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Philippe Guyot-Sionnest

7. PERFORMING ORGANIZATION NAMES AND ADDRESSES
University of Chicago
5801 South Ellis Avenue

Chicago, IL 60637 -5418

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14. ABSTRACT
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energy consistent with the generic gap law. Direct evidence of energy transfer to the CH stretch and overtone vibrations is apparent when
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The grant focused on the Photoluminescence efficiency of HgTe colloidal quantum dots. The photoluminescence quantum yield of HgTe colloidal quantum dots was measured from 1800 to 6500 cm-1 . There is a steep drop at low
energy consistent with the generic gap law. Direct evidence of energy transfer to the CH stretch and overtone vibrations is apparent when temperature tunes the PL wavelength of a given sample through the vibrational resonances. Calculations based on the radiative rate and resonant energy transfer to the ligand vibrations appear to account for much of the quantum yield drop. Power dependent photoluminescence lifetime measurements on 3.7 nm particles show fast , ~50 ps, biexciton lifetime similar to other colloidal quantum dot systems of similar sizes. Various synthetic modifications have been explored to increase the PL or the size of the particles, modify the particle composition, with interesting observations but moderate improvements

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Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received		Paper
06/11/2015	7.00	E. Lhuillier, S. Keuleyan, H. Liu, P. Guyot-Sionnest. Mid-IR Colloidal Nanocrystals, Chemistry of Materials, (04 2013): 0. doi: 10.1021/cm303801s
08/28/2012	2.00	Sean Keuleyan, Emmanuel Lhuillier, Philippe Guyot-Sionnest. Synthesis of Colloidal HgTe Quantum Dots for Narrow Mid-IR Emission and Detection, Journal of the American Chemical Society, (10 2011): 0. doi: 10.1021/ja2079509
08/28/2012	1.00	Philippe Guyot-Sionnest, Emmanuel Lhuillier, Sean Keuleyan. Optical properties of HgTe colloidal quantum dots, Nanotechnology, (05 2012): 0. doi: 10.1088/0957-4484/23/17/175705

TOTAL: **3**

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Received Paper

TOTAL:

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Number of Presentations: 0.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received		Paper
06/11/2015	6.00	Emmanuel Lhuillier, Sean Keuleyan, Philippe Guyot-Sionnest. colloidal quantum dots for mid-IR applications, conference. 13-AUG-12, . : ,

TOTAL: **1**

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received		Paper
08/28/2012	4.00	P. Guyot-Sionnest, S. Keuleyan, H. Liu, E. Lhuillier. Colloidal quantum dots for mid-infrared detection, Quantum Sensing and Nanophotonic Devices IX. , San Francisco, California, USA. : ,
08/28/2012	5.00	Emmanuel Lhuillier, Sean Keuleyan, Philippe Guyot-Sionnest. Transport properties of mid-infrared colloidal quantum dot films, Quantum Dots and Nanostructures: Synthesis, Characterization, and Modeling IX. , San Francisco, California, USA. : ,

TOTAL: **2**

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received	Paper

TOTAL:

Number of Manuscripts:

Books

Received	Book

TOTAL:

Received	Book Chapter

TOTAL:

Patents Submitted

Patents Awarded

Awards

Graduate Students

NAME	PERCENT_SUPPORTED	Discipline
sean keuleyan	1.00	
FTE Equivalent:	**1.00**	
Total Number:	**1**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
guyot-sionnest	0.08	
FTE Equivalent:	**0.08**	
Total Number:	**1**	

Names of Under Graduate students supported

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john kohler	1.00	
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Names of Personnel receiving masters degrees

NAME
Total Number:

Names of personnel receiving PHDs

NAME	
Sean Keuleyan	
Total Number:	**1**

Names of other research staff

NAME	PERCENT_SUPPORTED
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Total Number:	

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

see attachment

Technology Transfer

I. INTRODUCTION

During this year, HgTe Colloidal Quantum Dots (CQD) have been explored for mid-infrared photoluminescence, in view of applying it to LEDs, lasers or negative luminescence devices. Colloidal nanomaterials are already actively researched for fluorescence in the visible and near-IR for applications such as biological labeling[1] and solar energy.[2] In these spectral ranges, they compete with small organic molecules and polymers. However, organic molecules cannot sustain mid-IR electronic transitions due to intramolecular vibrational relaxation and therefore colloidal inorganic nanomaterials are unique solution-processed electronic materials in the mid and long wave IR. The surface chemistry can be adapted via core/shell systems[3] to allow some control of the electronic surface properties in order to remove electron/hole traps. In the infrared, molecular vibrations of ligands can still quench the nanocrystals electronic transitions.[4] The removal or replacement of organic ligands with inorganic matrices allows now fully inorganic nanocrystals solids.[5] [6] From a device point of view, ohmic conductivity in monodispersed colloidal nanocrystal films was observed first nearly a decade ago, [7] field-effect transistors achieve ever increasing mobilities,[8] there are reports of high sensitivity photoconduction,[9] and photovoltaic performance is improving with already ~100% quantum efficiency.[2] The combination of quantum confinement, all inorganic structures and reasonable mobilities make CQD films very promising for IR devices.

II. MATERIALS CANDIDATES

Both HgSe and HgTe nanocrystals colloids had been reported in the literature, prior to our work, with evidence of strong confinement and near-IR gaps.[10] [11] [12] [13] [14] HgTe was better characterized as a colloidal quantum dot material. The initial "HgTe" nanocrystals emitting in the near IR were made by the partial replacement of Cd by Hg in CdTe nanocrystals.[15] The aqueous synthesis of such small HgCdTe by Rogach *et al* led to efficient near-IR luminescence up to 2 μm. Their emission lifetime, in the 50 ns range, was much faster than for PbSe at a similar wavelength, reflecting the larger oscillator strength (HgTe Kane parameter E_p ~ 18eV) and weaker dielectric screening. Pure HgTe affords the same optical advantage while allowing better control a priori. [16] Kovalenko *et al* introduced a synthetic method that led to a fairly clean band-edge up to 3 μm and PL tunable from 1.2 to ~3 microns.[17] The Kovalenko *et al* strategy involved a low temperature reaction in aqueous solution to form small dots, followed by Ostwald ripening in nonpolar solvent. The Te source was in-situ electrochemically generated H_2Te. This procedure could make dots with an IR gap only up to 3 microns and in low yield.

III. RESULTS

Over the past two years, we investigated the colloidal synthesis of HgTe.[18] HgTe nanocrystals are now synthesized with an absorption edge up to 5 microns and slightly beyond, and in good yield.

The HgTe nanocrystals fluoresce at their band edge[18] and in this grant period we focused mostly on understanding the factors controlling the PL efficiency. The photoluminescence quantum yield of HgTe colloidal quantum dots was measured from 1800 to 6500 cm^{-1} . For the QY determination, we used an integrating sphere for a sample emitting at 1600nm, and obtained a QY of 7%. The other samples were measured relative to this absolute determination. In fig.1, the PL QYs of HgTe CQDs is compared to values reported by Kovalenko et al. (ref. 19). These are approximately 5 times higher than our measurements at the same frequencies, which may be due to synthetic method or particle shape. The quantum yield of PbSe CQDs of several reports are also shown confirming that the trends are similar.

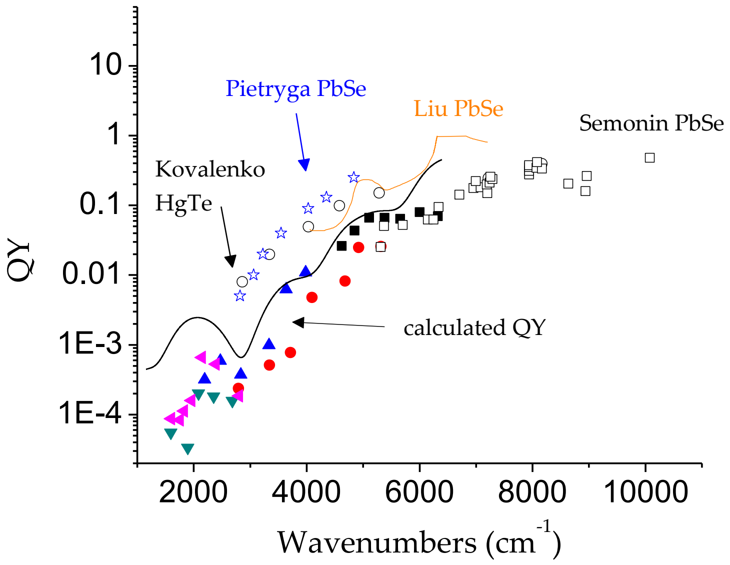


Figure 1: Quantum yield of HgTe samples in Tetrachloroethylene. Measured (solid symbols) and calculated room temperature solution PL QY (black solid line) ranging from the near-IR to beyond 5 µm. Also shown for comparison are values previously reported for HgTe and PbSe (open symbols). The orange solid line is the QY for PbSe previously calculated.

Similar to previous reports on infrared PL, the QY decreases sharply to smaller energies (larger particles).[19,20,] We observe a decrease of nearly an order of magnitude in QY every 1000 cm^{-1} between 5000 cm^{-1} and 2000 cm^{-1}. This is consistent with the generic gap law seen for visible and near-IR luminescent dyes and is attributed to energy conversion from the electronic to vibrational degrees of freedom. This usually relies on a specific electron-vibration coupling. With the extended wavefunctions of the dots, and the low frequency of their lattice vibrations, it seems unlikely that the energy relaxation be so effective. There is therefore the possibility of identifying other processes for the nonradiative decay.

PL Temperature Dependence

The temperature dependence of the PL is often a clue to the quenching mechanism. Typically, trapping processes are activated and the PL increases with lower temperature while energy transfer process will depend more specifically on the temperature dependence of the energy overlap. Low temperature PL measurements were made on films of nanocrystals. Films were prepared by precipitating a small amount of nanocrystals in TCE using methanol. The precipitate was dried and redispersed in chloroform, giving a clear, dark solution. This solution was filtered using a 0.2 µm pore filter and then spray coated onto a sapphire substrate. Spray-coating can give very uniform films up to at least 2 µm thick. The film on sapphire was then mounted in a closed-cycle helium cryostat with a CaF_2 window under vacuum and cooled.

Unlike Cd but similarly to Pb chalcogenides, HgTe exhibits a positive dependence of the bandgap on temperature, giving a red-shift of the PL on cooling. The red-shift of the absorption edge (and photoconductivity) and the size-dependence of the magnitude of the shift have been reported for HgTe CQD in the previous year. The PL shift with temperature is very large, covering about 800-1000 cm^{-1} and it allows to more directly probe the role of molecular vibrations in the quenching mechanism. The PL of HgTe CQDs of different sizes has therefore been measured over the temperature range of 3-300 K. Spectra for three sizes are shown in Fig.2. The changes in the PL intensity on cooling show no systematic effect of temperature, some showing increases, decreases or non-monotonous trends. In regions with weaker vibrational resonances (e.g. approx. 3300-4200 cm^{-1}) in Figure 4b the PL intensity does not change much as it shifts on cooling. However the spectra in figure 4a, and 4c, there is a clear dip associated with tuning through the CH stretch fundamental at 2850-2950 cm^{-1} and the CH stretch overtones around 6000 cm^{-1}. In particular, in fig 2a, near the C-H stretch absorption band, the samples show quenching much stronger and broader than can be attributed to reabsorption. Indeed, the film room-temperature transmission spectrum shows that the CH stretch reabsorption of the films is about 20% at the C-H peak and can only account for a sharp feature in the middle of the valley.

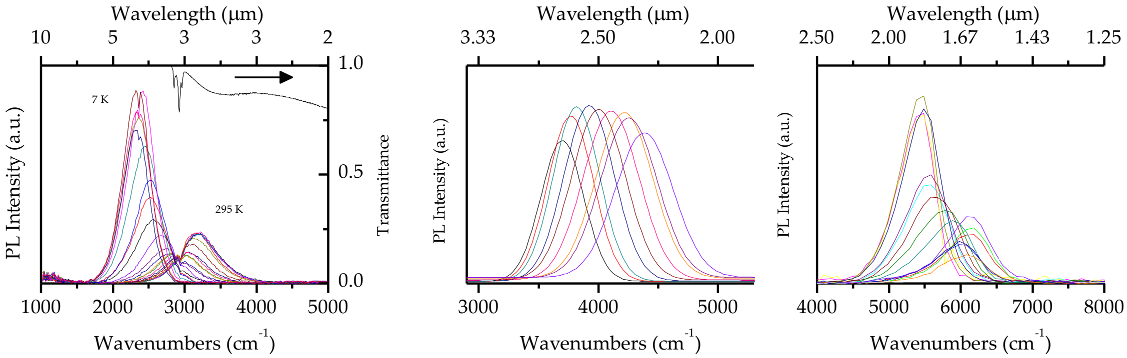


Figure 2: PL Spectra for 3 films of HgTe CQDs measured at temperatures between 300 and 7 K. (a) Through the resonance of the ligand C-H vibration band, there is a distinct valley. The transmittance of the sample is shown at the top-right for comparison to the valley near 2900 cm^{-1}. (b) Away from the resonances, the PL intensity is relatively temperature-independent. (c) Another valley is observed near the overtone of the C-H stretch band around 6000 cm^{-1}.

It is therefore clear that the ligand vibrations introduce some PL quenching. The mechanism could be some electron-vibration coupling, specific of the wavefunction leakage outside of the dots. However such mechanism is hard to model due to the lack of alternative measure of the coupling. There is a much more generic mechanisms that we introduced several years ago, which is the direct energy transfer, akin to Forster energy transfer, to the infrared absorbing vibrations. Such a mechanism can be calculated with no adjustable parameters, by knowing the coverage, the spectra and location of the IR absorbers. Using an effective shell of IR absorbing material of 1 nm, with imaginary optical constant representing the dodecanethiol ligands absorption, it is possible to simulate the QY. Fig. 1 shows that this parameter-free model seems to account for much of the overall PL drop. However, it predicts a greater QY above 2 microns and a somewhat larger PL drop right at the CH stretch. As described in the last section, much effort has been spent on reducing the ligand absorption. However, even a strong reduction of the CH absorbance using films processed with inorganic ligands or matrix, has yielded temperature dependent QY that are much flatter than in Fig 2a, but with a QY that has not improved yet. It is still a possibility that some other process quenches the PL, possibly interfacial states, or vibrations that are not readily observable if they have broad spectral resonances.

PL time resolved upconversion

In the previous grant, the Auger recombination rate was unknown for the HgTe colloidal dots and there was the possibility that the Auger rate would be much slower in the HgTe dots compared to the CdSe dots, due to the very low density of states, at least for the conduction band.

In this grant we performed time resolved PL upconversion as a function of the pump power to determine the biexciton Auger rate. Lifetime measurements were measured by up-conversion. A 1064 nm ~15ps 25 Hz Nd:YAG laser pulse was split into two paths. The first path included a delay stage and was used to excite the sample in a 1 cm fused silica cuvette. The second path was brought in line with the PL excitation but after the sample, recombining with a 45 degree 1064nm CaF_2 mirror, through a 14 mm long KTP nonlinear crystal that was angle tuned. This results in light being generated at the sum frequency. Narrow filters removed the 1064 nm and 532 nm and the sum frequency signal was then passed into a monochromator with a PMT at the output. The PMT allowed to detect the upconverted PL, typically a few detected photon/pulse. The delay between the PL excitation pulse and the upconversion pulse was limited to 350 ps due to a weak (< 1/100) satellite pulse.

These measurements are currently restricted to bluer samples by the PMT used to measure the sum frequency signal. All samples were measured under high and low excitation power. The slow time constant is about 100 times faster than the calculated radiative lifetime, suggesting a QY on the order of 1 %, which is roughly consistent with the data in for these wavelengths. However measurements with longer delay lines will be required to measure the lifetimes accurately. More interestingly, the samples exhibit a clear rise of a fast PL component at high pump power. As in other CQD systems, the high power fast time component is assigned to the biexciton decay rate. A "universal" trend has been proposed by Robel et *al*. where the biexciton lifetime (s) is given by $\tau = a 10^{10} R^3$ where R is the radius (cm) and a is a coefficient of order unity. For the two samples studied here here, 42 ps, R=3.5 nm, 3700 cm^{-1} a= 0.1 and 34 ps R=2.7 nm, 5000 cm^{-1} a=0.17. That the Auger rate is so fast even though the conduction band density of state is so sparse suggests that the positive trion, involving the heavy hole would be the dominant Auger recombination channel. This will need to be further investigated with measurements under electrochemical doping control. In particular, it will be important to determine if there is an advantage to choose electrons over holes as the majority carriers. Attempts at generating stimulated emission by optical pumping failed, presumably due the fast Auger recombination.

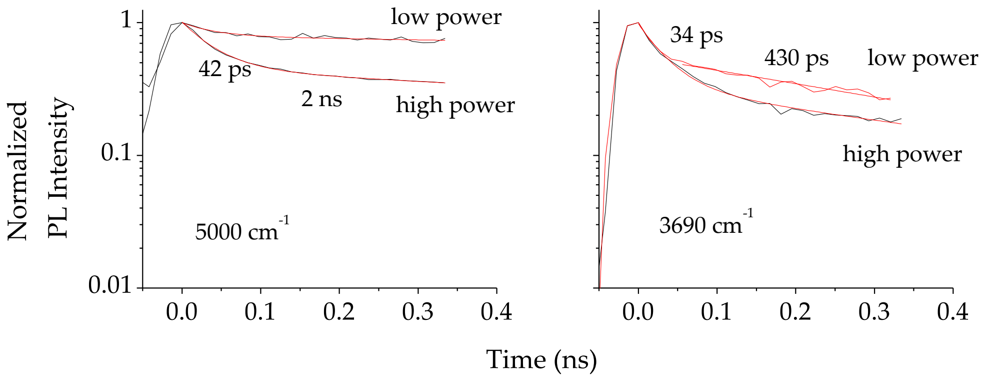
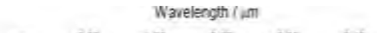


Figure 3. Time-resolved measurement of the PL decay for two solutions of HgTe CQDs emitting near 3690 cm^{-1} and 5000 cm^{-1}. Black lines are the measured intensity, red lines are biexponential fits with the labeled time constants. Over the small range of sizes measured the Auger biexciton lifetime is not changing significantly, being about 30-50 ps.

One issue with CQDs films for mid-IR detection will be to achieve noise limited by generation/recombination. Our first studies showed that at 1kHz, 1/f noise dominated starting at temperatures of 100K and increased dramatically with higher temperatures.[21] The magnitude, temperature dependence, carrier dependence and overall physical processes of the 1/f noise are not understood. We made some basic studies of the 1/f noise on another quantum dot system, CdSe, as part of a DOE grant on electrical transport in colloidal systems. From that study, it seems that the noise can be strongly decreased by improving the film quality, but some noise floor is inherent to the hopping process.

Synthesis

Using $HgCl_2$ and bis(trimethylsilyl)sulfide ($(TMS)_2S$), or thioacetamide, spherical HgS particles of large diameters reaching ~20 nm could be prepared although rather polydispersed. While HgS clearly will not give interband transitions in the mid-IR, an interesting broad mid-IR absorption feature is observed in the



range of 3-6 µm. A similar feature is seen in the absorption of HgSe particles prepared similarly. The peak frequency varies with particle size and bandgap, and is likely a sign of charge doping in the nanocrystals, though further experiments will be needed to confirm this.

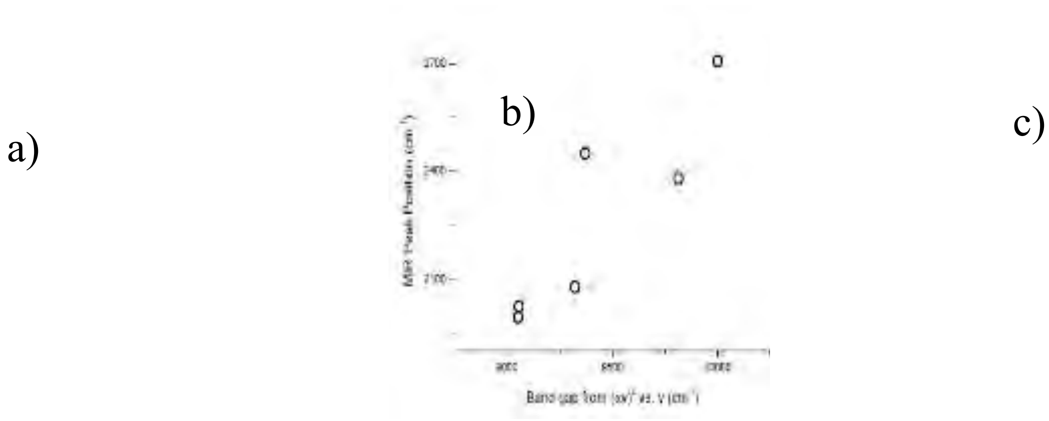


Figure 4: a) HgS particles show a mid-infrared absorption band, which may indicate charge doping. b) Energy of the low energy feature as a function of the estimated gap. c) TEM image of HgS nanoparticles of dimensions up to 20 nm.

The other direction explored has been the cation exchange for making larger HgTe particles or core-shell. Cation exchange has been demonstrated as a way to prepare particles of varying composition, including those which are difficult to synthesize directly. Since large particles of PbTe have been made, we investigated the possibility of cation exchange reactions to replace the Pb with Hg. Thus far, a direct exchange of Hg for Pb has not been possible, but similar transformations such as Cd to Pb have been seen to proceed more readily through monovalent Cu or Ag intermediates. To this end, we prepared 16 nm edge length PbTe particles, which are nicely monodisperse and exhibit self-assembly, but broad spectra. Exchange of an outer shell of the particle for Ag has produced PbTe/Ag_2Te core-shell particles shown below. Further work is needed to determine the limits of these exchange reactions and their application in achieving large and alternative shapes of HgTe nanocrystals.

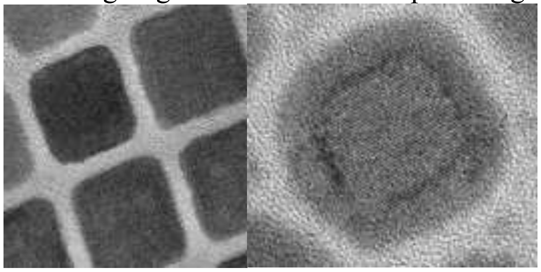
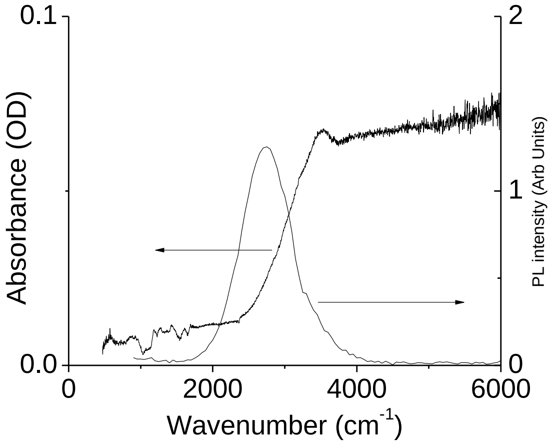


Figure 5: Left: PbTe particles with edge length ~16 nm. Right: PbTe particles of the same sample, having undergone partial cation exchange to Ag_2Te

Larger and more spherical particles of the HgTe have been synthesized using an alternative ligand than Octadecylamine, but the resulting samples are still more polydispersed than we would like. Luminescence has been detected up to the detection limit of our MCT detector (11 microns). Inorganic ligand exchange using ammonium sulfide, potassium thicyanate, as well as SeH-, TeH-, have been realized. Removal of the organic ligands has been successful. Shell growth of the CdS, CdSe, and CdTe have been attempted both in solution and as in-filling of films of HgTe quantum dots. Fig.6 shows the absorption and PL spectra of such a film. The improvement in the PL intensity has however so far not been as significant as hoped and work is ongoing.

Figure 6: Absorbance and PL spectra of a thin film of HgTe quantum dots (~ 150 nm) with a band edge at 3000 cm^{-1}, after 4 cycles of CdS liquid layer by layer deposition, processed at room temperature. The CH bands at 2850-



V. CONCLUSION

Colloidal quantum dots were started to be investigated in 2011 by our group for their potential as mid-infrared detectors. The chemistry is still under development to improve the range of materials, sizes and spectral characteristics, that can be achieved. We have measured the PL QY of HgTe CQDs through the range of 1800 to 6500 cm^{-1} and shown that it drops dramatically from ~0.1 to 10^{-4} at the lower energies.

The PL shows a redshift upon cooling and strong attenuation when tuning through the CH stretch resonance. In the absence of evidence for specific trapping, dark states, or phonon related processes, the PL quenching is tentatively and rather successfully attributed to the largely temperature independent energy transfer to the ligands and surface vibrations. Further development of the materials requires the elimination of the energy transfer process possibly through the growth of an epitaxial shell or the use of an inorganic ligand or matrix.

Personnel, Publications and Presentations: The grant supported Chemistry PhD student Sean Keuleyan. Sean is starting his 6th year and will likely graduate in the Fall 2013. The grant also supported John Koehler, a Physics BS graduate from the University of Chicago who worked as a technical assistant.

One paper is in preparation for submission to the Journal of Physical Chemistry.

Sean Keuleyan received the Best Paper Award for his work on HgTe infrared quantum dot at the "11th International Conference on Infrared Optoelectronics: Materials and Devices". Signatures by Profs. Manijeh Razeghi, Leo Esaki and Klaus Von Klitzing. Sean Keuleyan gave poster presentation at the Gordon conference on Nanocrytals in August 2013.

References

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[1] Medintz, I.L., Uyeda, H.T., Goldman, E.R., Mattoussi, H., "Quantum dot bioconjugates for imaging, labelling and sensing," Nature Mat. 4, 435-446 (2005)

[2] Hillhouse, H.W., Beard, M.C., "Solar cells from colloidal nanocrystals: Fundamentals, materials, devices, and economics," Curr. Op. Coll. Surf. Sci. 14, 245-259 (2009)

[3] Pandey, A., Guyot-Sionnest, P., "Slow Electron Cooling in Colloidal Quantum Dots," Science 322, 929-932 (2008)

[4] Guyot-Sionnest, ., Wehrenberg, B. and Yu, D., "Intraband relaxation in CdSe nanocrystals and the strong influence of the surface ligands," J. Chem. Phys. 123(7), 074709 (2005)

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[5] Pourret, A., Guyot-Sionnest, P., Elam, J., W., “Atomic Layer Deposition of ZnO in Quantum Dot Thin Films,” Adv. Mat. 21(2), 232-+ (2009)

[6] Kovalenko, M., V., Scheele, M. and Talapin, D., V.,“Colloidal Nanocrystals with Molecular Metal Chalcogenide Surface Ligands,” Science 324(5933), 1417-1420 (2009)

[7] Yu, D., Wang, C.J., Guyot-Sionnest, P., “n-type conducting CdSe nanocrystal solids,” Science 300, 1277-1280 (2003)

[8] Talapin, D. V., Lee J.S.; Kovalenko, M.V and Shechenko E.,V., “Prospects of Colloidal Nanocrystals for Electronic and Optoelectronic Applications,” Chem. Rev.110(1), 389-458 (2010)

[9] Konstantatos, G., Howard, I., Fischer, A., Hoogland, S., Clifford, J., Klem, E., Levina, L., Sargent, EH., “Ultrasensitive solution-cast quantum dot photodetectors,” Nature 442(7099), 180-183 (2006)

[10] Howes, P., Green, M., Johnston, C., Crossley, A., “Synthesis and shape control of mercury selenide (HgSe) quantum dots,”J. Mat. Chem. 18, 3474-3480 (2008)

[11] Kuno, M., Higginson, K.,A., Qadri, S.,B., Yousuf, M., Lee, S.,H., Davis, B.,L., Mattoussi, H., “Molecular clusters of binary and ternary mercury chalcogenides: Colloidal synthesis, characterization, and optical spectra ,” J. Phys. Chem. B 107, 5758-5767 (2003)

[12] Harrison, M.,T., Kershaw, S.,V., Rogach, A.,L., Kornowski, A., Eychmuller, A., Weller, H., “Wet chemical synthesis of highly luminescent HgTe/CdS core/shell nanocrystals,”Adv. Mat. 12, 1123-125 (2000)

[13] Rogach, A.,L., Harrison, M.,T., Kershaw, S.,V., Kornowski, A., Burt, M.,G., Eychmuller, A., Weller, H., “Colloidally prepared CdHgTe and HgTe quantum dots with strong near-infrared luminescence,”Physica Stat. Sol. B Bas. Res. 224 153-158 (2001)

[14] Li, L.,S., Wang, H.,Z., Liu, Y.,C., Lou. S.,Y., Wang, Y.,Q., Du, Z.,L., “ Room temperature synthesis of HgTe nanocrystals,”J. Coll. Inter. Sci. 308 254-257 (2007)

[15] Kershaw, S.,V., Burt, M., Harrison, M., Rogach, A., Weller, H., Eychmuller, A.,, ‘Colloidal CdTe/HgTe quantum dots with high photoluminescence quantum efficiency at room temperature,”Appl. Phys. Lett. 75, 1694-1696 (1999)

[16] Piepenbrock, M.,M., Stirner, T., Kelly, S.,M., O’Neill., M., “A Low-Temperature Synthesis for Organically Soluble HgTe Nanocrystals Exhibiting Near-Infrared Photoluminescence and Quantum Confinement,”J. Am. Chem. Soc. 2006, 128, 7087-7090 (2006)

[17] Kovalenko, MV., Kaufmann, E., Pachinger, D., Roither, J., Huber, M., Stangl, J., Hesser, G., Schaffler, F., Heiss, W.,’ Colloidal HgTe nanocrystals with widely tunable narrow band gap energies: From telecommunications to molecular vibrations,”J. Am. Chem. Soc. 128(11), 3516-3517 (2006)

[18] Keuleyan, S., Lhuillier, E. and Guyot-Sionnest, P., “Synthesis of Colloidal HgTe Quantum Dots for Narrow Mid-IR Emission and Detection,” J. Am. Chem. Soc. 133(41), 16422-16424 (2011)

[19] Kovalenko, M. V. *et al.* Colloidal HgTe Nanocrystals with Widely Tunable Narrow Band Gap Energies: From Telecommunications to Molecular Vibrations. *J. Am. Chem. Soc.* 128**,** 3516–3517 (2006).

[20] Pietryga, J. M. *et al.* Pushing the Band Gap Envelope: Mid-Infrared Emitting Colloidal PbSe Quantum Dots. *Journal of the American Chemical Society* 126**,** 11752–11753 (2004).

[21] Thermal properties of mid-infrared colloidal quantum dot detectors, Lhuillier E; Keuleyan S; Rekemeyer P, Guyot-Sionnest P. J. Appl. Phys. 110, Article Number: 033110 (2011)