Synthesis and Characterization of Colloidal PbS Quantum Dots in Gelatin

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***Abstract* – Colloidal solutions of lead sulphide (PbS) quantum dots (QDs) stabilized in gelatine were obtained using a novel simple method. Nanoparticle sizes were tuned during the synthesis by means of reaction temperature. In addition, the effect of acidity of solution, of reagents concentrations and of S to Pb molar ratio was investigated. Transmission electron microscopy (TEM) and energy-dispersive X-ray spectroscopy (EDX) was used to characterize the size and composition of PbS nanoparticles. Also, the peculiarities of photoluminescence (PL) spectra of PbS QDs in gelatine were studied. It was observed that PL spectrum consists of a relatively narrow excitonic band with the maximum located at 0.95– 1.3 eV depending on the QDs size.**

***Index Terms* – colloidal solution, gelatin, lead sulfide (*PbS*), photoluminescence, quantum dots.**

I. INTRODUCTION

Specific properties of nano-sized materials and the progress of the last two decades in nanotechnology necessitates to face the task of finding methods of commercial production of different nanomaterials with controllable properties for various applications, including those based on nanocrystals.

Among important group IV–VI semiconductors, *PbS* QDs have attracted considerable attention owing to their especially small direct band gap (0.41eV) and larger excitation Bohr radius (18 nm) [1] and have been widely used in many applications such as photography, Pb^{2+} ion-selective sensors, IR detectors and solar absorbers [2–4].

Recently, these nanomaterials have received great attention for their promising use in medicine. A key issue in evaluating the utility of these materials is assessing their potential toxicity - due to their inherent chemical composition [1]. In addition, *PbS* QDs are an example of nanomaterials that have been shown to be useful as an alternative to luminescent dyes for biological imaging, due to their bright luminescence, narrow emission, broad UV excitation and high photostability.

So far various methods for the preparation of semiconductor QDs in liquid media have been proposed [3, 5, 6]. Most of them use different surfactants as stabilizers for QDs, thus determining their chemical and physical properties, such as solubility, aggregative and kinetic stability, as well as stability against photocorrosion; they can change the position of the optical absorption edge or activate/suppress luminescence.

In this work, we propose a novel easy method of the synthesis of *PbS* QDs in aqueous solutions of a natural polymer, gelatin, and present the results of our investigation of their optical properties affected by synthesis conditions such as concentration of reagents, germination and growth temperature, molar ratio *S/Pb* and *pH* of the solution.

The modification of the reaction of formation *PbS* QDs offers a possibility to obtain the QDs sized in the range of 2-20 nm; the size can be estimated from the excitonic bands in photoluminescence/optical absorption spectra within the range of 800-1500 nm.

II. MATERIALS AND METHODS

Materials. The materials used in this work such as sodium sulfide $Na_2S{\cdot}9H_2O$ (ACS reagent), gelatin powdered (Ph. Eur.) and lead (II) nitrate (ACS reagent) were purchased from Aldrich and used without further purification.

Synthesis of colloidal solution of PbS QDs.

In a typical experiment, preparation of colloidal solutions of *PbS* QDs stabilized with gelatin consists of three steps:

I) producing an aqueous solution of gelatin (0.1-20 % by mass) and lead (II) nitrate (10^{-4}-0.1 M): 1 *gr* of gelatin was dissolved in 10 mL of 0.1 M $Pb(NO_3)_2$ upon slight heating in a conical flask;

II) heating the solution up to the required temperature (in the range 20 ÷ 90 °C) while stirring;

III) adding to the solution obtained 1 mL of the aqueous solution of 10^{-3}-1 M Na_2S dropwise, keeping stirring at the temperature indicated. This step lasts about 5 min.

Optical characterization.

The photoluminescence (PL) emission spectra were investigated using a grating monochromator and a photodetectors (IR photomultiplier ФЭУ-62, for wavelengths λ<1.1μm and/or InGaAs photodiode – 1μm <λ < 1.6μm).

Taking into account the fact that the emission spectrum of *PbS* QDs is located in the near IR region [7], He-Ne laser (λ_{L1} = 633nm) and the second harmonic of YAG:Nd laser (λ_{L2} = 532 nm) were used as excitation sources.

The absorption spectra in the same region were recorded by means of Shimadzu UV-3600 spectrophotometer. In order to ensure that the PL emission corresponds to the radiative recombination of excitons, the comparison between the emission and absorption spectra was carried out [8].

III. RESULTS AND DISCUSSION

Photoluminescence properties of gelatin stabilized PbS nanoparticles.

The PL properties of gelatin stabilized *PbS* nanoparticles in different applications are investigated and described in several papers and books [9-11].

In this work the PL spectra of the colloids prepared have been recorded and the QDs sizes correlated to the position of

the spectral maxima.

The solutions of *PbS* nanoparticles exhibit clear exciton peaks and bright band-edge exitonic luminescence at room temperature located in the near-IR spectral range (Fig. 1). The PL broad bands are mostly attributed to the recombination of the carriers trapped in surface states of bare *PbS* QDs. These surface defects are associated with Pb^{2+} and S^{2-} vacancies (such as nonstoichiometric defects and dangling bonds), that can induce nonradiative transitions or radiative emission [12], resulting in the degrading of luminescence properties.

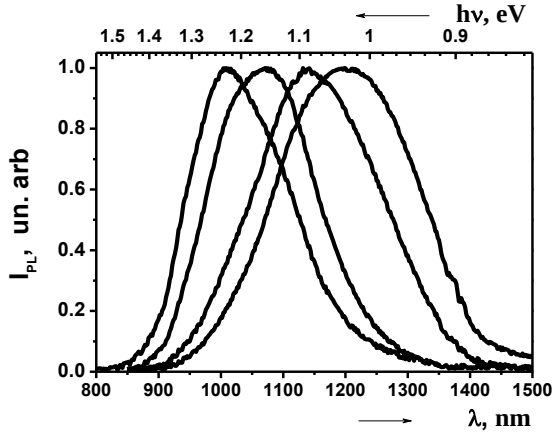


Fig. 1. Photoluminescence of PbS QDs synthesized in gelatin.

Generally, the PL of these QDs is intricate because it is sensitive to the synthesis conditions, crystalline sizes and shapes.

TEM analysis.

The particles sizes of the synthesized colloids were determined by TEM. The typical micrograph in Fig. 2 shows *PbS* QDs of about 4 nm in diameter coated with gelatin chains. This suggests that the core-shell products exhibit uniform sphere-shaped particles.

Fig. 3 shows the EDX spectrum of the synthesized *PbS* QDs in gelatin. The strong peaks for *Pb* and *S* in the spectrum confirmed the main components of the *PbS* QDs. EDX analysis also indicated the presence of copper (*Cu*) on the surface of *PbS* QDs, which was due to the copper substrate used.

Desirable changes in size of QDs in a broad range (2-20 nm) can be achieved by modifying the acidity of the solution, reagents concentrations, *S* to *Pb* molar ratio or the synthesis temperature. The changes in particle sizes were proved by the shift of the position of the maxima of excitonic luminescence spectra in the range 800-2000 nm.

Influence of gelatin concentration on PL properties.

The concentration of gelatin was varied in order to study its effect on the *PbS* QDs formed and on their optical properties.

In Fig. 4 the PL peak dependence on gelatin concentrations for the samples at ambient temperature are presented. The PL emission peaks are seen to shift to shorter wavelengths.

In our experiments, when the gelatin concentration was raised up to 12 – 20% a slight displacement of the maximum position of the band of excitonic PL towards the shorter wavelength was noticed, signifying a decrease of the average diameter of QDs.

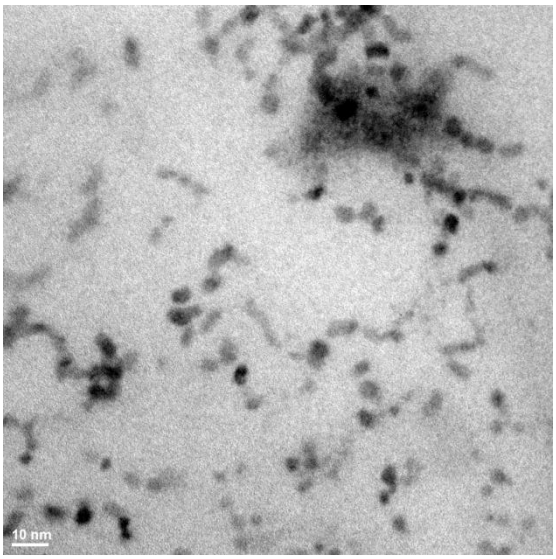


Fig. 2. TEM micrographs of *PbS* nanoparticles in gelatin.

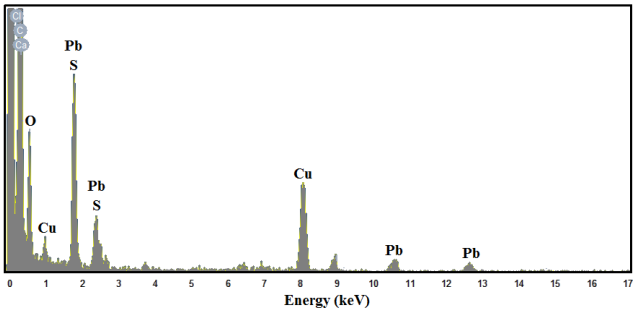


Fig. 3. EDX spectrum of the PbS nanoparticles in gelatin.

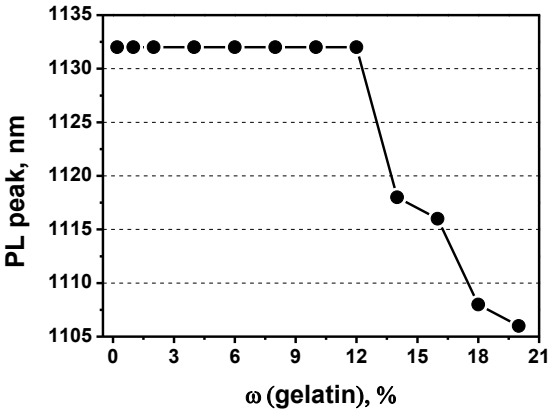


Fig. 4. PL emission peak dependence on gelatin concentration.

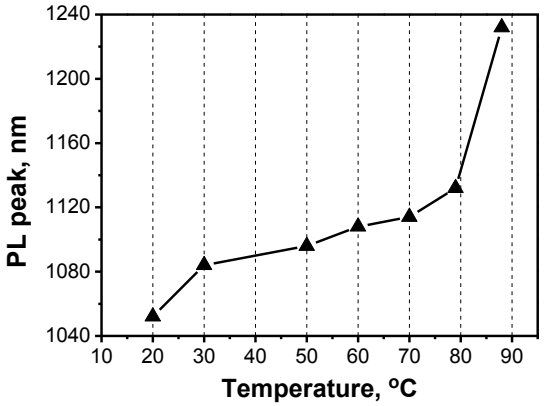
When the gelatin concentration was set in the range 0.5 - 12%, the maximum of the excitonic PL remained practically unchanged, which means that the final diameter of the particles was unaffected.

The results obtained might be interpreted by the increased efficiency of the passivation of surface states of the nanoparticles: greater concentrations of gelatine result in a larger number of chemical bonds between gelatine molecules and the surface atoms having dangling bonds. Besides, according to [13], gelatine immobilizes QDs, increasing their dipole interactions because of lower mobility.

Influence of the synthesis temperature on PL properties.

As can be seen in Fig. 5, with the raise of the synthesis

temperature from 20 to 90 °C, the maximum of the photoluminescence spectrum was found to become monotonously displaced from the lowest wavelength value of 900 nm to the highest of 1300 nm, by means of increasing the crystals diameter.



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ig. 5. PL emission peak dependence on reaction temperature.

Influence of *S* to *Pb* molar ratio on PL properties.

The growth of the ratio of *S:Pb* from 1:4 up to 4:1 leads, first, to the increase of the luminescence wavelength (crystal diameter), reaching the max. at the ratio 2:1, after which it starts to decrease (Fig. 6).

It is worthwhile mentioning that "better" synthesis conditions, in terms of narrower QDs' size distribution due to the improved separation of nucleation and growth stages, were found to lie in the region of smaller *S:Pb* ratios [14].

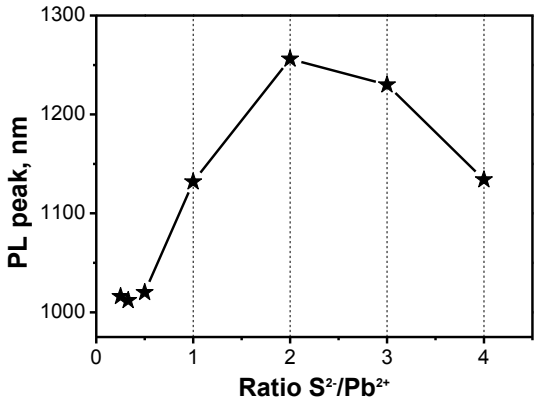

Fig. 6. PL emission peak dependence on S:Pb ratio.

Influence of pH solution on PL properties.

The experimental data presented in Fig. 7 show that the decrease of the solution *pH* from 13 to 4 did not result in a significant change in the dimensions of the produced QDs.

However, an increase of the crystals dimensions was observed at lower *pH*.

The method presented here has some advantages over other known synthetic procedures, namely:

- it is simple and fast;
- the final size of the QDs can be easily controlled;
- there is no need in complex and expensive equipment;
- it uses non-toxic and non expensive reagents;
- no harmful residues are formed and, last, but not least,
- the obtained nanocrystals are soluble in polar environments, such as water.

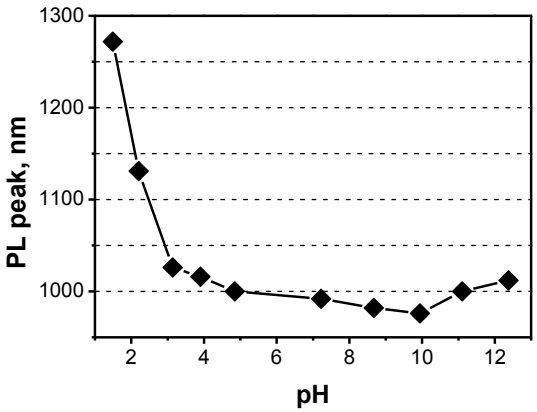

Fig. 7. PL emission peak dependence on solution pH.

IV. CONCLUSIONS

A novel easy method for the synthesis of colloidal lead sulphide nanocrystals in gelatin is presented. TEM studies showed that the sizes of QDs obtained were within 2 – 20 nm and EDX spectroscopy confirmed the elemental composition of nanoparticles. The sizes were tuned during the synthesis by modifying the acidity of the solution, reagents concentrations, *S* to *Pb* molar ratio and the synthesis temperature.

V. ACKNOWLEDGMENTS

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