

Synthesis of Quantum Dots and their Applications to (NIR) Photo-detectors

Eric Moyen,¹ Jin Jang¹

moyen.eric@gmail.com

¹Advanced Display Research Center, Department of Information Display, Kyung Hee University, Seoul 02447, South Korea

Keywords: quantum dots, photo-detectors, CsPbBr₃, PbS, CuInSe₂

ABSTRACT

Quantum dots (QDs) have gained attention for their potential applications in optoelectronic devices. Their bandgap as well as their electronics properties can easily be tuned and they are suitable for low-cost devices fabrication. We will detail various synthesis processes for QDs and show their applications in photo-detectors.

INTRODUCTION

Colloidal quantum dots (QDs) have gained attention for their potential applications in optoelectronic devices, such as solar cells, light-emitting diodes or photodetectors. Their bandgap is easily tunable by adjusting their size and composition. Their properties, such as the energy, the type, the concentration, and the mobility of the carriers can be further engineered via surface modifications due to their high surface-to-volume ratio. Moreover, they are suitable for low-cost large area devices fabrication since they can be dispersed in solvents making them compatible with low temperature spray, inkjet or spin coating techniques. Thus, QDs can be substitutes to traditional bulk Si or III-V-based technologies, in particular for flexible applications. Here we will show how quantum dots can be used in various types of photodetectors.

RESULTS AND DISCUSSION

Various synthesis methods are available for quantum dots, depending on the targeted material and application. In our talk, we will illustrate three synthesis methods. Firstly, zinc oxide (ZnO) nanoparticles, which find applications as electron transport layers in light emitting diodes or as active layer for photo-detectors in the UV range, are synthesized via a sol-gel process.[1] Simply varying the synthesis temperature enables to tune their size and their surface defect density, which are critical for the transport of carriers. Secondly, perovskite quantum dots (APbX₃, with A=Cs, Rb, MA... and X = Cl, Br or I) can be synthesized in a room temperature ligand assisted reprecipitation process (LARP).[2] Their synthesis is illustrated in Fig. 1 a. Their bandgap can easily be tuned from 2.8eV (~450nm) to 1.8eV (~700nm) by changing the halide (X) or the cation (A), see Fig. 1 c. Their excellent opto-electrical properties make them interesting candidates for future light emitting diodes or photo-

detectors in the visible range. Thirdly, lead sulfide (PbS) quantum dots are synthesized either in a hot injection or a heat up process. The bandgap of bulk PbS (~0.4eV) makes PbS QDs them great candidates for applications in the near infrared (NIR) range. The bandgap can be slightly widened by controlling the size of the quantum with the synthesis temperature, growth time as well as with the organic ligands used in the process. The synthesis method for PbS QDs is schematized in Fig. 2 a and more details can be found in [3].

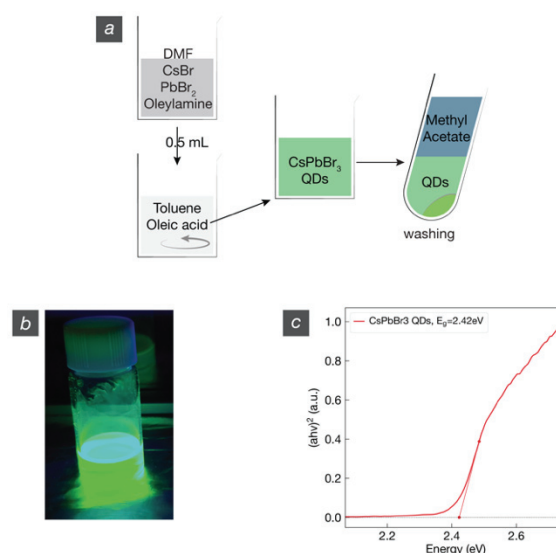


Fig. 1 Ligands assisted reprecipitation process for the synthesis of perovskites (CsPbBr₃) quantum dots – a) schematics illustrating the synthesis process. Briefly Cs and Pb halide precursors are dissolved in a mixture of oleylamine and DMF (N,N-Diméthylformamide), the resulting solution is injected at room temperature in a mixture of oleic acid and toluene. DMF is soluble in toluene while the perovskite precursors are not, which results in the local supersaturation of perovskite precursors and in the nucleation and growth of the CsPbBr₃ QDs. Oleylamine helps to limit the growth and control the size of the QDs while the oleic acid maintains the colloidal stability of the solution. The resulting solution is further washed multiple times with an antisolvent and the QDs are re-dispersed in toluene – b)

CsPbBr₃ QDs in toluene under 365nm UV illumination – c) Tauc plot obtained from absorption measurements on a CsPbBr₃ thin film, the optical bandgap is 2.42eV.

A key issue with commonly used QDs, such as perovskite, PbS, CdSe and CdTe, is the toxicity of Pb and Cd. Therefore, developing 'green' alternatives which exhibit comparable opto-electronic properties is crucial. Replacing Pb in perovskites QDs with Sn, Ge, Ag, Bi or Cu is subject to an ongoing research. Interestingly Sn-based perovskites have shown a bandgap as narrow as 1.2 eV making them potential candidates for NIR applications. However, the performance and the stability of photovoltaic devices or photo-detectors fabricated with Pb-free perovskites QDs are usually lower than those obtained with Pb-containing perovskites. One of the most promising 'green' alternative for PbS QDs are I-III-VI compounds. Among them, the CuInSe₂ (CISe) compound is stable, have a high absorption coefficient ($\sim 10^5$ cm⁻¹) and a narrow bandgap (1.2 eV in its bulk form). CISe QDs can easily be synthesized using the hot injection method.[4] We will discuss and compare the performance of photo-detectors which active layer is made of CuInSe₂ QDs and PbS QDs, and eventually Pb-free perovskite QDs.

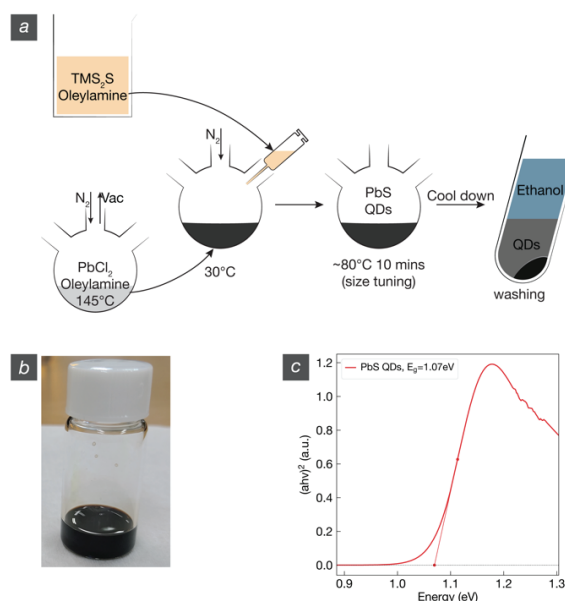


Fig. 2 Hot injection synthesis of PbS quantum dots – a) schematics of the process, Bis(trimethylsilyl)sulfide (TMS₂S) mixed with oleylamine is quickly injected at room temperature in a mixture of lead chloride (PbCl₂) previously dissolved in oleylamine at 145°C. Nucleation of PbS QDs immediately takes place as the solution turns black and the temperature is further increased to ~80°C for ~10 minutes to grow the QDs to the desired size; the resulting solution is further washed several times with ethanol and the precipitate is re-dissolved in

toluene – b) photograph of a 10 mg/ml ink of PbS QDs in toluene – c) Tauc plot (absorption) of a PbS QDs spin coated thin film, the optical bandgap of as synthesized QDs is 1.07eV

Moreover, to maintain their colloidal stability QDs are surrounded by insulating ligands, which are usually long carbon chains (see Fig. 3 b). Those cannot be fully removed in QDs films which limits the performance of opto-electronic devices. Consequently, they should be replaced with shorter more conducting ligands (see Fig. 3 c). A proper choice of ligand can also passivate the surface of the QDs. As shown in Fig. 3 d,e,f and g in the case of a photo-transistor based on CsPbBr₃ coated on a n-type metal oxide channel, using shorter ligands usually results in a dramatic improvement of the photo-detectors performance, such as their detectivity and response time. We will show how the choice of ligands can affect the performance of photo-detectors and discuss several possible configurations (photo-transistors, p-i-n diodes, ...) of colloidal quantum dots based photo-detectors.[5]

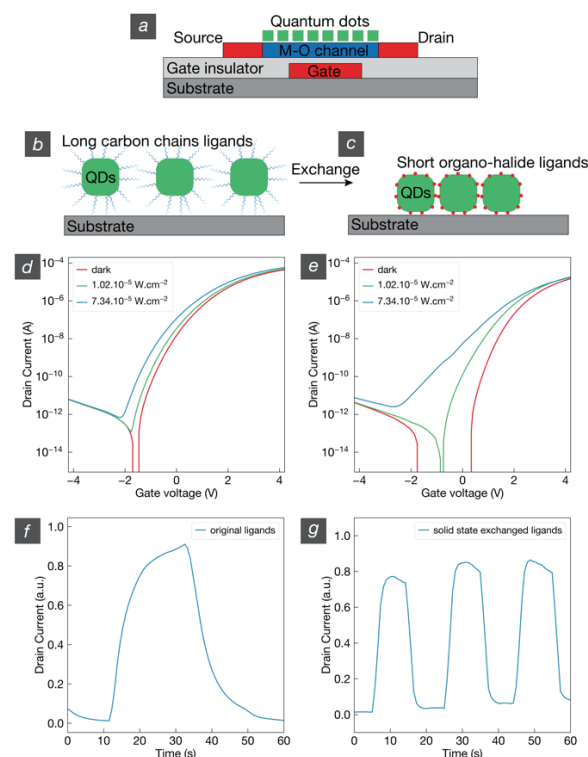


Fig. 3 CsPbBr₃ based photo-transistors – a) device structure – b) illustration of a CsPbBr₃ thin film where the QDs are surrounded by long organic ligands – c) solid state ligands exchange, after exchange the QDs are surrounded by short organic or inorganic ligands which facilitates the carriers transport in the film and eventually passivates the QDs surface preventing electron-holes recombinations at the QDs surface – d) Transfer curves

of a device with long chain organic ligands in the dark and under green (525nm) illumination at various powers – e) after ligands exchange the drain current increases under illumination as a result of a better electron transport to the metal-oxide channel – f) the rising and falling times are in the >10 seconds range as long chain organic ligands are present in the CsPbBr₃ QDs film – g) the rising and falling times decrease below 1 second when using shorter ligands.

CONCLUSION

Colloidal quantum dots can reach and outperform the performance of bulk photo-detectors while using cheaper solution process that are eventually compatible with flexible technologies.

REFERENCES

- [1] E. Moyen, J. H. Kim, J. Kim, and J. Jang, "ZnO Nanoparticles for Quantum-Dot-Based Light-Emitting Diodes," *ACS Appl. Nano Mater.*, vol. 3, no. 6, pp. 5203–5211, Jun. 2020, doi: 10.1021/acsanm.0c00639.
- [2] E. Moyen, H. Jun, H. Kim, and J. Jang, "Surface Engineering of Room Temperature-Grown Inorganic Perovskite Quantum Dots for Highly Efficient Inverted Light-Emitting Diodes," *ACS Appl. Mater. Interfaces*, vol. 10, no. 49, pp. 42647–42656, Dec. 2018, doi: 10.1021/acsami.8b15212.
- [3] Z. Huang, G. Zhai, Z. Zhang, C. Zhang, Y. Xia, L. Lian, X. Fu, D. Zhang, and J. Zhang, "Low cost and large scale synthesis of PbS quantum dots with hybrid surface passivation," *CrystEngComm*, vol. 19, no. 6, pp. 946–951, 2017, doi: 10.1039/C6CE02471H.
- [4] R. Guo, J. Meng, W. Lin, A. Liu, T. Pullerits, K. Zheng, and J. Tian, "Manganese doped eco-friendly CuInSe₂ colloidal quantum dots for boosting near-infrared photodetection performance," *Chem. Eng. J.*, vol. 403, no. May 2020, p. 126452, 2021, doi: 10.1016/j.cej.2020.126452.
- [5] R. Saran and R. J. Curry, "Lead sulphide nanocrystal photodetector technologies," *Nat. Photonics*, vol. 10, no. 2, pp. 81–92, 2016, doi: 10.1038/nphoton.2015.280.