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CONDENSED-MATTER SPECTROSCOPY

The Influence of the Polymer-Stabilizer Molecular Weight on the Spectral Luminescence Properties of Composite Sols and Coatings Containing PbS Quantum Dots

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Abstract—The influence of the polyvinylpyrrolidone (PVP) molecular weight on the stability and spectral luminescence properties of sols of lead sulfide nanocrystals and the related composite coatings has been studied. It is shown that the spectral properties of PbS sols stabilized with low-molecular (PVP) and the related coatings are determined to a great extent by the formation of large particle aggregates in these materials and, accordingly, high level of light scattering. It is effective to use low-molecular PVP for preparing powder materials containing PbS quantum dots (QDs), because it allows one to perform fast powder precipitation and form small semiconductor particles. High-molecular PVP provides high aggregative and sedimentation stabilities of semiconductor nanocrystal sols. This polymer is effective for use in preparing stable QD sols and homogeneous coatings transparent in the visible spectral range.

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INTRODUCTION

Lead-sulfide quantum dots (QDs) can be considered a promising material for photonics, medicine, solar power engineering, and development of sensors [1–11]. It is well known that the optical properties of QD-containing materials depend on the concentration and size of nanoparticles and their near environment, which often plays the role of a stabilizer impeding the uncontrolled growth and aggregation of particles.

Liquid colloidal chemical methods [3, 4, 10, 11] are widely used for synthesizing semiconductor QDs. The synthesized suspensions contain semiconductor nanoparticles stabilized with organic compounds and dispersed in the liquid phase.

Organic compounds and polymers, which are present in the reaction mixture during the synthesis, play an important stabilizing role thus providing the formation of nanoparticles and impeding their coarsening and aggregate formation. Polyvinylpyrrolidone (PVP) has been widely applied for stabilizing QD suspensions of different chemical compositions: PbS [3, 4, 10, 11], CdSe [12], ZnS [13–16], and CdS [17–19].

PVP of varying molecular weight was used in [3, 4, 10–19] to stabilize QDs of different chemical compositions. The methods for synthesizing and stabilizing QDs, as well as the experimental conditions, were different in these studies. Therefore, it is difficult to compare the results obtained in different publications and estimate the role of the PVP molecular weight in the QD stabilization.

The purpose of this study was to analyze the influence of the PVP molecular weight on the spectral luminescence properties and stability of sols of lead sulfide nanocrystals and the related composite coatings.

EXPERIMENTAL

We synthesized sols and composite coatings containing PbS QDs and stabilized PVPs with different molecular weights and compared their stabilities and spectral properties. These materials were synthesized based on the same technique and had an identical chemical composition expressed in weight percent.

The total number of structural groups in PVP molecules that can interact with nanoparticles is identical for PVPs with different molecular weights at the same PVP weight content in solutions. Comparison was performed using different PVP contents. Each solution pair was characterized by an identical PVP weight content but different polymer molecular weights. The

Chemical compositions of the PbS sols stabilized with PVPs of different molecular weights

No.	Chemical composition, wt %							PbS concentration, c_{PbS} 10^3 mol/L	Molar ratio $k = [\mathrm{PbS}]/[\mathrm{PVP}]$
	PbS	Propanol-2	H_2O	$Pb(NO_3)_2$	$NaNO_3$	PVP-L	PVP-H		
C1	0.07	34.03	64.95	0.03	0.05	–	0.87	2.5	3
C2	0.07	34.03	64.95	0.03	0.05	0.87	–	2.5	433

PVP-L is low-molecular polyvinylpyrrolidone, and PVP-H is high-molecular polyvinylpyrrolidone.

chemical compositions of the PbS sols stabilized with PVP additives of different molecular weights are listed in the table.

In this study, we used $Pb(NO_3)_2$ (concentration 0.005 M) and Na_2S (concentration 0.13 M) aqueous solutions as the initial components for the QD synthesis. Solutions of high-molecular PVP (PVP-H, M_s = 1300000) or low-molecular PVP (PVP-L, M_s = 10000) in propanol-2 were added to the reaction mixture to stabilize metal-sulfide nanoparticles. The liquid phase of the sol obtained upon mixing the initial solutions was a mixture of propanol-2 and water at the volume ratio of 1 : 1.7.

The as-prepared sols were used for depositing coatings on the surface of alkali silicate glass samples. The coatings were deposited by immersing the glass samples into the sols with subsequent extraction and drying for 24 h at room temperature. The chemical composition of the obtained composite coatings included PVP modified by lead-sulfide nanocrystals and a small amount of the residual liquid phase.

The absorption spectra of the sols and composite coatings were measured on a Shimadzu UV-3600 spectrophotometer in the range of 200–2000 nm.

The material photoluminescence was excited using HPR40E-50UV (emission-band maximum is at 370 nm) and HPR40E-43KR (625 nm) LEDs. The luminescence spectra were analyzed on an SDH-IV spectrometer (SOLAR Laser Systems, Belarus).

The coating morphology and inhomogeneities were investigated at the level of several units and tens of micrometers using a Mikmed-6 optical microscope (LOMO, Russia).

RESULTS AND DISCUSSION

Figure 1 shows the light-attenuation spectra of as-prepared (kept for 30 min after synthesis) sols C1 and C2 (curves *1* and *2*, respectively). The spectrum of sol C1 stabilized with PVP-H is a curve monotonically decaying with an increase in the wavelength. A similar spectrum shape was previously observed in [4, 10, 11], which may be due to the combination of light absorption by PbS nanoparticles having a wide size distribution [5] and light scattering by the colloidal solution.

The spectrum of sol C2 stabilized with PVP-L exhibits much higher light attenuation in the visible spectral range, which can be explained as due to the low stability of this colloidal solution and rapid formation of large particle aggregates therein, which caused the significant light scattering.

Long PVP-H chains separate nanoparticles much more efficiently in comparison with PVP-L molecules, thus hindering the formation of large inhomogeneities in the sol. It is also well known that the viscosity of polymer solutions (as well as the colloidal-solution kinetic stability to sedimentation) significantly increases with an increase in the size of polymer molecules [20]. Therefore, the use of PVP-H facilitates the QD stabilization in sols.

The appearance of these sols retained for 2 h after the synthesis is shown in Fig. 2. It can be seen that sol C1 is a homogeneous slightly opalescent liquid, whereas sol C2 is inhomogeneous, and individual precipitating dark particles can be observed therein.

Figure 3 shows the absorption spectra of the glass samples with composite PbS/PVP coatings prepared from sols C1 and C2 (curves *1* and *2*, respectively). It can be seen that the coating made of sol C1 is characterized by fairly high transparency in the visible spectral range (curve *1*). The transparency of the coating

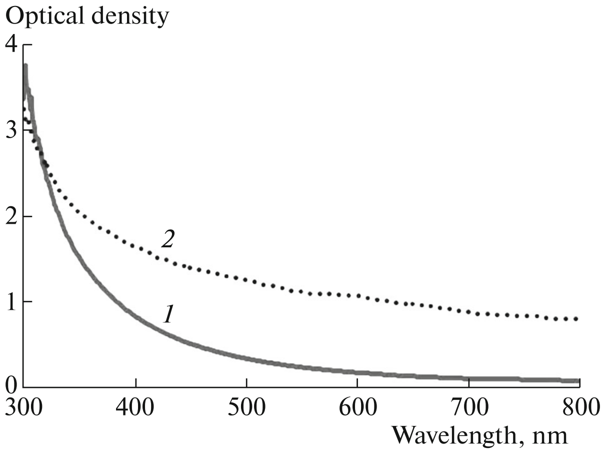

Fig. 1. Light-attenuation spectra of sols (*1*) C1 and (*2*) C2 kept for 0.5 h after the synthesis.

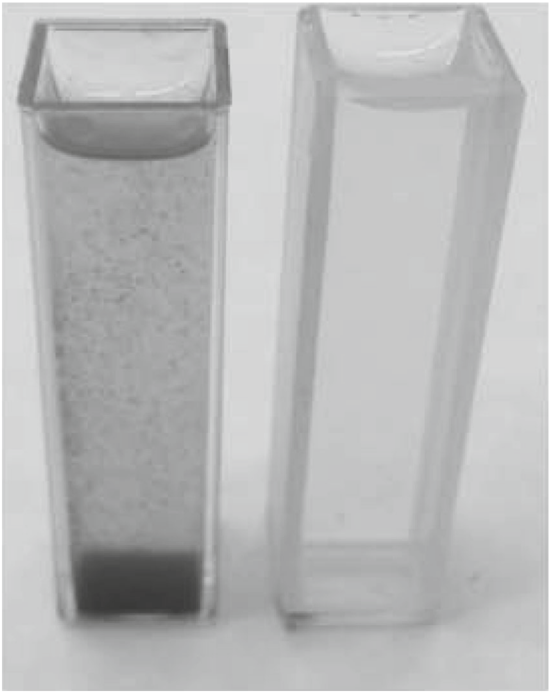

Fig. 2. Photographs of sols C1 (on the right) and C2 (on the left) kept for 2 h.

made of sol C2 stabilized with PVP-L is much lower (curve *2*).

Figure 4 demonstrates micrographs of the surface of the composite coatings prepared from sols (a) C1 and (b) C2 on the glass surface. It can be seen that the coating made of sol C1 stabilized with PVP-H is characterized by fairly high homogeneity and contains no large inclusions. On the contrary, the coating made of sol C2 contains large particle aggregates and its homogeneity is much lower. This fact suggests that the higher light attenuation observed for the coating made of sol C2 is determined by the presence of these large inhomogeneities in the coating structure.

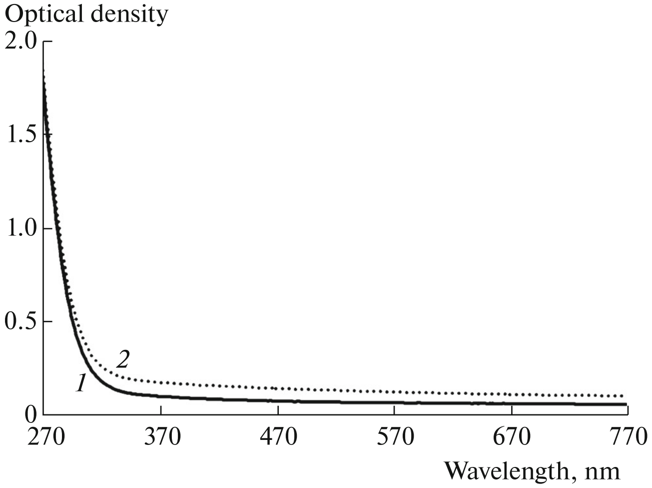

Fig. 3. Light-attenuation spectra of the samples with the composite PbS/PVP coatings made of sols (*1*) C1 and (*2*) C2.

Figure 5 shows the photoluminescence spectra upon excitation of the glass samples with coatings made of sols (*1*) PbS31 and (*2*) PbS32 by light with wavelengths λ_{ex} = (a) 370 and (b) 625 nm. The intense luminescence in the near-IR range was observed under irradiation of the samples with coatings by both blue (370 nm) and red (625 nm) light. The specific features of photoluminescence of PbS/PVP nanocomposites were studied in detail in [4, 10, 11]. The shape of the spectra presented in Fig. 5 is similar to that of the spectra recorded in these studies. The proximity of the luminescence-band peaks for the coatings suggests, based on [8, 21], that the sizes of PbS nanoparticles only slightly differ in the coatings made of the sols stabilized with PVP-H and PVP-L. It is noteworthy that the luminescence spectra of the coatings made of sols C1 and C2 differ only slightly. This fact suggests that the structures of PbS/PVP emission centers in the coatings are close.

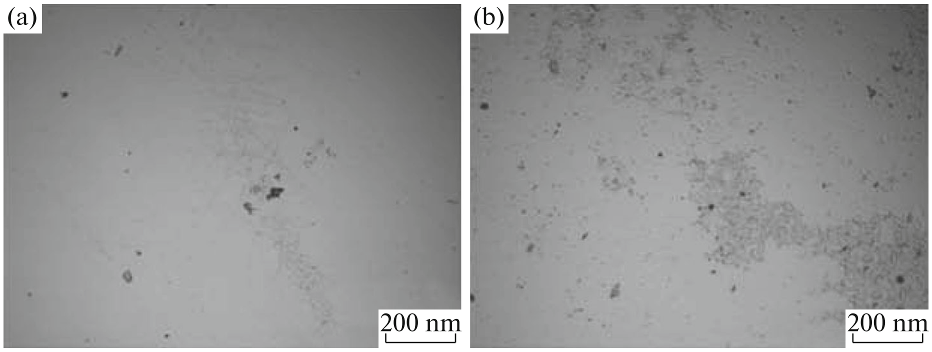

Fig. 4. Micrographs of the surface of the composite coatings prepared from sols (a) C1 and (b) C2 on the glass surface.

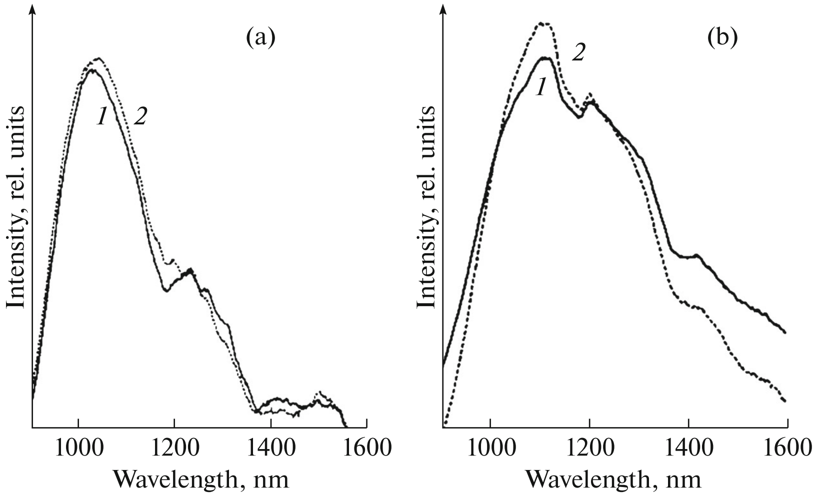

Fig. 5. Photoluminescence spectra (λ_{ex} = (a) 370 and (b) 625 nm) of the samples with coatings made of sols (*1*) C1 and (*2*) C2.

Based on the obtained experimental data, we can conclude that the size of lead sulfide nanoparticles forming in the solution and their luminescence properties weakly depend on the molecular weight of the polymer stabilizer. At the same time, the weak stabilizing ability of PVP-L causes the rapid formation of large particle aggregates in the sol, which determine the significant light scattering and low sedimentation stability. These large particle aggregates are retained in the structure of the coating made of this sol, which causes its low homogeneity and high light attenuation.

CONCLUSIONS

Based on the obtained experimental results, we can conclude the following.

The spectral properties of PbS sols stabilized with PVP-L and the related coatings are determined to a great extent by the formation of large particle aggregates in these materials and, accordingly, the high level of light scattering. It is expedient to use PVP-L for preparing powder materials containing PbS QDs because it allows to perform rapid powder precipitation and obtain small semiconductor particles.

PVP-H provides high aggregative and sedimentation stabilities of semiconductor nanocrystal sols. This polymer is effective for use in preparing stable QD sols and homogeneous coatings transparent in the visible spectral range.

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