1. **DE-FG0206ER46326. Grant ER 46326**
2. **Project Title and name of the PI:** Conductivity and Magnetism in Strongly Coupled Quantum Dot Solids. PI: Philippe Guyot-Sionnest, James Franck Institute, 929 E. 57th Street, The University of Chicago, Chicago, IL 60637. pgs@uchicago.edu

3. **Date of the report** 28/04/2016. **Period covered until the end of the grant**

4. **Brief description of recent accomplishments**.
   The goal of the program is to understand and optimize charge transport in colloidal quantum dot solids and to develop magneto electrical properties.
   a. 1/f electrical noise in Nanocrystals solids: Data were taken until Dec. 15 2013 and the paper was finalized and submitted on February 25 2014. The work was published in J. Appl. Phys.
   This is the first detailed study of 1/f noise in nanocrystal solids for a range of materials. We initially expected that 1/f noise could be reduced by film processing, by the choice of the materials comprising the nanocrystals, and by the choice of the matrix. We did find that cracks in films increased the 1/f noise. However, for good films of all the different materials studied, we found a "universal" 1/f noise floor, with a noise scaling as the number of nanocrystals in the system, i.e. extensive as for bulk systems, and approximately proportional to the interdot conductance, irrespective of the materials. We qualitatively concluded that the noise is an intrinsic effect of the granularity in conduction, where charges moving in weakly connected part of the network modify the transport in the higher conductivity regions.

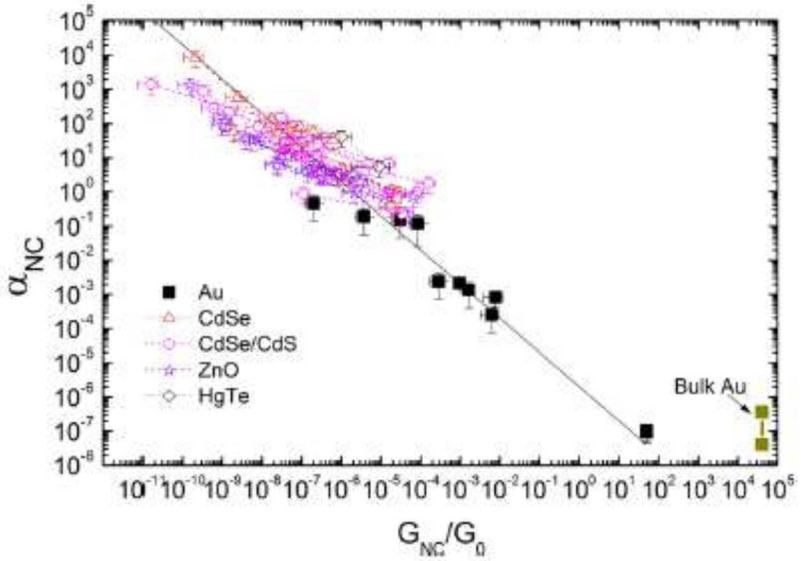

Figure 1: 1/f noise effective Hooge parameter for nanocrystal films as a function of the average conductance between nanoparticles normalized to the quantum conductance. The data extend across the metal-insulator regime.

b. Magnetoresistance of Semiconductor Quantum Dots Films.

In this work, we searched for enhanced magnetoconductivity effects in quantum dot arrays as electrons transfer and spin alignment are affected by an external magnetic field. A magnetic polaron is expected when a quantum dot doped with magnetic impurities is charged with an odd number of electrons..

The magnetoresistance of films of manganese-doped colloidal quantum dots of CdSe, ZnO, HgS, and ZnTe was therefore investigated. At low concentration of manganese ions (1% or less), the hyperfine splitting of the Mn2+ electron spin resonance is resolved and similar to that of the bulk doped materials, indicating successful doping into the nanocrystals. At high Mn concentration (~ 10%), the hyperfine splitting disappears because of interaction between the Mn^{2+} ions. Thin films of Mn:CdSe, Mn:ZnO, and Mn:HgS quantum dots are charged negative by applying an electrochemical potential, and the magnetoresistance is measured down to 2 K and up to 9 T. At low charging level, the magnetoresistance of thin films is positive, exhibits little effect of the manganese dopant, and is instead consistent with predictions from the variable range hopping model and the squeezing of the wave function of the quantum dots. At high charging level, the magnetoresistance becomes linear both for Mn:CdSe and Mn:ZnO, an this is not explained. At high Mn doping and low temperature, the positive magnetoresistance is greatly increased at low fields. This is proposed to be a signature of electron-magnetic polarons on the transport properties of the quantum dot films.

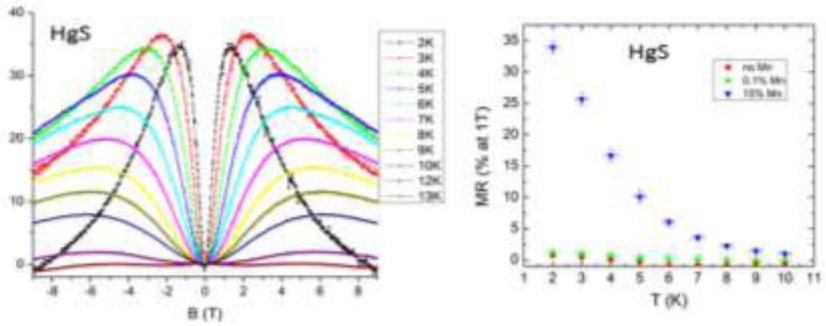

Figure 2: Left: For highly Mn^{2+}-doped β-HgS quantum dots in the strong confinement regime, but not very mono-dispersed, a strong negative MR was observed. Right: The strength of the negative MR was strongly affected by the Mn concentration.

c. Ligand Exchange and Electrolytes.

This work was being pursued by a chemistry PhD student, Guohua Shen, who joined the group in March 2014. We were searching for simple surface modifications that increase the conductivity, while preserving good optical properties and clear quantum confinement. This led us to surface passivation using halides ions (figure 3a). In prior work, we tuned the charging and conductivity of quantum dot solids with an electrochemical control applied through a liquid electrolyte. The drawback is that for any study at room temperature, the electrochemical potential needs to be maintained. For studies of time of flight as a function of doping, which would be a good measure of the mobility distribution, the applied electrochemical potential is an unwanted complication. We are now investigating ionic liquids that have melting points around 100°C so that a permanent charging level can be maintained at room temperature as well as salt eutectic electrolytes (Figure 3b). The project however took a longer turn when we realized that the quantum dots would sinter at 100-170°C required to melt the electrolyte. This led us to revisit the synthesis of the quantum dots and develop core/shell structures. That work did not lead to a finished result before the end of the grant.

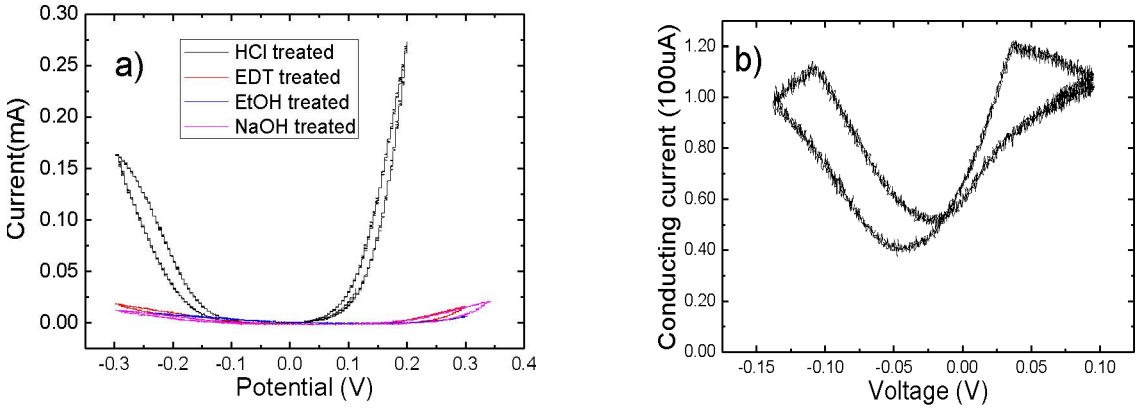

Figure 3: a) conduction *vs* electrochemical potential gate for HgTe quantum dot films. The ligand exchange by treatment in HCl leads to the largest increase in mobility compared to ethanedithiol (EDT). The electrolyte is $LiClO_4$ in Formamide, liquid at 300K. The ambipolar response reflects the similar mobility of n and p carriers. b) A similar film in a $AlCl_3$:NaCl:KCl electrolyte liquid above 100°C with evidence of remaining ambipolar response at that temperature. The electrolyte is solid below 100°C.

5. List of papers

(Include an excerpt of the acknowledgement section. Instructions regarding BES acknowledgement guidelines are contained in the attached document "Acknowledgement of support and delineating BES-funding in publications".)

- *1/f noise in semiconductor and metal nanocrystal solids*, Liu, H; Lhuillier, E. Guyot-Sionnest P. J. Appl. Phys. 115, 154309 (2014). **Acknowledgement:** The research was supported by the DOE under Grant No. DE-FG02- 06ER46326. The authors made use of shared facilities supported by the NSF MRSEC Program under DMR-0820054.
- *Small Bright Charged Dots*, Qin W., Heng L. Guyot-Sionnest P. ACS Nano, 8, 283-291, (2014) **Acknowledgement:** W.Q. acknowledges the financial support from the Petroleum Research Fund under Grant ACS-PRF 51312-ND10. H.L. acknowledges the support from the DOE under Grant No. DE-FG02-06ER46326.
- *Magneto-Resistance of Manganese Doped Quantum Dot Solids,* Heng Liu, P. Guyot-Sionnest. The Journal of Physical Chemistry C 119 (26), 14797-14804 (2015). **Acknowledgements :** The research was supported by the DOE under Grant No. DE-FG02- 06ER46326. The authors made use of shared facilities supported by the NSF MRSEC Program under DMR-0820054.