Controlled Synthesis of Near IR Emitting Metal Chalcogenide Quantum Dots for the Opto-electronic Applications

Ibrahim Hocaoglu,* Leyla Eral Dogan,* and Pinar Dagtepe*

*Kuantag Nanotechnologies Development and Production Inc., Turkey,

ibrahim.hocaoglu@kuantag.com, leylaeral.dogan@kuantag.com, pinar.dagtepe@kuantag.com

ABSTRACT

In the study, QDs are synthesized colloidally in a single operation by continuous flow reactor. Reaction parameters affect the QD quality and quantity. The reaction parameters have been studied to prepare high quality particles in terms of optical and colloidal properties. These parameters are type and amount of reagent, capping agent and solvent, reaction time and, reaction temperature. In continuous flow reactor effective heat and mass transfer can be achieved. The size distribution of Near IR emitting metal chalcogenide QDs is highly monodisperse. These QDs have emission profile over 700 nm. These QDs are optically and colloidally stable in different solvent in the long term even at low concentration with high PLQY.

INTRODUCTION

Studies on the synthesis of Near IR emitting Quantum Dots have increased due to their potential in fiber optic communication systems, in photovoltaic cells, solar cell conversion, in NIR detectors-cameras, in biological applications including in vitro and in vivo cell and tissue imaging and tagging, cell tracking and so on.[1-4]

There are few series of semiconductors made up of metal chalcogenides utilized in preparation of NIR-QDs. Especially the semiconductors having band gap energies at least 1.5 eV and less than 1.5eV such as InP, InAs, Ag_2S, PbS, PbSe and so on have been used. Several problems are encountered in the preparation and within the material itself in terms of colloidal and optical stability and quantum efficiency.

Preparation method and the system plays important role in producing high quality particles. Choice of precursors, capping agents and reaction medium was one of the influential parameters in a reaction. These parameters were studied with the efficient heat and mass transfer in a set time and the temperature. Also, the differences between the batch reactor and the continuous flow reactor were observed. The continuous flow reactor is advantageous over a batch reactor in terms of mono-disperse high quality particles due to efficient heat and mass transfer with a controlled mixing of the precursors. Beside these, easy and continuous operation allows scalability of the production and also altering reaction condition.

Syntheses of metal chalcogenides nanoparticles were attained in this system with a high yield and quality, mono-disperse size, colloidal and optical stability and high quantum yield. Specifically PbS nanoparticles were studied. The reaction conditions were optimized via continuous flow reactor and those particles emitting in the Near-IR-region above 700nm with high quantum yield at above 30%.

PREPARATION of METAL CHALCOGENIDE NANOPARTICLES

In a typical synthesis, Metal and Anion precursors were prepared and stored before run the continuous flow system.[5-7]

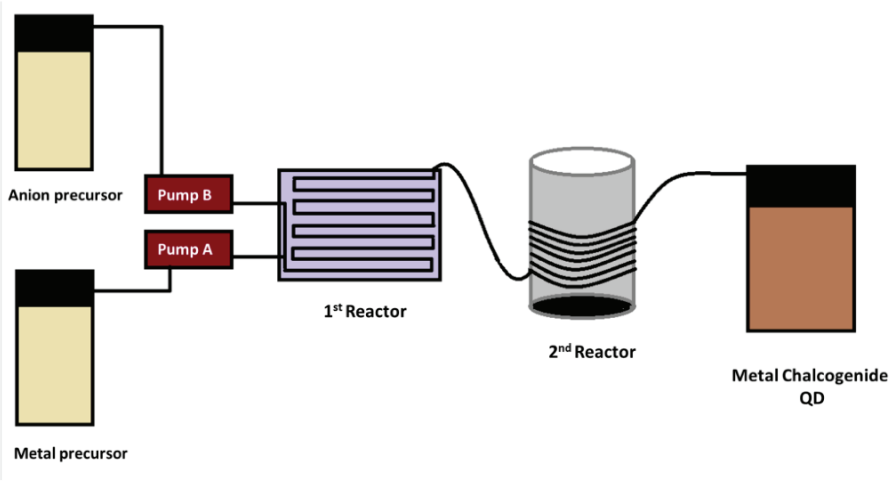
Metal Precursors prefentially metal oxides or salts were dissolved with oleic acid in the presence of other stabilizer or capping agents at above 120 ^{o}C under inert atmosphere in the reaction medium (Picture 1). In our study, PbO was used as a metal source dissolved in 1-octadecene. A clear solution was obtained.

Picture 1: Metal precursor preparation

Anion precursor prefentially sulfides were dissolved in reaction medium at a required temperature (Picture 2). In our study, Trimethylsilylsulfide was dispersed in 1-Octadecene.

Picture 2: Anion precursor preparation.

TechConnect Briefs 2016, TechConnect.org, ISBN 978-0-9975-1170-3



Picture 3: Continuous Flow system scheme for the production of Metal Chalcogenide QDs.

Metal chalchogenide QDs were synthesized by continuous flow reactor in a controlled way. Prepared metal and anion precursors were mixed in the micro-channels of 1st reactor. Metal Chalchogenides nucleates in the reactors and growth take places in the 2nd reactor (Picture 3). Temperatures, Flow rate, Residence Time, Ratio of the reactants were the influential parameters in the production of the high quality particles. In our study, PbS QDs were synthesized from Lead(II) and sulfur precursors emitting between 700-1000nm near-IR-emission range. Studied parameters (Table 1) were 30-120 ^{o}C for the temperature, 1,125 ml/min.-6ml/min. for the flow rates and 10s-180s for the residence time.

RESULTS

Production of metal chalcogenides was studied by continuous flow reactors. Especially, PbS nanoparticles were synthesized and their optical properties were evaluated for versatile application as well as opto-electronic applications.

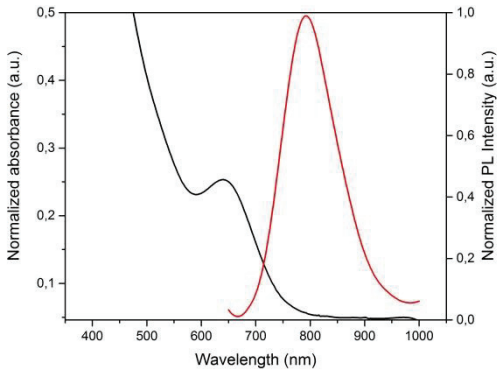
Table 1: Reaction parameters controlled by continuous flow reactor.

	Volume (A) ml	Volume (B) ml	Ratio A:B	T(^{o}C) 1st reactor	T(^{o}C) 2nd reactor	Total Flow Rate ml/min
1	8	8	1:1	50	30	2.25
2	8	8	1:1	50	30	4.5
3	8	8	1:1	70	50	2.25
4	8	8	1:1	70	50	4.5
5	8	8	1:1	70	50	9
6	8	8	1:1	90	70	2.25
7	8	8	1:1	90	70	4.5
8	8	8	1:1	90	70	9
9	8	8	1:1	110	90	12

Product quality can only be optimized by the reaction parameters which can be easily controlled by continuous flow reactors. Some examined parameters and optimization studies for the PbS QD production are stated on table1. Two important parameters affecting particle properties/quality are temperature and flow rate as well as residence time were altered in the flow system under keeping the reactant ratios constant. Reactant ratios and the concentrations are also influential indeed. These two parameters are meaningfully influential for the property of the particles with high mass and heat transfer performance ability of the flow system. Hence, Size of the particles directly related to emission tunability, can be easily controlled and tuned. Synthesized PbS QDs in brown color are seen in the picture 4 with different reaction condition. These QDs emit between 700-1000nm Near IR window.

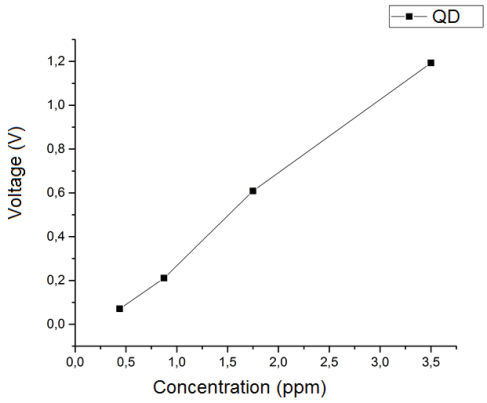
Picture 4: Synthesized PbS QDs with different control parameters via continuous flow reactor.

A typical synthesized PbS QD has band edge emission profile as seen on graph 1. PbS QD has absorption band covering the visible region and has an explicit excitonic at above 600nm. This profile may changes or shift according to particle size and quality. This particle emits at 800nm with a PhotoLuminescent Quantum Yield (PLQY) around 40%. PLQY of the particles were measured by collecting absolute emission with an integrating sphere rather than comparing to a reference dye.



Graph 1: Absorbance and Photoluminescence spectra of PbS QDs.

PbS QDs synthesized by flow system are colloidally and optically stable at low concentration in organic medium. A sample of PbS QD emitting at 850nm was dispersed in tetrachloroethylene and after serial dilution (From 12000ppm-0.5ppm) emission maximum was recorded at 850 nm (Graph 2). 3,5-0,5 ppm concentration levels with the PL intensities were ploted in the graph 2.



Graph 2: Concentration based photoluminscence intesity of PbS QD in tetrachloroethylene.

CONCLUSION

Metal chalcogenide nanoparticles can be successfully by continuous flow reactor advantageous over batch reactors in terms of controlling over reaction parameters. Efficient mass and heat transfer and conventional processing and operation make the system useful for the nanoparticle synthesis as well as with the microchanells. Synthesized particles have higher quality in the meaning of size, absorbance and emission profile and tunability and PLQY. Also, They are optically and colloidally stable in low concentrations in different solvent. In the study, Production of PbS QDs were reported. These QDs have broad absorbance band up to Near IR field and tunable emission band between 700-1000 nm. In addition, these particles are stable in low concentrations in a solvent medium. Hence, PbS QDs have a great potential for both biotechnology and the opto-electronic applications.[8-10]

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