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RPPR Final Report
as of 17-Aug-2018

Agency Code:

Proposal Number: 66695EL **Agreement Number: W911NF-15-1-0110**

INVESTIGATOR(S):

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Report Date: 30-Jun-2018 Date Received: 08-Aug-2018
Final Report for Period Beginning 31-Mar-2015 and Ending 30-Mar-2018

Title: Electronic Relaxation and Doping in Smal Gap Colloidal Quantum Dots

Begin Performance Period: 31-Mar-2015 **End Performance Period:** 30-Mar-2018
Report Term: 0-Other

Submitted By: Philippe Guyot-Sionnest Email: pgs@uchicago.edu
Phone: (773) 702-7461

STEM Degrees: 2 **STEM Participants:** 6

Major Goals: The major goal of the work is to advance the basic understanding of the infrared optical properties of colloidal quantum dot materials with a view towards applications for photodetection and emission. This is motivated by the need for fast, low cost, low power consumption IR sources and thermal infrared detection for military and civilian applications. While bolometers are getting cheaper, they have lower detectivity and slower response (<30Hz) than semiconductor detectors. With the present technology, semiconductor detector materials are expensive, grown by MBE, and suffer from Auger recombination, which degrades operation at room temperature. Cooled cameras are very expensive not only because of the requirement for cooling and the infrared optics but also because the active chips are expensive.
The use of colloidal quantum dots which may be deposited as thin films on silicon integrated read-out circuits is an alternative approach that could much reduce the cost fabrication. However, the performances of colloidal quantum dots in the infrared have barely started to be investigated.
There are many issues toward bringing such materials to a practical end product. The work funded is specifically about two topics: First understanding and ultimately controlling the carrier lifetimes, and in particular the exciton and Auger lifetimes. Second understanding and controlling the effect of surface modification on the doping level of the quantum dots. The systems that are investigated are primarily mercury and cadmium chalcogenides quantum dots.
For the first aim of the project, we focus on measurement of the mid-infrared photoluminescence of various quantum dots, the efficiency/lifetime/temperature/Auger effects, and the role of the environment/ligands/matrix,
For the second aim of the project, we focus on measurements of the doping concentrations, the sign of the dopant as a function of particle size, surface and environment.
Finally, we apply the knowledge gained on both aspects to the construction of mid-infrared photodetectors with improving performances.

Accomplishments: 1) Over the course of the grant, we very significantly improved the performance of HgTe CQD photodetector. We started with the first reported PV MIR device, with which background limited photodetection (BLIP) was achieved at 5 microns. Notably, that work at he beginning of the grant was started with only one undergraduate, John Roberts, working closely with the PI. John was a top physics undergrad at Chicago and he went on to the Stanford applied physics PhD program where he received the NDSAG fellowship. The work was then taken over completely by a new graduate student, Mr. Matt Ackerman, who was joined a year later by a Postdoc, Dr. Xin Tang. Over the next two years of their dedicated effort, they improved performances enormously, achieving at low temperature 45% EQE and 3x1011Jones. Even larger improvements were achieved at elevated temperatures, with 1010Jones at 220K. This was a benefit from our growing understanding of the doping process and the fabrication of better devices, using plasmonic and interference enhancement to collect more of the light in thin devices, compatible with the depletion layer width that can be achieved. They arrived at the conclusion that striving to make PV devices using electron and hole barriers was not a fruitful approach, even though the concept is typically used for organic PV. This is because the gap is so small in the mid-infrared that there are no likely barriers. Rather, they found success by using electron and hole doping , as in standard homojunctions. One particular finding was the possibility of cation exchange by Ag+ to achieve high concentration hole doping profile starting from the film surface or interfaces. The procedures they developed led to great improvements in the reliability of the device fabrication, with ~ 100% yield of rectifying devices and ~ 20% performance variability. As a result of the reliability of the process, substrates and overlayers could be varied systematically. They explored dielectric overlayers to increase the light collection efficiency as well as made plasmonic structures on the substrates for the same purpose. They provided imaging demonstrations using a scanning imaging system, and an NEDT of 14 mK was observed with a 1kH bandwidth, 200x200 microns detector, 5 micron cut-off, and F/1.3 at 90K. It is most exciting that these performances approach those of InSb single crystals, and that there are likely many more potential improvements. As a result of their excellent work, presentations to single-session conferences were both upgraded to contributed talks for Matt Ackerman at QD-2018 (June 2018) and Dr. Xin Tang at MIOMD-18 (October 2018).

2) We performed a broad range of studies on the other chalcogenides HgS and HgSe, exploring their intraband transitions as well as the effect of additional doping and we learned many interesting things.
a) We studied 4.5-7 nm diameter HgSe colloidal quantum dots and their core/shells. This work was carried out by Mr. Zhiyou Deng, who has since received his PhD and is currently working in a start-up company in the Boston area. The electron doping of HgSe CQDs gives rise to an intense intraband absorption at 5 microns for ~2 electrons/dot. Zhiyou Deng found that the transition also fluoresces and he explored for the first time the synthesis of a shell of CdS and CdSe on the HgSe quantum dots in order to enhance the fluorescence. He found that the shell growth could be performed with good control. However, upon the growth of the shell, he also observed that the doping was lost, and the dot reverted to the intrinsic undoped systems, with clear excitonic features and fluorescence around 2 microns and no longer an intraband absorption nor luminescence. We attributed this effect to the shell effectively lifting the quantum dots states above the environment Fermi level. He also discovered that when the dots were dried as a film, the intraband absorption and fluorescence partially recovered. Upon annealing, up to 200C, he found that core/shells were robust and that the 5 microns features increased in strength, and corresponded to a doping of ~ 1 electron per dot. Such films show a much more robust and much more intense intraband fluorescence compared to the original HgSe cores. They will form the basis for future work investigating the possibility of 5 micron stimulated emission.
b) We explored the synthesis and optical properties of HgS colloidal quantum dots. Using a fixed synthetic procedure, graduate student Mr. Guohua Shen was able to tune the dot size from 3 nm to 14 nm. Over this size range, he found that all the dots exhibited an intense intraband absorption. However the absorption energy tuned more weakly with size than we expected. Using sulfide exposure of the dots, from 3 to 7 nm, in solutions, we were able to remove the intraband absorption, and therefore calculate the doing level of the dots. It was found to be close to 2/dot across that size range. However for the larger dots, it was not possible to remove the electrons. Furthermore, for the larger dots, the intraband absorption took on a definitely Lorentzian lineshape at 10 microns, suggestive of homogeneous broadening. However the width, 300 cm-1, remained too large to be compatible with single electron transition. We therefore concluded that the large HgS quantum dots are heavily doped and that the collective excitation of the electrons results in a plasmon resonance. The effects evolves from a simple local field correction to the initial transition energy. This work showed how this smoothly leads to a collective surface plasmon resonance as the number of electrons is increased.
c) In order to understand the differences in doping of CQDs of the three mercury chalcogenides, HgTe, HgSe, and HgS, we performed electrochemical measurements as a function of sizea and surface processing. This work carried by graduate student Ms. Menglu Chen, put a solid basis for the rational discussion of the doping in terms of the absolute positions of the electronic states of the dots, in relation to the environmental Fermi level. She found out that, for the CQD as we synthesized them, the bulk valence bands are at− 5.85,− 5.50, and− 4.77 eV (±0.05 eV) for zinc-blend HgS, HgSe, HgTe, respectively, in the same order as the anions p-orbital energies. The electron Fermi level in ambient conditions is about -4.7eV, and Menglu could therefore explain the ease of electron doping for HgS and HgSe CQDs, even with significant confinement (conduction band at -5.25eV and -5.50eV respectively) and the difficulty for the HgTe (conduction band at -4.77eV).
d) Most of our work on HgTe CQD is using a synthesis that we developed in 2011. It is a simple scalable synthesis with cheap reagents, but it produces CQDs with some degree of aggregation that can render the processing more difficult. We therefore strived to develop a synthesis that would lead to more dispersed CQDs. This work was carried out by graduate student Mr. Guohua Shen. He discovered a new synthesis, using excess HgCl2 and a more reactive, non Hg-chelating, tellurium source, Trismethylsilyltelluride. With his new procedure, he produced very well dispersed HgTe colloids with a broad range of sizes. This new synthesis has allowed to explore

the further development of HgTe/CdX core shell materials, which is a work in preparation. It has also led to the highest mobility ever observed for simply drop-cast CQD films which retain their clear quantum confined states, also observable in the transport measurements by state-filling signatures, another work in preparation. It is also interesting that as synthesized, these HgTe CQDs are n-doped at least for large enough sizes (weaker confinement). This is attributed to the Hg-rich surface which lowers the conduction state energy, and verified by electrochemical measurements by Ms. Menglu Chen.

Training Opportunities: The grant trained several students.
Graduate students:
-Zhiyou Deng: developed synthetic skills. He learned elemental analysis technique. He travelled to the Gordon Conference on Nanocrystals as well as to the MRS meeting in Phoenix. He wrote a paper as first author. He graduated in Fall 2016 and is employed
-Guohua Shen: developed synthetic skills. He learned XPS analysis technique. He travelled to the Gordon Conference on Nanocrystals in 2016, 2018, to the MRS conference in Phoenix in 2017 and he wrote two papers as first author. He should be graduating in Fall 2018.
-Matt Ackerman: developed synthetic skills, device fabrication and detector characterization. He is the key student making 5 microns PV detectors. He published one paper as a first author and one paper as a second author. He gave a poster at the II-VI workshop in Chicago October 2017, and contributed talks at the MRS-Phoenix 2018 and QD-2018.
-Menglu Chen: developed electrochemical expertise, synthetic skills, detector characterization and low-temperature Hall and conduction measurements. She published a first author paper and is the lead co-author on two other papers in preparation. She travelled to the Gordon Conference on Nanocrystals in 2018 and to the MRS conference in Phoenix in 2017.
-Dr. Xin Tang: joined the group in June 2017. He developed further his skills at optical simulation, synthesis, device fabrication and characterization. Dr. Xin Tang is the lead expert in microfabrication, device modelling and characterization. He published one paper as first author and will travel to his first conference for a contributed talk at MIOMD 2018.
Undergraduates:
-John Roberts: (4th year) moved to Stanford Applied Physics PhD program in September 2016. He developed skills to set up pulsed diode lasers at 808nm and 1500 nm, and set-up a fast digital oscilloscope to acquire time of flight data in photoconductive devices. He developed Python codes to calculate the optical properties of a multilayer devices, thus simulating photovoltaic devices. He wrote labview programs to control several instruments and perform measurements in the lab.
-Zane Rossi (1st year) joined us this summer and he built on John's python code and developed a "Lumerical" simulation of the optical properties of the multilayer devices, with an optimization program to determine the best thicknesses of the various materials in order to optimize the light absorption and minimize the thickness of the active quantum dot layer.

RPPR Final Report
as of 17-Aug-2018

Results Dissemination: 9 papers acknowledging the grant were published
1. Thermal Imaging with Plasmon Resonance Enhanced HgTe Colloidal Quantum Dots Photovoltaic Devices, X Tang, MM Ackerman, P Guyot-Sionnest, ACS nano 2018
2. Recent Progresses in Mid Infrared Nanocrystal Optoelectronics, E Lhuillier, P Guyot-Sionnest, IEEE Journal of Selected Topics in Quantum Electronics 23 (5), 1-8 2017
3. Synthesis of Nonaggregating HgTe Colloidal Quantum Dots and the Emergence of Air-Stable n-Doping, G Shen, M Chen, P Guyot-Sionnest, The journal of physical chemistry letters 8 (10), 2224-2228
4. Reversible Electrochemistry of Mercury Chalcogenide Colloidal Quantum Dot Films, M Chen, P Guyot-Sionnest, ACS nano 11 (4), 4165-4173 2017
5. Mid-IR colloidal quantum dot detectors enhanced by optical nano-antennas, Y Yifat, M Ackerman, P Guyot-Sionnest, Applied Physics Letters 110 (4), 041106 2017
6. HgS and HgS/CdS colloidal quantum dots with infrared intraband transitions and emergence of a surface plasmon, G Shen, P Guyot-Sionnest, the Journal of Physical Chemistry C 120 (21), 11744-11753 2016
7. Intraband luminescence from HgSe/CdS core/shell quantum dots, Z Deng, P Guyot-Sionnest, ACS nano 10 (2), 2121-2127 2016
8. Mid-infrared photoluminescence of CdS and CdSe colloidal quantum dots, KS Jeong, P Guyot-Sionnest, ACS nano 10 (2), 2225-2231 2016
9. Background limited mid-infrared photodetection with photovoltaic HgTe colloidal quantum dots, P Guyot-Sionnest, JA Roberts, Applied Physics Letters 107 (25), 253104 2015

Conference presentations:
-Zhiyou Deng, contributed talk at MRS -Phoenix. April 2016.
-Guohua Shen, Zhiyou Deng, posters at the GRC-Nanocrystals, in Vermont. August 2016.
-Philippe Guyot-Sionnest, keynote lecture at the GRS-Nanocrystals, invited lecture at the following GRC. August 2016.
-Guohua Shen and Menglu Chen, posters at MRS-Phoenix, April 2017.
-Philippe Guyot-Sionnest, invited talk, Matt Ackerman, poster, II-VI workshop Chicago October 2017.
-Matt Ackerman, contributed talk, Philippe Guyot-Sionnest, invited talk, MRS-Phoenix, April 2018.
-Matt Ackerman, contributed talk QD-2018, Toronto June 2018
-Guohua Shen and Menglu Chen, posters GRC-nanocrystals, June 2018.

Honors and Awards: Matt Ackerman received the best presentation award at the MRS-Phoenix 2018 symposium in which he presented his paper. Symposium NM12 (Transitioning Quantum Dots from Benchtop to Industry)

Protocol Activity Status:

Technology Transfer: The group collaborated with Sivananthan Labs in 2014- June 2016. We provided HgTe quantum dot materials for their tests of IR cameras and we provided our knowledge on film processing. The results were very promising in the MWIR with 5 microns camera already achieving 100mK NEDT at 90K. The work highlighted the simplicity of the process where the device is simply obtained by dropcasting a solution of quantum dots on existing commercial ROICs followed by cross-linking with our recommended solution.
We collaborated with Voxtel in the context of the Wired Darpa program from June 2106 to Dec. 2017. We provided data on exciton lifetime, mobility, doping, diffusion length and ideas on the possible junction materials in photovoltaic devices based on the HgTe colloidal quantum dots. We explored the PV devices and that grant provided a major impetus for the present performances.

PARTICIPANTS:

Participant Type: PD/PI
Participant: Philippe Guyot-Sionnest
Person Months Worked: 8.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Zhiyou Deng
Person Months Worked: 8.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Guohua Shen
Person Months Worked: 15.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: menglu Chen
Person Months Worked: 15.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Matt Ackerman
Person Months Worked: 15.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Undergraduate Student
Participant: John Roberts
Person Months Worked: 3.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Undergraduate Student
Participant: Zane Rossi
Person Months Worked: 2.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)
Participant: Kwang Seob Jeong
Person Months Worked: 9.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)
Participant: Xin Tang
Person Months Worked: 6.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

ARTICLES:

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
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Date Submitted: Date Published: 6/30/18 8:00PM
Publication Location:
Article Title: Thermal Imaging with Plasmon Resonance Enhanced HgTe Colloidal Quantum Dot Photovoltaic Devices
Authors: Xin Tang, Matthew M. Ackerman, Philippe Guyot-Sionnest
Keywords: Colloidal quantum dot, infrared, HgTe, HgSe, self-doping, photoresponse
Abstract: Over the past few years, colloidal nanoparticles have started to be investigated for their optical properties in the midinfrared, past 3 μm. Research on detector application has led to background limited detection and fast video imaging at 5 μm. With further development, one could imagine that these new materials could vastly reduce the costs of infrared technology and this would lead to a trove of new applications for infrared imaging into our daily lives. This paper reviews the progress regarding the optical, transport, and photodetection properties of thin film based on these materials, and the three different ways by which infrared resonances have been realized with colloidal nanoparticles: interband absorption with small gap semiconductor quantum dots, intraband absorption in lightly doped quantum dots, and plasmonic resonances in heavily doped nanocrystals.
Distribution Statement: 1-Approved for public release; distribution is unlimited.
Acknowledged Federal Support: **N**

Award Information

Title: Electronic Relaxation and Doping in Small Gap Colloidal Quantum Dots

Contract Number: W911NF1510110

Period of Performance : Start: June 01 2015 **End:** April 2018

MAJOR GOALS:

The major goal of the work is to advance the basic understanding of the infrared optical properties of colloidal quantum dot materials with a view towards applications for photodetection and emission. This is motivated by the need for fast, low cost, low power consumption IR sources and thermal infrared detection for military and civilian applications. While bolometers are getting cheaper, they have lower detectivity and slower response (<30Hz) than semiconductor detectors. With the present technology, semiconductor detector materials are expensive, grown by MBE, and suffer from Auger recombination, which degrades operation at room temperature. Cooled cameras are very expensive not only because of the requirement for cooling and the infrared optics but also because the active chips are expensive.

The use of colloidal quantum dots which may be deposited as thin films on silicon integrated read-out circuits is an alternative approach that could much reduce the cost fabrication. However, the performances of colloidal quantum dots in the infrared have barely started to be investigated.

There are many issues toward bringing such materials to a practical end product. The work funded is specifically about two topics: First understanding and ultimately controlling the carrier lifetimes, and in particular the exciton and Auger lifetimes. Second understanding and controlling the effect of surface modification on the doping level of the quantum dots. The systems that are investigated are primarily mercury and cadmium chalcogenides quantum dots.

For the first aim of the project, we focused on measurement of the mid-infrared photoluminescence of various quantum dots, the efficiency/lifetime/temperature/Auger effects, and the role of the environment/ligands/matrix,

For the second aim of the project, we focused on measurements of the doping concentrations, the sign of the dopant as a function of particle size, surface and environment.

Finally, we applied the knowledge gained on both aspects to the construction of mid-infrared photodetectors with improving performances.

ACCOMPLISHMENTS:

1) Over the course of the grant, we very significantly improved the performance of HgTe CQD photodetector. We started with the first reported PV MIR device, with which background limited photodetection (BLIP) was achieved at 5 microns. Notably, that work at he beginning of the grant was started with only one undergraduate, John Roberts, working closely

with the PI. John was a top physics undergrad at Chicago and he went on to the Stanford applied physics PhD program where he received the NDSAG fellowship. The work was then taken over completely by a new graduate student, Mr. Matt Ackerman, who was joined a year later by a Postdoc, Dr. Xin Tang. Over the next two years of their dedicated effort, they improved performances enormously, achieving at low temperature 45% EQE and $3x10^{11}$Jones. Even larger improvements were achieved at elevated temperatures, with 10^{10}Jones at 220K. This was a benefit from our growing understanding of the doping process and the fabrication of better devices, using plasmonic and interference enhancement to collect more of the light in thin devices, compatible with the depletion layer width that can be achieved. They arrived at the conclusion that striving to make PV devices using electron and hole barriers was not a fruitful approach, even though the concept is typically used for organic PV. This is because the gap is so small in the mid-infrared that there are no likely barriers. Rather, they found success by using electron and hole doping , as in standard homojunctions. One particular finding was the possibility of cation exchange by Ag^+ to achieve high concentration hole doping profile starting from the film surface or interfaces. The procedures they developed led to great improvements in the reliability of the device fabrication, with ~ 100% yield of rectifying devices and ~ 20% performance variability. As a result of the reliability of the process, substrates and overlayers could be varied systematically. They explored dielectric overlayers to increase the light collection efficiency as well as made plasmonic structures on the substrates for the same purpose. They provided imaging demonstrations using a scanning imaging system, and an NEDT of 14 mK was observed with a 1kH bandwidth, 200x200 microns detector, 5 micron cut-off, and F/1.3 at 90K. It is most exciting that these performances approach those of InSb single crystals, and that there are likely many more potential improvements. As a result of their excellent work, presentations to single-session conferences were both upgraded to contributed talks for Matt Ackerman at QD-2018 (June 2018) and Dr. Xin Tang at MIOMD-18 (October 2018).

2) We performed a broad range of studies on the other chalcogenides CQD, HgS and HgSe, exploring their intraband transitions as well as the effect of additional doping.

a) We studied 4.5-7 nm diameter HgSe colloidal quantum dots and their core/shells. This work was carried out by Mr. Zhiyou Deng, who has since received his PhD and is currently working in a start-up company in the Boston area. The electron doping of HgSe CQDs gives rise to an intense intraband absorption at 5 microns for ~2 electrons/dot. Zhiyou Deng found that the transition also fluoresces and he explored for the first time the synthesis of a shell of CdS and CdSe on the HgSe quantum dots in order to enhance the fluorescence. He found that the shell growth could be performed with good control. However, upon the growth of the shell, he also observed that the doping was lost, and the dot reverted to the intrinsic undoped systems, with clear excitonic features and fluorescence around 2 microns and no longer an intraband absorption nor luminescence. We attributed this effect to the shell effectively lifting the quantum dots states above the environment Fermi level. He also discovered that when the dots were dried as a film, the intraband absorption and fluorescence partially recovered. Upon annealing, up to 200C, he found that core/shells were robust and that the 5 microns features increased in strength, and corresponded to a doping of ~ 1 electron per dot. Such films show a much more robust and much more intense intraband fluorescence compared to the original HgSe cores. They will form the basis for future work investigating the possibility of 5 micron stimulated emission.

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d) Most of our work on HgTe CQD is using a synthesis that we developed in 2011. It is a simple scalable synthesis with cheap reagents, but it produces CQDs with some degree of aggregation that can render the processing more difficult. We therefore strived to develop a synthesis that would lead to more dispersed CQDs. This work was carried out by graduate student Mr. Guohua Shen. He discovered a new synthesis, using excess $HgCl_2$ and a more reactive, non Hg-chelating, tellurium source, Trismethylsilyltelluride. With his new procedure, he produced very well dispersed HgTe colloids with a broad range of sizes. This new synthesis has allowed to explore the further development of HgTe/CdX core shell materials, which is a work in preparation. It has also led to the highest mobility ever observed for simply drop-cast CQD films which retain their clear quantum confined states, also observable in the transport measurements by state-filling signatures, another work in preparation. It is also interesting that as synthesized, these HgTe CQDs are n-doped at least for large enough sizes (weaker confinement). This was attributed to the Hg^{2+}-rich surface which lowers the conduction state energy, and it was verified by electrochemical measurements by Ms. Menglu Chen.

4) We explored the possibility of intraband emission in the less toxic Cadmium chalcogenides quantum dots. This work was carried out by Dr. Kwang Seob Jeong, who then

received a position of assistant professor at the prestigious Korea University in Seoul, where he has by now built a vigorous research program also on mid-IR CQD materials. While the CdX systems are not doped in ambient conditions, he found that a two-step photoexcitation, first a "photodoping" followed by a high energy intraband excitation, led to a measurable photoluminescence at 5 microns. It was found that the systems were very sensitive to air, such that upon photoexcitation, sulfide or selenide were oxidized to sulfonates or possibly selenate, and concurrently led to the strong increase of infrared vibrational features in the films. As this was concurrent with the rapid drop in photoluminescence, it was concluded that this was an effect of the photochemical creation of these new surface vibrations. Using core/shells of the CdSe quantum dots, the infrared photoluminescence could be enhanced. This work provides the impetus for looking for other wide gap CQD materials that could be used as mid-infrared materials via their intraband transitions.

TRAINING:

The grant trained several students.

Graduate students:

-Zhiyou Deng: developed synthetic skills. He learned elemental analysis technique. He travelled to the Gordon Conference on Nanocrystals as well as to the MRS meeting in Phoenix. He wrote a paper as first author. He graduated in Fall 2016 and is employed

-Guohua Shen: developed synthetic skills. He learned XPS analysis technique. He travelled to the Gordon Conference on Nanocrystals in 2016, 2018, to the MRS conference in Phoenix in 2017 and he wrote two papers as first author. He should be graduating in Fall 2018.

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-Menglu Chen: developed electrochemical expertise, synthetic skills, detector characterization and low-temperature Hall and conduction measurements. She published a first author paper and is the lead co-author on two other papers in preparation. She travelled to the Gordon Conference on Nanocrystals in 2018 and to the MRS conference in Phoenix in 2017.

-Dr. Xin Tang: joined the group in June 2017. He developed further his skills at optical simulation, synthesis, device fabrication and characterization. Dr. Xin Tang is the lead expert in microfabrication, device modelling and characterization. He published one paper as first author and will travel to his first conference for a contributed talk at MIOMD 2018.

Undergraduates:

-John Roberts: (4th year) moved to Stanford Applied Physics PhD program in September 2016. He developed skills to set up pulsed diode lasers at 808nm and 1500 nm, and set-up a fast digital oscilloscope to acquire time of flight data in photoconductive devices. He developed Python codes to calculate the optical properties of a multilayer devices, thus simulating photovoltaic devices. He wrote labview programs to control several instruments and perform measurements in the lab.

-Zane Rossi (1st year) joined us this summer and he built on John's python code and developed a "Lumerical" simulation of the optical properties of the multilayer devices, with an optimization program to determine the best thicknesses of the various materials in order to optimize the light absorption and minimize the thickness of the active quantum dot layer.

DISSEMINATION:

9 papers acknowledging the grant were published

1. ***Thermal Imaging with Plasmon Resonance Enhanced HgTe Colloidal Quantum Dots Photovoltaic Devices****, X Tang, MM Ackerman, P Guyot-Sionnest, ACS nano 2018*
2. ***Recent Progresses in Mid Infrared Nanocrystal Optoelectronics****, E Lhuillier, P Guyot-Sionnest, IEEE Journal of Selected Topics in Quantum Electronics 23 (5), 1-8 2017*
3. ***Synthesis of Nonaggregating HgTe Colloidal Quantum Dots and the Emergence of Air-Stable n-Doping****, G Shen, M Chen, P Guyot-Sionnest, The journal of physical chemistry letters 8 (10), 2224-2228*
4. ***Reversible Electrochemistry of Mercury Chalcogenide Colloidal Quantum Dot Films****, M Chen, P Guyot-Sionnest, ACS nano 11 (4), 4165-4173 2017*
5. ***Mid-IR colloidal quantum dot detectors enhanced by optical nano-antennas****, Y Yifat, M Ackerman, P Guyot-Sionnest, Applied Physics Letters 110 (4), 041106 2017*
6. ***HgS and HgS/CdS colloidal quantum dots with infrared intraband transitions and emergence of a surface plasmon****, G Shen, P Guyot-Sionnest, the Journal of Physical Chemistry C 120 (21), 11744-11753 2016*
7. ***Intraband luminescence from HgSe/CdS core/shell quantum dots****, Z Deng, P Guyot-Sionnest, ACS nano 10 (2), 2121-2127 2016*
8. ***Mid-infrared photoluminescence of CdS and CdSe colloidal quantum dots****, KS Jeong, P Guyot-Sionnest, ACS nano 10 (2), 2225-2231 2016*
9. ***Background limited mid-infrared photodetection with photovoltaic HgTe colloidal quantum dots****, P Guyot-Sionnest, JA Roberts, Applied Physics Letters 107 (25), 253104 2015*

Conference presentations:

-Zhiyou Deng, contributed talk at *MRS -Phoenix*. April 2016.

-Guohua Shen, Zhiyou Deng, posters at the *GRC-Nanocrystals*, in Vermont. August 2016.

-Philippe Guyot-Sionnest, *keynote lecture at the GRS-Nanocrystals, invited lecture at the following GRC.* August 2016.

-Guohua Shen and Menglu Chen, posters at *MRS-Phoenix*, April 2017.

-Philippe Guyot-Sionnest, invited talk, Matt Ackerman, poster, *II-VI workshop* Chicago October 2017.

-Matt Ackerman, contributed talk, Philippe Guyot-Sionnest, invited talk, *MRS-Phoenix*, April 2018.

-Matt Ackerman, contributed talk *QD-2018*, Toronto June 2018

-Guohua Shen and Menglu Chen, posters *GRC-nanocrystals*, June 2018.

TECH TRANSFER:

The group collaborated with Sivananthan Labs in 2014- June 2016. We provided HgTe quantum dot materials for their tests of IR cameras and we provided our knowledge on film processing. The results were very promising in the MWIR with 5 microns camera already achieving 100mK NEDT at 90K. The work highlighted the simplicity of the process where the device is simply obtained by dropcasting a solution of quantum dots on existing commercial ROICs followed by cross-linking with our recommended solution.

We collaborated with Voxtel in the context of the Wired Darpa program from June 2106 to Dec. 2017. We provided data on exciton lifetime, mobility, doping, diffusion length and ideas on the possible junction materials in photovoltaic devices based on the HgTe colloidal quantum dots. We explored the PV devices and that grant provided a major impetus for the present performances.