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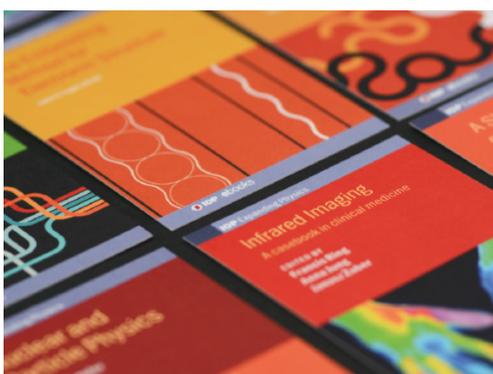
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Engineering the synthesis procedure for PbS nanosheets with controlled optical properties in the near-infrared region

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Abstract. This work discloses routes of obtaining two-dimensional PbS nanostructures by chemical synthesis methods. Using the techniques of absorption and luminescence spectroscopy, their optical characteristics are revealed. Special attention is paid to the evolution of nanoplates in a colloidal solution. The processes of growth and degradation of the structure of nanoplatelets, as well as the corresponding changes in the optical properties of nanocrystals are considered.

1. Introduction

There is currently a trend in Materials Science to pay closer look to the two-dimensional materials. That is especially important for optoelectronics since it aims for better compatibility with the existing device designs. In colloidal photonics this addresses two-dimensional analogues of well-proven semiconductor nanocrystals. For example, in the visible range, nanoplatelets and nanoribbons of cadmium chalcogenides thanks to their unique features, such as thickness-dependent optical transitions [1], rapid charge carrier cooling [2], and anisotropic electron-phonon interaction [3], have now replaced quantum dots for many applications [4,5]. A promising task is to obtain two-dimensional analogues for semiconductor nanocrystals of the near-IR range as well. Lead and mercury compounds are excellent for this purpose. In the previous years, numerous nanostructures of lead and mercury chalcogenides were reported [6] as well as their alloys [7] and core/shell structures [8]. Their practical applications are abundant and breath-taking [9,10]. However, the growth mechanisms and synthesis procedures of the two-dimensional nanostructures for these materials are in a certain way more complex and significantly less studied than for cadmium compounds [11,12]. Development of the efficient and reproducible synthesis protocols for lead sulfide nanoplatelets and nanosheets of the desired optical parameters, is thus a field in the urgent need for improvement. Such structures are in demand to enrich the creation of LEDs, solar cells, as well as the study of nonlinear effects in the near IR range [13]. In this work we demonstrate the reliable synthesis conditions for obtaining PbS nanosheets with two different exciton transition energies, look into their stability issues and their influence on the optical responses of nanostructures. Among our goals was also expanding the wavelength range available for two-dimensional structures to shorter wavelengths. Thus, the thinner structures described here are new to the family of PbS nanosheets and were never reported before.

2. Synthesis

PbS nanosheets were obtained using a procedure described in [14] with significant modifications for the smaller thickness. In a 50 ml three-neck flask a mixture of 10 ml diphenyl ether, 3.5 ml oleic acid and 860 mg of lead acetate trihydrate was prepared. The flask was kept under vacuum at 85 °C for 1 h, and



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then cooled to 35 °C under argon flow. At this temperature the 1.5 ml of chloroalkane (dichloromethane or chloroform) was added to the reaction flask. Subsequently the solution was heated under Ar atmosphere until it reached the reaction (65 or 90 °C). At this temperature sulfur precursor was injected as a solution containing 12 mg of thioacetamide, 930 μ l of trioctylphosphine and 100 μ l of dimethylformamide. The reaction mixture was kept at this temperature for 30 minutes in the case of dichloromethane and 7 minutes for chloroform, after which it was slowly cooled to room temperature. The reaction mixture was redissolved twice in double volume of toluene and centrifuged at 6000 rpm for 10 minutes.

3. Optical properties

It was determined experimentally that at the reaction temperatures in the ranges of 60-70 and 71-90 °C, two different populations of nanocrystals with constant optical responses are formed. For an accurate assessment of the optical parameters of two-dimensional lead sulphide nanocrystals, their electronic energy structure was characterized by absorption and photoluminescence spectroscopy. Detailed parameter values for four syntheses are given in Table 1.

Table 1. Spectral parameters of PbS nanoplatelets in CCl₄.

	T, °C	Abs. peak, nm	Abs. edge, nm	PL peak, nm	FWHM, nm	Stokes shift, nm
PbS1	90	1383	1510	1462	190	79
PbS2	75	1380	1520	1482	160	102
PbS3	69	1290	1380	1380	210	90
PbS4	65	1240	1380	1335	160	95

Typical spectra for two different populations of nanosheets represented by samples PbS1 and PbS4 are shown in Figure 1.

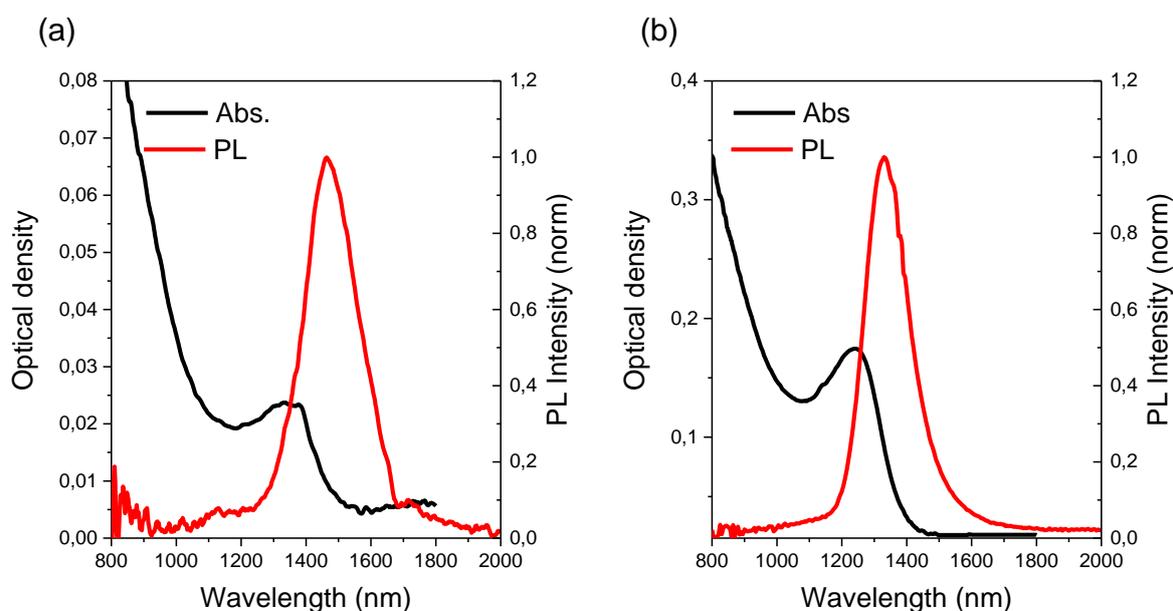


Figure 1(a, b). Photoluminescence (PL) and Absorption (Abs.) spectra of (a) PbS1 and (b) PbS4 nanosheets.

As can be seen from the graphs, the clearly defined edges of the absorption band at 1510 or 1380 nm with maxima at 1383 or 1240 nm overlap with the photoluminescence bands. The photoluminescence bands of nanosheets are characterized by maxima at 1462 nm and 1335 nm and full width at half maximum (FWHM) of 190 and 160 nm. Nanosheets PbS1 and PbS2 are in good accordance with published data for PbS nanosheets with thickness of 1.2 nm. Samples PbS3 and PbS4 correspond to thinner nanosheets that have not been reported before. Estimated size using the fitting curves is around 1.0 nm [14]. For each pair of the nanosheets the sample obtained at a lower temperature demonstrates narrower PL band and larger Stokes shift. That indicates the temperature conditions to be better suitable for nanocrystals of this particular thickness.

These results are fully consistent with the literature data for this class of nanoobjects. They demonstrate a number of fundamental differences from cadmium compound nanoplatelets, due to the different energy structures of nanocrystals having a zinc blende crystal structure in the case of cadmium compounds and a cubic salt one in the case of lead.

4. Morphology and degradation dynamics

Lead sulphide nanosheets present a certain difficulty in maintaining their stability. Without special measures, the stock solution degrades with the transition of nanosheets into quantum dots. The reason for this behaviour lies in the fundamental mechanisms of growth of two-dimensional nanocrystals. Cadmium chalcogenide nanoplatelets are formed during crystal growth due to the ongoing reaction of precursors [15]. In contrast, in the case of lead chalcogenides, nanosheet growth occurs by the directional attachment of grains or smaller islands formed by nanocrystal grains [11] with the subsequent rearrangement of surface atoms. The main difference of these structures from a well-studied self-assembled highly ordered superlattices lies in them being substrate-free, but more importantly in the formation of the homogeneous crystal structure of the nanosheets rather than a [16–18]. This process is easily reversible; therefore, for early samples, we observed the degradation of nanoplates into smaller clusters and individual nanocrystals. This process is illustrated on images from an scanning electron microscope (Merlin, Carl Zeiss).

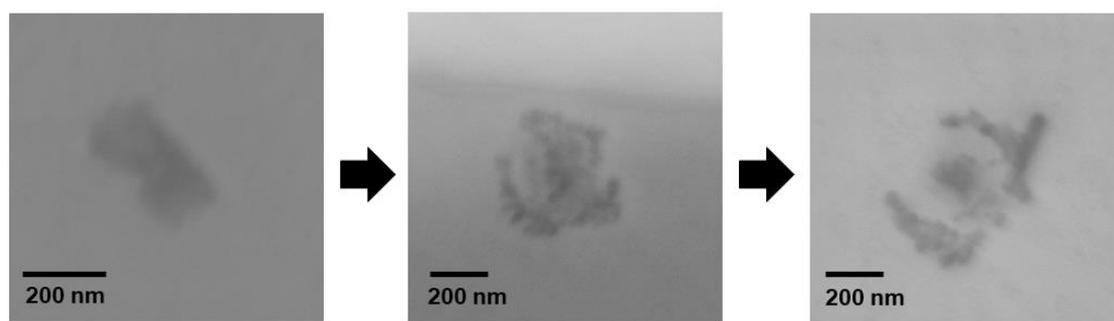


Figure 2. Images of nanosheets in PbS2 sample taken with an electron microscope, which reflect different stages of degradation of nanosheets.

Such a crucial change in the morphology of the nanocrystal leads to a change in the conditions of quantum confinement and, therefore, the optical responses. The graphs on the Figure 3 (a) show the spectra of PbS nanosheets on day 1 right after preparation and taken after 7 days. By this time, as represented on Figure 3 (b) there can be almost no nanosheets found in the sample, only small nanocrystals 8-9 nm in diameter and their 60 nm large aggregates. The solution to this problem lays in finding the right storage environment. Transferring nanosheets to carbon tetrachloride solution,

preserves the position of the PL band, as can be seen from Figure 3 (c). The contribution to the PL from quantum dots, indicating their amount, has grown, but on a negligible scale.

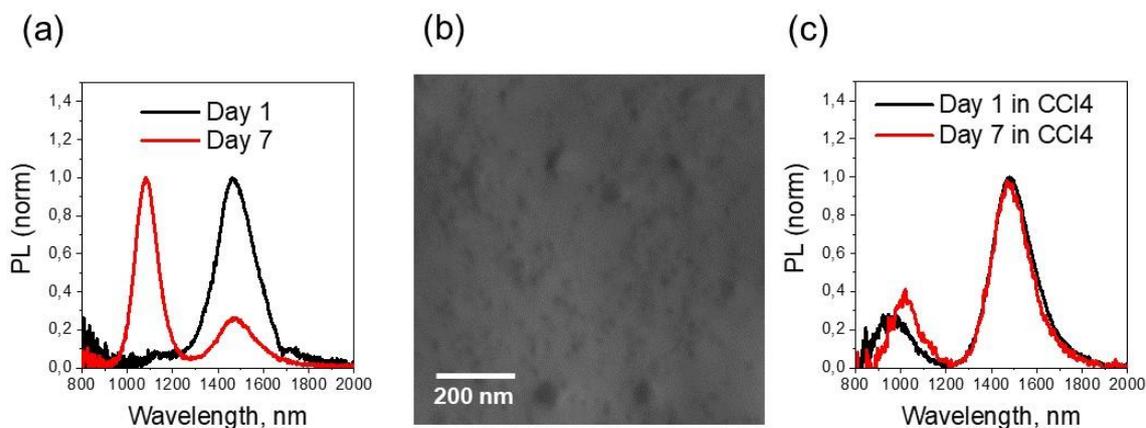


Figure 3. a) The photoluminescence spectra of the stock unwashed solution of PbS1 nanosheets on the first day after the synthesis and a week later; b) Image of nanostructures in the stock solution of the PbS1 sample after 7 days of storage; c) Spectra of a sample of PbS nanosheets, which were redissolved in carbon tetrachloride taken at the time of transfer and 7 days after it.

5. Conclusion

Samples of nanosheets in a colloidal solution were obtained by organic synthesis methods which allowed their optical properties to be tuned in accordance with study goals. Their optical properties were studied using absorption and luminescence spectroscopy techniques and suggest promising nanomaterial for IR range. We also showed dynamics of the morphology degradation of nanostructures in a sample that was carried out by means of electron microscopy and linked it with a change in their optical responses. Using the information obtained in this work, it is possible to create high-quality nanostructures with controlled optical properties in the near-IR range, which would be stable in a colloidal solution and present great interest for solving various tasks of modern optoelectronics and photovoltaics.

Acknowledgements

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