The flow reactor system for in-line synthesis of semiconductor nanoparticle

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Abstract. A flow reactor nanoparticle synthesis technique is proposed as replacement for «hot injection» synthesis of semiconductor nanocrystals in a glass flask. The main advantages are possibility of continuous nanoparticles production, technology flexibility and lower cost of the final products in comparison with currently applied methods.

1. Introduction
The traditional synthesis in a chemical glass flask allows to obtain a variety of nanoparticle types with different functional properties: luminescent quantum dots [1], magnetic structures [2], plasmonic active elements [3] etc. In some of these methods materials are synthesized at room temperature, while others require a heating step. For instance, in the case of “hot-injection” synthesis of colloidal quantum dots temperatures about 200–300°C are used. Nucleation and growth stages dividing allows to obtain monodisperse nanoparticles. However, in the case of chemical flask it is impossible to separate these stages completely, because the reaction takes place in a restricted volume. This technique also limits the product yield – a single synthesis gives only a limited amount of particles, and for large quantities it must be repeated many times. This factor limits the creation of industrial systems for production of colloidal quantum dots and hinders development of their applications.

1.1. Types of flows
Flow reactors are divided into two basic types: continuous and segmented flow reactors. The latter type is conventionally divided into two groups: the “gas/liquid” and “liquid/liquid”.
The reactors of the continuous flow type (Figure 1a) are the first system which has been implemented in the synthesis of nanoparticles in a stream mode. Along with the manufacturing ease of such reactors they have some disadvantages: firstly, they are soiled over time and secondly, the liquid front has a parabolic velocity profile. The reason for such profile known as Hagen-Poiseuille is the friction between flow and wall which results in a corresponding decrease in velocity near the walls. That leads to a fatal issue of relatively large nanoparticles size dispersion. In low viscosity solvents the velocity dispersion effect is partly compensated by lateral diffusion through the channel – growing nanoparticles and reagents cross channel numerous times thereby experiencing all speeds equally. But in case of high-temperature synthesis we must use solvents with high boiling point, which usually expect a high viscosity solvent. Particle size dispersion reducing can be achieved by the transition from a continuous flow to a segmented one.

A segmented stream is created by introducing to it an additional component which is immiscible with the reactive basic solutions (liquid or gas) so that discrete droplets stream of a liquid is separated by layers of another liquid or gas. Using the segmented flow is becoming increasingly popular for the synthesis of nanoparticles. The method has been applied to a wide range of materials [4 – 7].

When it is used the “gas/liquid” mode viscous friction of the channel walls causes convective mixing within each segment, providing chemical homogeneity, important to obtain monodisperse nanoparticles product. The particles pass through the reactor at the same speed, therefore dispersion of particles size is reduced in comparison with a continuous stream. Not only inert gases can be used for segmentation, but also, for example, volatile amines or just air.

However, a disadvantage of using “gas/liquid” mode is a contact of the reaction mixture with the walls, resulting in gradual clogging of the channel. This problem can be solved by using the next type of flow regime “liquid/liquid”, where the reactants move in a series of discrete droplets which are separated not only from each other but also from the channel walls by an immiscible liquid (Figure 1c). This occurs when the separating phase is a liquid, preferably wetting the channel walls and being in excess in relation to the reactive components.

This type of flow has an important advantage over the above described: the reaction mixture isolated from the channel walls, any reaction products reliably enclosed in the droplet volume, thus minimizing the risk of reactor fouling. Therefore, this type of synthesis is the most interesting for the industrial implementation of the entrained flow reactor.

2. Experiment
In comparison with traditional chemical synthesis in a flask, a flow chemistry nanoparticle synthesis is performed in a stream of fluid flowing in a narrow capillary. Precursors can be solutions of water soluble salts or organic compounds in a nonpolar medium. There are two organic immiscible fluids in
our system: one fluid serves as the liquid carrier with good wetting of capillary wall, while the other consists of precursor solution drops which are distributed in the flow of medium. Syringe pumps are used for setting transfer rates of components (carrier liquid and precursors). Number of pumps equals to the number of independent components that are placed in corresponding syringes.

Our system works as follows: 1) the precursors A and B are moved by syringe pumps to the mixing cell, 2) the mixed solution gets into a coil with a temperature $T_n$ corresponding to the nucleation of nanocrystals, 3) the core particles solution flows into the coil with a temperature $T_g$ corresponding to the particles growth stage, 4) in the last step the solutions are selected and cooled to room temperature. Time control of the particle growth is determined by the flow rate of carrier fluid. Due to the immiscible nature of the carrier and the solvent, the liquids separates into two layers of different density, so nanoparticles are isolated from the solvent by standard flocculation technique by polar liquid such as acetone or methanol.

At the last stage and each of the intermediate steps the solutions can be tested by optical spectroscopy. For this purpose we have developed a compact optical spectrophotometer Eltech-M-14 allowing to obtain in situ luminescence spectra. The syringe pumps flow rate and the heating devices temperatures $T_n$ and $T_g$ are controlled by computer program, microcontroller board and several additional printed circuit boards created ourselves.

2.1. Implementation of precursors flow in the capillary
An important part of the reactor is precursors mixing module. The scheme of such a module is shown in Figure 2.

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Figure 2 – Scheme module for mixing: 1, 2 – needle precursors; 3 – needle with a liquid carrier; 4 – capillary
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Two precursors flow through the needles 1 and 2 (angled 90°), mixes together and forms droplets in a stream of carrier liquid from needle 3 and go in the polytetrafluoroethylene capillary 4. Since the capillary has a diameter less than 1 millimeter, it is the best to use needle from the insulin syringes. The feed rate of the carrier fluid should be higher than the rate of precursors feed to control the distance between drops.

2.2. Software implementation management syringe pump
Syringe pump system is based on a stepper motor and transmission system of movement to the syringe, which is printed using the 3D-printer UP Plus 2. The appearance is shown in Figure 3. Inject syringes can have different volumes: 5 ml, 10 ml, 20 ml.
Pump control is done by a single-board microcontroller Arduino Uno and software developed in NI LabVIEW with LabVIEW Interface for Arduino. Figure 3 shows a flowchart of this program. Work can be divided into three stages of the pump: 1) “initialization” – attaching the movable unit with an internal thread (element 2 in Figure 3) to its initial position, which depends on the filling of the syringe being used; 2) a syringe pump setup; 3) “start operation” – extruding the solution from a syringe at a determined speed.

Figure 3 – The syringe pump model: 1 – a syringe, 2 – the movable unit with an internal thread, 3 – the threaded rod, 4 – the stepping motor, 5 – module housing

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Figure 4 – Schematic diagram of the software is running for pump control

Set all the parameters:
1. Model syringe
2. Setting the total volume of the liquid
3. Setting the liquid flow rate (ml / sec)
4. Setting the reagent extrusion volume

Reading values from the switch after clicking the "Initialize"

Switch OFF » («0»)

Stepper motor (SM) performs one revolution

Switch ON » («1»)

SM reverses direction and performs a count N1 of steps in accordance with the type of syringe and the filling volume

Installing a syringe with a solution of a user after the withdrawal of the dialog pop-up window with the message "Secure syringe"

Calculation of time during which the liquid is used up in the syringe by pressing the "Prediction time of the pump"

SM performs N2 number of steps in accordance with the type of syringe and reagent extrusion volume. Speed of movement corresponds to the "liquid flow rate"
2.3. **Diagnosis of the optical properties of nanoparticles**

The new technology of synthesis is needed to measure the optical characteristics of produced quantum dots in situ. At the same time photometric device on the output of the reactor should be very compact and economically competitive with the total cost of the reactor. Spectrophotometric instruments for the diagnostics of such materials are traditionally used. So there was a need to create a compact device for the rapid analysis of the luminescence of colloidal quantum dots.

When measuring the luminescence spectra of the exciting radiation (excitation by LED) passes through the cell and causes the sample photoluminescence. Secondary radiation passes through a narrow slit and divides by diffraction grating to different wavelengths with intensities registered by CMOS webcam. CMOS sensor allows to simultaneously record the entire wavelength range of the visible spectrum, which reduces analysis time and allows the measurement of the optical spectrum in a continuous mode. In addition, webcam is fully prepared to host that does not require additional electronic components. Adjacent rows of pixels can increase the number of experimental points and accordingly improve the measurement accuracy.

As a result of analysis on the computer receives a radiation image of the diffraction pattern, the next stage of the work was to develop a program that transforms the spectrogram (two-dimensional array of pixels) in the spectrum. During the analysis program in the form of two-dimensional array of picture, data transmitted diffraction pattern. The position of a pixel corresponds to a particular wavelength value, while the brightness of the pixel is proportional to the intensity of the light coming on cell CMOS sensor. Signal is formed of three colors (red, green, blue), brightness is due to the averaging of the intensity values on the three channels:

\[
I = \frac{R + G + B}{3}
\]  

where \(I\) – brightness (intensity) of the pixel; \(R, G, B\) – the intensity of red, green, and blue channel of the pixel, respectively. Three modes of the device are implemented:

1. In the “Calibration” mode conversion factors are being identified diffraction. As a gauge used emission spectrum compact fluorescent lamp having a fixed characteristic intensity peaks at known wavelengths. To determine the scaling factors in the resulting emission spectrum of the fluorescent lamp two selected intensity maxima are assigned their own wavelengths and calculated ratios of corresponding pixels of the wavelength of the diffraction pattern. In fact, it is necessary to know the left border of the spectrum and the coefficient corresponding to step (a kind of dividing the price of one pixel). The last factor is calculated as follows:

\[
h = \frac{P_2-P_1}{N_2-N_1}
\]  

where \(P_i\) and \(N_i\) – respectively the position of the \(i\)-th maximum of the selected pixel relative to the left boundary and the position of that peak, expressed in nanometers.

Calculation of the left end of the spectrum in nanometers is made, taking into account the calculated ratio:

\[
L = \frac{N_1-hP_1+N_2-hP_2}{2}
\]  

The calculated data are used as calibration data in other modes of operation of the program.

2. In the “Emission spectrum” mode – measured photoluminescence spectrum of a solution of nanoparticles. When measuring the luminescence spectra of the exciting radiation (LED \(\lambda = 365\) nm) passes through the sample and causes the photoluminescence. Software converts the captured image in dependence of the emission intensity of the wavelength, assigning each pixel column wavelength based calibration data.
3. In the “Time response” mode luminescence intensity is measured on the same wavelength with respect to time. This mode is particularly interesting for the in situ measurement and research questions degradation of quantum dots under the influence of high-energy excitation.

The software also realized the possibility of averaging analysis results for several consecutive spectra measurements. The body of device is also made by 3D-printer. The cell may be of arbitrary shape, its role in the synthesis reactor stream may carry functional nozzles allowing fast move without any difficulties spectrofluorimeter at different reactor units. Thus, the developed device can measure the optical characteristics of the nanoparticles at a nucleation step and during the analysis of growth of quantum dots.

3. Results
The reactor uses the principle of separation of nucleation and growth of nanoparticles. The offered technique increases the production rate, makes synthesis more reproducible and reduces the reagents consumption. Such system allows to obtain nanoparticles of metal chalcogenides $A_2B_6$, $A_4B_6$.

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