engineering. Although I had a long standing interest in basic chemistry and physics, I decided to study chemical engineering instead of chemistry or physics because I thought this would be a good combination of both disciplines and also because in the 1950s chemical engineering was considered a premier field for employment opportunities, it was experiencing a shortage of graduates, and it seemed I would have an abundance of good job offers upon graduation; it wasn't clear to me as a 17 year old whether the same would be true with a degree in either chemistry or physics.

### 1953–1967

Cornell was an exhilarating experience, but after the first 2 years, depleted savings and insufficient scholarship support forced me to interrupt my education. I took a leave of absence to earn additional money working as a junior scientist at the Monsanto Chemical Company complex in Springfield. Fortunately, my financial resources improved dramatically when I received a large private scholarship from generous Jewish philanthropists in Springfield, allowing me to return to Cornell after only a one semester break. Another enormous improvement in my life shortly thereafter was my marriage in 1958 to my lovely wife Rhoda, a devoted companion and dedicated supporter for the past 48 years; Rhoda landed a job as a research assistant in the laboratories of Hans Bethe, further enhancing our resources picture. Other famous scientists I encountered at Cornell either at seminars or in the classroom and who provided great stimulation were Peter Debye, Paul Flory, Harold Scheraga, Michael Sienko, and Ben Widom. I graduated from Cornell with a B.Ch.E. in June, 1959.

After graduation, I accepted a position doing engineering research on rocket propellants in the aerospace industry (Douglas Aircraft Company) in southern California. However, after only a short time I recognized clearly that I much preferred basic science to engineering and in 1960 enrolled in the Ph.D. program at Yale in physical chemistry. My research advisor was Richard Wolfgang, a nuclear chemist working on the kinetics of hot atom reactions. During my first year at Yale, Rhoda and I were happy to learn that Rhoda was pregnant, and a baby girl named Eva arrived in New Haven in 1961. I decided to again interrupt my educational path to work to support my family and left Yale in 1961 with an M.S. degree that was awarded the following year. I took a position as a chemical engineer at the Central Research Laboratories of the American Cyanamid Company (one of the large chemical companies of the day) in Stamford, Connecticut, working on a pilot plant project making melamine from urea. After 1 year I transferred to the Engineering Research Department to do more fundamental type of research on plasma jet chemistry and the kinetics of ammonia decomposition; the latter work resulted in my first scientific publication.<sup>1</sup>

After 3 years at Cyanamid I was fortunate to win a company scholarship that paid for the continuation of my graduate

education. I returned to Yale in 1964, but at that time Richard Wolfgang was in Boulder, Colorado (where ironically I moved to in 1978), establishing kinetics in interacting molecular beams as a primary research area at the University of Colorado. I therefore resumed my Ph.D. studies at Yale as the first graduate student of a new assistant professor, Morton Kaplan, who was working on Mössbauer spectroscopy (recoilless nuclear resonance fluorescence). The subject of my thesis was Mössbauer spectroscopy of divalent and trivalent iron and europium ions trapped in ice.<sup>2–5</sup> My office and lab was next to that of Lars Onsager, who later served on my thesis committee because of his current work explaining the conductivity of ice. His unusual personality led to many interesting and memorable stories, including how he forgot to show up at my thesis defense, and when told about this after my exam was completed, he came into the exam room and had me go through the defense for a second time; his way of hosting a visit to Yale by Paul Dirac was also quite amusing.

During my second period at Yale, Rhoda and I were again happy to welcome into the world my second daughter, Jane, born in New Haven in 1966 at the same Yale–New Haven hospital as Eva was, 4 years earlier. I graduated from Yale with a Ph.D. in Physical Chemistry in 1967. Thus, the most important personal events in life—marriage and the birth of children—all occurred while I was a student; somehow this seemed to be very appropriate.

### 1967–1975

Although I had no formal or legal obligation to do so, I returned to work for Cyanamid after graduation out of a sense of obligation and to express my gratitude for their critical support of my graduate studies. I introduced Mössbauer spectroscopy as a new analytical tool at Cyanamid and conducted research in the area of optical properties of semiconductors and applications to pigment technology; Cyanamid was a major producer of pigments and especially TiO<sub>2</sub>, which is the foremost white pigment. It was during this time that I learned about the extremely powerful photo-oxidizing power of illuminated TiO<sub>2</sub> that can essentially oxidize any chemical species on its surface; in 1972<sup>6</sup> I used Mössbauer spectroscopy to show that photo-excited TiO<sub>2</sub> could oxidize Fe<sup>+3</sup> to Fe<sup>+4</sup>, a reaction requiring a strong oxidizing redox potential >2.8 V (vs NHE). A few years later this background in TiO<sub>2</sub> photochemistry/photophysics led me into the field of photoelectrochemistry and photoelectrolysis, where photoexcited TiO<sub>2</sub> was shown to be able to photo-oxidize H<sub>2</sub>O to O<sub>2</sub> and thus opened the door to the possibility that H<sub>2</sub>O could be photolytically split into H<sub>2</sub> and O<sub>2</sub> by semiconductors. This was a very important new realization because the first energy crisis of 1973–1974 was about to paralyze the U.S. and this new approach to solar energy conversion and solar hydrogen production offered a potential solution (and it still does). More about this is discussed further below.

At Cyanamid I also used Mössbauer spectroscopy to study new magnetic semiconductors (Fe<sub>1–x</sub>Cu<sub>x</sub>Cr<sub>2</sub>S<sub>4</sub>) and new magnetic materials for information storage (Fe<sub>4</sub>N).<sup>7,8</sup> I also discovered a new defect oxide semiconductor, Cd<sub>2</sub>SnO<sub>4</sub>, which has outstanding properties as a transparent conductor.<sup>9</sup> I received several patents for this discovery and its applications, and Cd<sub>2</sub>SnO<sub>4</sub> is currently being used in CdTe-based solar cells as the best transparent conductor for this commercially produced photovoltaic cell.

A very fortunate result of my stay at Cyanamid was my meeting and befriending Ferd Williams, a brilliant, very creative condensed matter physicist who was actually trained as a

chemist. Ferd was a frequent consultant and a well-known theorist in the field of solid state luminescence; he was Chair of the Physics Department at the University of Delaware and Editor-in-Chief of the *Journal of Luminescence*. Ferd was my first and only mentor and a wonderful human being—we developed a long and continuing productive collaboration even as I moved on after 1975 to two other laboratories.

At Cyanamid I also befriended Satyen Deb, who had discovered electrochromism in WO<sub>3</sub>, which is currently being commercialized as a “smart” window for energy conservation, and who subsequently moved to Colorado in 1978, as I did, to join the newly created Solar Energy Research Institute. Satyen became the Director of the Basic Sciences Center where I presently reside.

In 1973–1974, the world experienced its first energy crisis. At the same time a new Materials Research Center was established by Jack Gilman, a well-known materials scientist from the University of Illinois, at the Allied Chemical Corporation campus in Morristown, New Jersey. The famous letter in *Nature* by Fujishima and Honda<sup>10</sup> had just appeared in 1972 that claimed TiO<sub>2</sub> could photolytically split water into H<sub>2</sub> and O<sub>2</sub> (a process later termed photoelectrolysis), and in 1973 this paper stimulated a tremendous amount of interest in this possibility and in the general area of semiconductor–electrolyte interfaces for solar energy conversion—a field called photoelectrochemistry. Jack Gilman was open to beginning research in this area and I joined the Materials Science Center at Allied in 1974 to lead the effort.

### 1975–1979

In 1975, after a few months at Allied, I published a paper in *Nature*<sup>11</sup> on the photoelectrolysis of water using a TiO<sub>2</sub> semiconductor anode that was one of the first publications that followed the 1972 Fujishima and Honda paper; I showed for the first time that an external bias voltage (0.3 V) was required to split water with near-UV (375 nm) light using semiconducting TiO<sub>2</sub> photoelectrodes; thus, the system exhibited “photo-assisted electrolysis”. The original Fujishima and Honda paper implied that no bias was necessary. (They actually had an internal bias present in the form of a large pH difference between the anodic and the cathodic compartments.) The required bias of 0.3 V was still much less than the bias required in the dark (1.6–1.8 V) using catalytic metal electrodes like platinum. However, in 1976, I showed for the first time that the external bias could be eliminated if two semiconductor photoelectrodes were used as the anode and cathode in a photoelectrolysis cell.<sup>12</sup> The two semiconductors that I used were n-type TiO<sub>2</sub> and p-type GaP. With this system, water could be decomposed with sunlight at about 0.5% efficiency without the need for any external voltage source. The system was shown to be an inorganic analog to the mechanism of biological photosynthesis, in that there are two photosystems each absorbing one photon to produce one separated electron–hole pair with an enhanced photopotential and where one electron–hole pair is lost through recombination. The n-type semiconductor electrode is analogous to Photosystem II, and the p-type semiconductor electrode to Photosystem I. A highlight of this period was a visit to my lab by Margaret Thatcher, a chemist by training but then the leader of the British Conservative Party and Prime Minister to be, to see a demonstration of photoelectrolysis as a potential answer to the troubling energy crisis of that time.

In 1976, I also conceived of the “photochemical diode”, which is a monolithic semiconductor structure that can spontaneously photolytically split water and drive other chemical reactions

upon simple immersion in the appropriate solution and illumination with light of an appropriate wavelength matched to the bandgaps of the semiconductors.<sup>13</sup> Photochemical diodes were the forerunners of the colloidal semiconductor photoconversion systems in use and under development today for photodetoxification/photopurification applications based on particulate TiO<sub>2</sub> photocatalysts as well as the high-efficiency multigap tandem structures for photolytic water splitting. Several patents were issued for this discovery. In 1978, I hired C. R. (Bob) Dickson from Richard Zare's lab at Columbia to work with me and we soon demonstrated for the first time the photoreduction of dinitrogen with visible light using a p-type semiconductor electrode.<sup>14</sup> Ferd Williams continued to collaborate with me while at Allied, and in 1978 we were the first to propose the possibility of hot electron photoinjection processes at semiconductor–molecule interfaces.<sup>15–18</sup>

### 1979–Present

In 1977 President Jimmy Carter signed legislation to establish the Solar Energy Research Institute (SERI), a new Department of Energy (DOE) Laboratory, in Golden, Colorado. This new institute interested me very much since I had been working on scientific issues related to solar energy for 4 years, and I decided in 1978 to join it to continue working on novel approaches to solar photon conversion, including hot electron processes. The early days at SERI were quite turbulent—it was a new DOE lab starting from scratch, and the staff grew from 0 to 1200 persons in less than 3 years. However, its growth was abruptly halted by the election of President Reagan in 1980, and the staff shrank to about 450. But the work in basic energy science, funded by the DOE Office of Basic Energy Sciences, was relatively unaffected, and excellent progress was maintained, even as further ups and downs for SERI occurred because of political forces at work in the area of solar and renewable energy.

In 1979, I hired electrochemist John A. Turner, a Fred Anson student from Cal Tech, and Gerry Cooper, a masters degree student from Colorado State, to work with me in photoelectrochemical energy conversion; I was appointed Branch Chief of the Photoconversion Branch in 1980, which encompassed the research of about 25 scientists in photoelectrochemistry, photochemistry, photobiology, and synthesis and catalysis. At SERI I also continued my collaborations with Ferd Williams, and in 1980 Ferd and I, together with Daryl Boudreaux, a theorist from Allied, were the first to propose the idea that in quantized semiconductors the cooling time might be increased due to reduced electron–phonon coupling (now called a phonon bottleneck) and that the slowed hot electron cooling would favor hot electron transfer;<sup>17,18</sup> the quantization in our analysis was the result of carrier confinement in the space charge layer of heavily doped semiconductors. I also teamed with Robert Ross from Ohio State University, who had done early groundbreaking work on the thermodynamics of biological photosynthesis with Melvin Calvin at Berkeley, and in 1982 we showed through a thermodynamic analysis<sup>19</sup> of hot carrier photoprocesses in illuminated semiconductor junctions that the maximum theoretical conversion efficiency could be more than doubled from the 32% limit established by Shockley and Queisser in 1960 to 66%. Setting out to achieve and demonstrate this theoretical result in various configurations using photoactive semiconductor and molecular structures became a major aspect of my research from 1978 to the present day. This area of research has grown in recent years, and advanced concepts for exceeding the Shockley–Queisser limit of 32% by such effects

as hot electron injection and other approaches are now labeled Third Generation Solar Photon Conversion.<sup>20,21</sup> In 1982–1983 Turner, Cooper, and I, along with Bruce Parkinson who had recently joined SERI, demonstrated the first hot electron injection processes from illuminated semiconductors (InP) into strongly negative supra-band-edge molecular redox acceptors in an electrolyte.<sup>22,23</sup>

In 1982, I also had the good fortune to team up with Olga Mičić, an outstanding chemist at the Boris Kidric Institute in Belgrade, who collaborated with SERI under the Joint U.S.–Yugoslavia Research Program, to conduct research on small semiconductor particles that could exhibit quantization effects. In 1984, Ferd and I were among the first to propose quantization effects in small semiconductor nanoparticles,<sup>18</sup> and in 1985 we, together with Olga and Tijana Rajh (a student of Olga's now at Argonne National Laboratory), experimentally verified quantization effects in small colloidal semiconductor particles (now called semiconductor quantum dots or nanocrystals).<sup>24</sup> Our experimental paper on this topic was the first one published in the *Journal of Physical Chemistry*<sup>24</sup> dealing with semiconductor nanocrystals. Subsequently, this has been followed by a continuing series of papers by myself, Olga Mičić, and various other colleagues at SERI on nanocrystals and quantum dots,<sup>25–54</sup> and this area currently represents a major research field in physical chemistry, materials science, and solid state physics. In 1990, SERI was designated a National Laboratory of the Department of Energy by President George H. W. Bush and renamed the National Renewable Energy Laboratory (NREL).

Sadly, I suffered a great loss of my two closest collaborators discussed above: In 1985, Ferd Williams died suddenly at age 63 while playing tennis during the afternoon break at a Gordon Conference on solid state physics, and Olga Mičić died recently in April, 2006, from complications due to cancer.

For hot electron transfer to occur from semiconductors to redox molecules in solution, it is necessary that the rate of hot electron cooling in the semiconductor be comparable to or slower than the rate of electron transfer across the semiconductor–solution interface. Therefore, my colleagues and I set out in 1988 to measure both the hot electron cooling rate, first in bulk semiconductors, superlattices, and quantum wells (1988–1995), and more recently in quantum dots (2001–present), and also the electron transfer rate (1993–2001) to see if the latter can compete with the former.

The hot electron cooling rates in superlattices and quantum wells were measured using picosecond and femtosecond time-resolved transient photoluminescence (TRPL) spectroscopy to obtain photoluminescence (PL) spectra as a function of time. The TRPL measurements were obtained using either ultrafast (femtosecond) laser upconversion techniques or time-correlated single photon counting (picosecond to nanosecond). The ability to do these experiments evolved from a collaboration with Chung Tang at Cornell, an expert in nonlinear ultrafast spectroscopy, together with his graduate students Randy Ellingson, Wayne Peloch, and Dan Edelstein. Fortunately for NREL, Randy Ellingson became a postdoc at NREL after his graduation in 1993 and was responsible for building and setting up our own state-of-the-art capabilities in ultrafast time-resolved spectroscopy.

From time-resolved PL spectra, line-shape analyses could be performed to obtain the electron temperature as a function of time.<sup>55–58</sup> From these analyses a cooling curve for hot electrons could be generated, and a characteristic cooling time established. For bulk semiconductors (e.g., GaAs), the characteristic cooling time was found to within a few picoseconds. However, because



of our prediction in 1980 that in quantized semiconductors the cooling time should be increased due to reduced electron–phonon coupling, we began to study cooling dynamics in quantized systems.<sup>59–61</sup> The work was initially conducted, and a phonon bottleneck was confirmed based on TRPL experiments with semiconductor quantum wells (one-dimensional confinement) and superlattices (electronically coupled multiple quantum wells). It was found that the hot electron cooling time could be increased by up to 2 orders of magnitude (up to 500 ps) in GaAs/AlGaAs quantum wells or superlattices. However, it was found that this phonon bottle neck only appeared at very high photogenerated carrier densities, namely, above about  $5 \times 10^{18} \text{ cm}^{-3}$ . The explanation for this is that the slowed cooling is caused by a *hot* phonon bottleneck effect (hot phonons created by the high hot electron density keep the electrons hot via hot phonon absorption), and this process is enhanced in quantized semiconductors because of phonon confinement.<sup>62</sup> However, the carrier density required to achieve slowed hot electron cooling corresponds to solar concentrations of several thousand suns and is therefore not practical for solar energy conversion. However, in 1997, I anticipated that with three-dimensional confinement in semiconductor nanocrystals hot electron cooling could be slowed even at low light intensity (i.e., one sun).<sup>62,63</sup> This idea led Olga and me to begin a program to synthesize and study a variety of semiconductor quantum dots for this purpose.

Knowledge of the electron transfer (ET) rate across semiconductor–molecule interfaces is needed to determine how slow the hot electron cooling rate must be to permit significant hot electron transfer. At NREL my colleagues and I conducted both extensive experimental and theoretical work on this critical and relatively unexplored scientific issue.<sup>63–80</sup> The experimental work involved measurements of the photoinduced minority electron transfer rate from p-type semiconductors using fast transient PL spectroscopy; postdoc Yossi Rosenwaks made extensive and critical contributions to these studies. This experiment is based on the quenching of the PL decay characteristic produced by electron transfer. Analysis of the PL decay with and without the redox acceptor yields information on the rate of ET. Success in this experiment requires passivation of the semiconductor surface to avoid domination of the PL decay by surface recombination. Extraction of the ET rate constant, especially with electric fields present, also requires a complicated analysis of the PL decay involving solution of the Poisson and continuity equations. There are no analytical solutions to this problem with field terms present, and a very extensive modeling and computation effort was undertaken. The presence of hot electron effects also necessitated the use of Monte Carlo calculations to take care of nonequilibrium of the electron transport. These calculations were successfully applied to a semiconductor–molecule interface consisting of p-GaAs (passivated with sulfide) in contact with cobaltocenium acceptor molecules in acetonitrile. The characteristic time for electron transfer was found to be a few picoseconds or less.

Another system that was investigated in these studies was p-GaAs passivated with a thin layer of GaInP<sub>2</sub> in contact with either cobaltocenium or ferrocenium.<sup>68</sup> This system produced nearly ideal behavior in photoelectrochemical cells and showed the theoretically expected concentration dependence, which is very rarely seen at semiconductor–liquid junctions.

Another important method to measure ET rate constants is to do the experiments with majority electrons in n-type semiconductors in the dark. The technique uses electrochemical impedance spectroscopy and current–voltage measurements.

These experiments were performed with n-GaAs in contact with cobaltocenium acceptors in acetonitrile.<sup>77,78</sup> The impedance of the system was measured as a function of frequency from 1 Hz to 1 MHz. The resulting impedance plane plots of the imaginary part of the impedance versus the real part produced ideal single semicircles. These data, together with quartz crystal microbalance (QCM) measurements made by a postdoc Don Selmarten, showed for the first time that ultrafast ET was occurring in this system and that this was due in large part to adsorption of the cobaltocenium acceptor on the GaAs surface. This was an unexpected result since metallocenes had always been believed to be classical outer-sphere, nonadsorbing redox species. The characteristic ET times were in the sub-picosecond to several picosecond range. These ET rates were thus found to be competitive with hot electron cooling rates and led to the conclusion that hot ET is indeed feasible.

In 1995, Barton Smith, a theorist postdoc, joined NREL and initiated theoretical studies of ET dynamics at semiconductor–liquid interfaces. An extremely ambitious approach was undertaken that invokes a very high-level theory using first principles molecular dynamics and model Hamiltonians to solve the quantum mechanics of the coupled total system comprising the semiconductor, the redox molecules, and the solvent. This approach was never attempted previously and required simultaneous consideration of the electronic band structure of the semiconductor, the electronic structure of the redox acceptor molecules, the electronic coupling between the semiconductor and the electron-acceptor molecule, and the solvation dynamics. Solution of the wave functions for this problem yields the ET rate constant, the energetics of the interfacial chemistry, the molecular structure and geometry of molecules at the interface, the adsorption characteristics, and a complete time–energy–molecular configuration profile of the ET process. The results of these calculations were been presented in a series of papers beginning in 1996.<sup>62,71–73,78,80,81</sup>

In addition to the study of the ET dynamics from semiconductors to redox acceptors, our group at NREL collaborated with Tim Lian of Emory University to conduct studies of ET from photoexcited dye molecules adsorbed on semiconductor surfaces to the semiconductor conduction band (i.e., the dye-sensitized nanocrystalline (Grätzel) solar cell).<sup>75,76,79</sup> The technique used was time-resolved transient absorption spectroscopy in the mid-IR region. This technique probes the arrival of injected electrons into the conduction band by virtue of the IR absorption of conduction band electrons and thereby avoids complications in other methods where the oxidized or excited dye state is monitored. For the system of nanocrystalline TiO<sub>2</sub> with an adsorbed Ru–bipyridyl-dicarboxyl-thiocyanate complex (the famous N3 dye of the Grätzel cell), the injection time was found to be less than 50 fs. This time scale means that hot electron injection occurs from hot dye molecules.

Olga Mićić and I studied the fundamental properties of group III–V colloidal semiconductor quantum dots (QDs) from 1991 to 2006, and together with various postdocs and NREL colleagues synthesized for the first time high-quality colloidal GaN, InP, GaP, and GaInP<sub>2</sub> quantum dots, and greatly improved the synthesis of GaAs colloidal quantum dots. The bulk of the work in the literature on QDs has been with group II–VI semiconductors; group III–V QDs are much more difficult to prepare since the synthesis requires nonaqueous and air-free environments. It was found that InP QDs can be treated to completely eliminate surface recombination, resulting in quantum yields for PL emission at the band edge (no red shift) of 60% at liquid He temperatures and 30% at 300 K. The colloidal

quantum dots could also be “crystallized” from solution to form ordered arrays of quantum dots, which are expected to be the three-dimensional equivalent of semiconductor superlattices. Strong electronic coupling between the QDs is expected to result in miniband formation and good electrical transport. A new theoretical approach to electronic coupling in QD arrays was published by Barton Smith and myself in 2001.<sup>81</sup> A new effect that was also found from the work of postdocs Ehud Poles and Don Selmarten was efficient anti-Stokes photoluminescence (upconversion) in a variety of QDs.<sup>44</sup>

In 2001, research to explore the predicted slowed cooling of high-energy (i.e., hot) electrons in QDs even at low light intensities (the phonon bottleneck) was initiated; this research, conducted with Randy Ellingson taking the lead, benefited enormously from the efforts of one of my graduate students from the University of Colorado, Jeff Blackburn.<sup>51,53,62,82,83</sup> Femtosecond pump–probe transient absorption experiments were performed on InP QDs to determine the cooling dynamics under various conditions. It was found that the cooling of hot electrons photogenerated in higher electronic states of the QD could be slowed to 3–7 ps if the photogenerated holes are rapidly removed by fast charge transfer to efficient hole traps at the QD surface; this idea was first proposed by Philippe Guyot-Sionnest at the University of Chicago and advanced further by Victor Klimov at Los Alamos National Laboratory. We found that if the electron and hole are confined to the QD core by passivating the InP surface with HF and eliminating hole traps, then the hot electron cooling time is 350–450 fs, at least an order of magnitude faster than that for the case where the holes are removed. This indicates that Auger cooling, which can break the phonon bottleneck, can be blocked to re-establish the phonon bottleneck. This was an encouraging result for the prospects of utilizing hot electrons to enhance conversion efficiency.

Cooling dynamics studies were also conducted on free electrons injected into InP QDs from an external reducing agent with a redox potential above the InP conduction band;<sup>53,82</sup> this experiment was also based on previous work by Guyot-Sionnest. In this case, holes are always absent from the QDs. The transient absorption was done by pumping the free injected electrons with an IR pulse to higher energies and probing (with band gap excitation) the time for the electrons to relax to the bottom of the conduction band. The cooling times were also found to be much longer (3–4 ps) than those when electrons and holes are simultaneously generated upon photoexcitation of the QDs (350 fs).

Collaborations under a U.S.–Israel Binational Science Foundation project with Efrat Lifshitz of the Technion in Haifa and with Tijana Rajh and Marion Thurnauer at Argonne led to a new approaches to determine the defect chemistry at the surface and in the core of InP QDs as a function of photoexcitation and QD history.<sup>49,50</sup> These techniques were electron paramagnetic resonance (in collaboration with T. Rajh and M. Thurnauer at Argonne)<sup>49</sup> and optically detected magnetic resonance (in collaboration with E. Lifshitz);<sup>50</sup> Olga Micić also played a key role in these studies. These two powerful methods produced consistent results and allowed for the detailed determination of the chemical nature of QD surface and core defects, which play a major role in the optical and electrical properties of QDs.

An unusual spectroscopic anomaly was found during a collaboration with Garry Rumbles during his sabbatical visit to the NREL from Imperial College in that the photoluminescence excitation spectra of InP QDs did not always follow the absorption spectra.<sup>47</sup> This is a violation of Kasha’s rule as

applied to molecules and indicates that an unusual nonradiative channel can open up in QDs at high photon energies under certain conditions.

QD arrays that exhibit efficient electron transport (photoconductivity) through the array are important for applications of QDs in certain solar cell configurations. Barton Smith and I demonstrated theoretically that even in cases where the electronic coupling between two QDs is small, this level of coupling can nevertheless lead to dense miniband formation in a large array composed of dots held at comparable separation distances to the two dot case, and the phenomenon is directly analogous to the process of band formation in atomic systems as the system size grows larger.<sup>81</sup> All real world arrays are disordered to some extent, and this causes electronic state localization. Theoretical analyses show that the “dimensionality” of the array systems (characterized as linear, planar, or markedly three-dimensional QD configurations) can have a profound influence on the degree of state localization. (This is analogous to the well-known effects of dimensionality on localization in arrangements of atoms.) We found that the degree of localization dramatically influences transport since it can vary from hopping to extended state transport even in various energetic regions of the bands (band tails versus interiors). But we also found evidence that even in highly spatially disordered arrays it is still possible to have extended state “wormholes” for transport that span the entire array. Experimental verification<sup>84,85</sup> of photoconductivity and hence good electron mobility in QD arrays has been obtained using time-resolved THz spectroscopy through a collaboration with Charles Schmuttenmaer at Yale and his grad student Matt Beard (who subsequently joined NREL to apply THz spectroscopy to various fundamental problems), together with grad student Jim Murphy working at NREL.

In addition to colloidal group III–V QDs, my collaborators and I also investigated a host of other QD materials including II–VI compounds, HgI<sub>2</sub>, Cu<sub>2</sub>O, and layered metal chalcogenides as well as strain-induced GaAs QDs produced from GaAs quantum wells with InP stressor islands formed on the quantum well barrier by Stranski–Krastinow growth in a organometallic chemical vapor deposition reactor built and operated by Mark Hanna. For single strain-induced GaAs QDs produced by forming Stranski–Krastinow islands of InP on GaAs/AlGaAs quantum wells an unusual transient, two-color photoluminescence blinking was observed and reported based on work by postdoc Dietrich Bertram.

Finally, in very recent experiments my collaborators (Randy Ellingson, postdocs Matt Beard, Justin Johnson, and Kelly Knutsen, and grad students Jim Murphy and Pingrong Yu) and I have shown that very efficient formation of multiple excitons can be formed in PbSe, PbS, and PbTe quantum dots.<sup>86–88</sup> Quantum yields of 300% have been observed at photon energies 4 times the quantum dot band gap (HOMO–LUMO energy), indicating the formation of three excitons per photon. This exciting new result yields great promise for the possibility of increasing solar photon conversion efficiencies through the utilization of high-energy photons and hot charge carriers to produce additional electrical or chemical free energy (here in the form of multiple excitons from a single absorbed photon) rather than heat. This important result finally represents success after over 25 years of research that I conducted to utilize hot electrons and high-energy photons to produce enhanced solar photon conversion.

The formation of multiple electron–hole pairs per absorbed photon in photoexcited bulk semiconductors is a process that is known and explained by a mechanism called impact ioniza-

tion. In this process, an electron with kinetic energy greater than that of the semiconductor band gap can produce an additional electron–hole pair by scattering off an electron in the valence and promoting it across the band gap. However, impact ionization in bulk semiconductors cannot contribute to improving the efficiency of solar cells because impact ionization cannot occur until the photon energy is in the mid-UV region (4–5 eV) of the solar spectrum, where essentially no solar photons exist. This happens because of two reasons: (1) In bulk semiconductors crystal momentum must also be conserved in addition to the conservation of energy, and this requires the photoexcited electron to be created at high energy in the conduction band, and (2) the rate of impact ionization does not become competitive with the rate of hot electron cooling by phonon emission until the photon energy is also very high, typically in the UV (4–5 times the semiconductor band gap). Finally, even when impact ionization does occur in bulk material, the efficiency of the process is low (for example, a maximum quantum yield of approximately 130% in Si at photon energies of 5 eV).

However, in late 1997, I attended a seminar by Sasha Efros in which he proposed an explanation of the phenomenon of transient photoluminescence (PL blinking) in single quantum dots by an enhanced Auger process in QDs caused by strong Coulomb interactions in QDs. In this process when two photogenerated excitons are created in a single quantum dot, one exciton recombines nonradiatively and transfers the recombination energy to either the electron or the hole of the remaining exciton, producing a highly excited single exciton. It occurred to me that this is just the inverse of exciton multiplication by a highly excited single exciton and if the enhanced Coulomb coupling causes enhanced Auger processes, then exciton multiplication should also be enhanced since it is also an Auger-like process. Furthermore, we had found at NREL that in quantized systems the rate of electron relaxation through phonon emission can be greatly reduced because of the discrete character of the quantized energy levels; and the increased Coulomb interaction will increase the rate of exciton multiplication because the rate of Auger processes are increased by Coulomb interactions by the sixth power of the inverse quantum dot size. Furthermore, crystal momentum need not be conserved in QDs because momentum is not a good quantum number for QDs and only energy must be conserved. These effects mean that the onset (threshold) for exciton multiplication need only be 2 times the bandgap and that the process will be very efficient.

Therefore, in 2000, we began to search for efficient exciton multiplication in III–V QDs, such as InAs and InP, using as a probe transient absorption spectroscopy and photocurrent spectroscopy. While this search was on, we learned of the successful work by Richard Schaller and Victor Klimov at Los Alamos who found very efficient (220% quantum yield) exciton multiplication in PbSe QDs. This result was confirmed shortly at NREL, where we found a quantum yield of 300% (three excitons per photon) at approximately 4 times the QD bandgap for PbSe, PbS, and PbTe QDs. We also reported a threshold photon energy for multiple exciton generation (MEG) that was 2 times the quantum dot band gap, consistent with the expectation that only energy need be conserved in QDs.

To explain these results a collaboration with Sasha Efros and postdoc Andrew Shabaev at the Naval Research Laboratory resulted in a unique quantum mechanical theory for MEG that invokes a coherent superposition of multiple excitonic states,<sup>89</sup> meaning that multiple excitons are essentially created instantly upon absorption of the high-energy photons; this model also

explains the threshold energy for MEG at twice the QD band gap. However, alternative models for MEG have recently been proposed by Alex Zunger, Alberto Franceschetti, and J. M. An; Klimov, Schaller, and Agranovich; and Guy Allan. Further experimental and theoretical work is required before a widely and generally accepted mode for MEG will be established.

The next critical advance for QD solar cells based on MEG is to demonstrate quantum yields greater than one in the photocurrent of these cells; no reports of such quantum yield values have yet appeared in the literature. At NREL we are actively pursuing studies of QD solar cells with various configurations, such as QD-sensitized nanocrystalline TiO<sub>2</sub> cells, QDs dispersed in heterogeneous blends of electron- and hole-conducting phases, and electronically conducting QD arrays that form the i-region of a p–i–n PV cell structure. We are hopeful that this approach to Third Generation solar photon conversion will prove to be very fruitful and that solar energy conversion will make a major contribution to the world's global energy needs in the near future, and also alleviate the growing problem of global climate change.

In closing, I wish to again express my great appreciation to all of my colleagues and collaborators, most of whom have been mentioned above or are listed in the following pages, both at NREL and outside of NREL, for their critical contributions to the science that I have described. The importance and value of doing the kind of research that we have all been conducting over the past few decades on the basic science related to solar energy utilization is now finally beginning to receive widespread appreciation, recognition, and increased support. The issue of introducing renewable energy to moderate to a great extent our present near total reliance on (addiction to) fossil fuels represents an enormous challenge that must be met, and I am proud and happy to have made a contribution to this effort. And this contribution during my 28 year stay at SERI and NREL was only made possible by the absolutely steady and generous support of the Solar Photochemistry Program managed by Mary E. Gress since the early 1980s and before that by Dick Kandel, both at the Division of Chemical, Geothermal, and Biosciences of the DOE Office of Basic Energy Sciences.

I wish to also express my gratitude to the Guest Editors of this Festschrift, my NREL colleagues Mike Heben and Randy Ellingson. Both started at NREL as postdocs with me and subsequently became regular NREL staff. Early in his NREL career Mike Heben shifted his focus from photon conversion to carbon nanoscience, a field in which he has made many important contributions.

I would like to end this history by again expressing my deep love to my wife, Rhoda, and my children, Eva and Jane, for their rock-solid support over the many decades that I have been engaged in study and in scientific research.

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