Lead sulfide quantum dots and their application for solar cells

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Dedication

This thesis is dedicated to my loving mom and dad Uma and Arun Shrestha, my sister Agya Shrestha nd my wife Reshma Shakya.

Declaration

I certify that this work contains no material which has been accepted for the award of any other degree or diploma in my name, in any university or other tertiary institution and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference has been made in the text. In addition, I certify that no part of this work will, in the future, be used in a submission in my name, for any other degree or diploma in any university or other tertiary institution without the prior approval of the University of Adelaide and where applicable, any partner institution responsible for the joint-award of this degree.

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Abstract

Quantum dot sensitized solar cells (QDSSCs) are interesting third generation solar cells that have potential to address the current energy related issues due to their low manufacturing cost, ease of fabrication as well as good performance. Quantum dots (QDs) offer several advantages such as size tunable band gaps across a wide range of energy levels, high molar extinction coefficients and enhanced stability. Among them, colloidal near infrared (NIR) QDs of lead sulfide (PbS) are attractive due to their narrow bulk bandgap, large exciton Bohr radii and the possibility of multiple exciton generation. Utilizing these QDs in solar cells with extendable IR absorption is promising. However, the progress of PbS QDSSCs is lacking due to the limited understanding regarding the synthesis and surface chemistry of QDs. The development of QDSSCs is also hindered by lack of proper counter electrode materials for the reduction of electrolytes. Hence, further developments in the synthesis and application of new materials for QDSSCs are necessary.

This PhD project focuses on the materials development for PbS QDSSCs such as PbS QD synthesis, surface ligand exchange of PbS QDs, and the development of new counter electrode materials. The following researches are included in this thesis:

1) A robust method to synthesize monodisperse lead sulfide (PbS) QDs is presented. PbS QDs with different sizes is produced by stepwise heating of the preformed seed QDs in the presence of excess oleic acid. A combination of "living" monomer addition and Ostwald ripening is identified as the mechanism for such QD growth processes.
2) The detailed synthesis mechanism of PbS QDs is investigated. Here, the various synthesis parameters influencing the nucleation and growth of PbS QDs are elucidated.

In addition, the detailed understanding of the synthesis mechanism is used to guide the synthesis of PbS QDs at ultra-small regime.

3) A versatile solution phase ligand exchange of PbS QDs in the presence of Pb-thiolate as the exchanging ligands is presented. The ligand exchange procedure better preserves the optical properties of PbS QDs and is applicable to a number of ligand/solvent systems.
4) The implementation of PbS QDs in QDSSCs is presented. The treatment of PbS QD photoelectrodes with cadmium salts is necessary to maintain the stability of PbS QDs in polysulfide based electrolytes. In addition, the number of cycles of CdS and ZnS treatment is optimized to achieve a photoconversion efficiency of 1.77 %.
5) Finally, N-doped CN_x/CNT hetero-electrocatalyst materials using polydopamine is synthesized, which are explored as counter electrode materials for dye-sensitized solar cell (DSSC). These CN_x/CNTs material show excellent electrocatalytic activities towards the reduction of tri-iodide electrolytes with the optimized solar devices using CN_x/CNTs showing comparable performance (7.3 %) to reference Pt based devices (7.1 %).

List of publications

This doctoral thesis is prepared in "Publication" format according to the "specifications for Thesis (2016)" of the University of Adelaide. The thesis includes the following publications that have been published, submitted for publication, or ready for submission:

1) Aabhash Shrestha, Shizhang Qiao, Sheng Dai, "Near infrared (NIR) lead chalcogenide QDs- recent progress in their synthesis, post-synthesis ligand exchange and applications in solar cells" (To be submitted)
2) Aabhash Shrestha, Bo Jin, Tak Kee, Shizhang Qiao, and Sheng Dai, "A Robust Strategy for Living Growth of Lead Sulphide Quantum Dots", Published in Journal ChemNanoMat (DOI: 10.1002/cnma.201500110)
3) Aabhash Shrestha, Nigel A. Spooner, Shizhang Qiao, and Sheng Dai, "Mechanistic insight into the nucleation and growth of oleic acid capped lead sulfide quantum dots", Submitted to Journal Physical Chemistry Chemical Physics (Submission ID: CP-ART-03-2016-002119)
4) Aabhash Shrestha, Nigel A. Spooner, Shizhang Qiao, and Sheng Dai, "Versatile PbS quantum dot ligand exchange systems in the presence of Pb-thiolates", Submitted to Journal Small (Submission ID: smll.201601046)
5) Aabhash Shrestha, Munkhbayar Batmunkh, , Cameron J. Shearer, Yanting Yu, Gunther Andersson, Joseph G. Shapter, Shizhang Qiao, Sheng Dai, "Nitrogen-doped CN_x/CNTs hetero-electrocatalysts for highly efficient dye sensitized solar cells", (To be submitted in Journal Advanced Energy Materials)

6) Aabhash Shrestha, Munkhbayar Batmunkh, Joseph G. Shizhang Qiao, Shapter, Sheng Dai, “Enhancing the stability of pre-synthesized PbS quantum dot sensitized solar cells in polysulfide electrolyte by treating with cadmium salts”, (To be submitted)

Some relevant components of the work have also been presented in the following conferences:

1) Aabhash Shrestha, Munkhbayar Batmunkh, Joe Shapter, Shizhang Qiao, Sheng Dai “Hybrid carbon nanomaterials for highly efficient dye sensitized solar cells (DSSCs)” MRS 2015, Fall Meeting, Boston, USA, 2015

2) Aabhash Shrestha, Shizhang Qiao, Sheng Dai “ Understanding the nucleation and growth mechanism towards synthesis of Lead Sulphide Quantum Dots” ICONN 2014, International Conference on Nanoscience and Nanotechnology, Adelaide Conventional Center, Adelaide, Australia, 2014

3) Aabhash Shrestha, Shizhang Qiao, Sheng Dai, “Precursor and ligand influenced growth mechanism and living chain polymerization of post focused Lead Sulfide Quantum dots” SA Polymer and Biotechnology Symposium, Flinders University City Campus, Adelaide, Australia, 2013

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