Evolution of CdS:Mn nanoparticle properties caused by pH of colloid solution and ultrasound irradiation

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The effects of pH value and precursors concentrations in the growth solution as well as of ultrasound irradiation on the properties of CdS:Mn nanoparticles in PVA matrix are studied. Analysis of the photoluminescence spectra indicates that the increase of the pH value in the growth solution leads to the increase of the density of surface electron states that participate in radiative transitions and to the enlargement of CdS:Mn nanoparticles.

We discuss a stabilization of the sizes of CdS:Mn nanoparticles at pH=6 and change of nanoparticle size with decreasing pH value at elevated concentrations of ions HS⁻. It is shown that in the ultrasound-treated samples the size of the particles does not depend on pH value. The effects of ultrasound result primarily from acoustic cavitation. It is demonstrated that the action of two external factors (the value of the medium pH and ultrasound treatment) on the characteristics of nanoparticles is correlated.

1 Introduction Nanocomposites such as polymer/semiconductor nanoparticles have been intensely studied during last decades due to their quantum-dimensional properties and prospective applications. Combined control over the sizes, surface properties and aggregation of nanoparticles permits to obtain high-quality low-dimensional materials, opening up new possibilities of their use in optics, electronics, biology [1, 2].

The production of II-VI semiconductor nanoparticles with predicted physicochemical properties remains a challenge. In order to minimize the effect of uncontrolled factors the nanoparticles can be covered with the layers of organic and inorganic substances [3, 4]. Organic passivation is often reversible and incomplete. In addition, the largely mismatched core/shell structures may result in the formation of defects that cause a degradation of optical properties of nanoparticles [5, 6].

One of the effective trends of nanotechnology development is to use external factors that permit to control the growth process and modification of nanostructures. Examples of the influence of such factors as pressure, pH of the medium, where the synthesis occurs, X-ray irradiation, high-energy electron irradiation have been investigated [7-11].

It has been ascertained [12] that the specific feature of the action of ultrasonic vibrations on the qualitative and quantitative characteristics of nanoparticles is a continuous formation and collapse of bubbles within a static fluid. It has been established that in the process of bubble collapsing in water the temperature reaches the values 2000-4000 °C and pressure 100-400 atm [13].

Here we report the influence of the precursors concentration, pH values, and ultrasound (US) treatment on the properties of the nanocomposite polyvinyl alcohol (PVA) / CdS:Mn nanoparticles.

2 Experimental CdS:Mn nanoparticles were obtained at room temperature by using chemically pure sodium sulfide, cadmium and manganese chlorides as the precursors. The synthesis took place in 5% aqueous solution of PVA which played the role of a stabilizing agent.

The physicochemical properties of nanoparticles were controlled by variation of pH of colloid solution within the range of 4-6 as well as by US treatment of the colloid during 30 min. Frequency of ultrasonic irradiation was kept 22 kHz. The synthesis occurred under the conditions of an excess of Cd^{2+} ions. The films of the PVA/CdS:Mn nanoparticles composite were formed by adsorptive dessication method. For this purpose the colloid solution was transferred to glass Petri dishes which were placed in a pressure-tight vessel that contained an absorbent. The temperature of drying was 20 ^{o}C.

The photoluminescence (PL) spectra were measured using the grating spectrometer with a spectral resolution of 0.5nm and LED source (λ=375 nm) for excitation at room temperature.

3 Results and discussion The PL spectra of nanocomposites PVA/CdS:Mn nanoparticles obtained at various synthesis conditions are shown in Figs. 1-3. All spectra can be pretty well fitted by four Gaussian curves peaking at ~ 430 nm, ~470 nm, ~565 nm, and ~ 625 nm (see the insert in Fig. 1). Relative intensities of the bands depend on the conditions of synthesis (concentration of precursors, values of pH) and post-synthetic US processing. The band at ~470 nm is the near-band-edge luminescence. The bands at ~565 nm and at ~625 nm correspond to the transitions involving d-electrons of Mn^{2+} ions and recombination via surface localized states, respectively. The weak high-energy band at ~430 nm arises due to radiative transitions in PVA [14,15].

Figure 1 shows the influence of the pH value of the colloid solution on the PL spectra. It is seen that the increase in the pH leads to a decrease in the ratio of the 470 nm PL band intensity over the 630 nm PL band intensity (I_{470}/I_{630}). This indicates that the density of surface electron localized states that participate in the radiative transitions increases. It can be caused by the adsorption of OH^{-} ions on the surface of CdS:Mn nanoparticles. Moreover, with the increase of pH, the spectral position of the

near-band-edge PL band is shifted to longer wavelengths thus pointing to the enlargement of the CdS:Mn nanoparticles and surface terminations, such as OH^{-} [16]. This shift can be related to:

i) An elevated concentration of OH^{-} ions. It increases from $1 \cdot 10^{-10}$ mol·l^{-1} at pH=4 to $1 \cdot 10^{-8}$ mol·l^{-1} at pH=6.0.

ii) A change of a sulphurizing agent concentration. It is known that in aqueous solutions Na_2S is hydrolyzed, the products of hydrolysis being either HS^{-} ions or H_2S molecules, depending on the pH value. Calculations show that the ratios of equilibrium concentrations of sulphurizing agents in an aqueous solution of Na_2S at pH=4 are equal to $[H_2S]:[HS^{-}]:[S^{2-}]=1000:1:(2,5 \cdot 10^{-7})$, whereas at pH=6 $[H_2S]:[HS^{-}]:[S^{2-}]=10:1:(2,5 \cdot 10^{-5})$. Since the concentration of sulfide-ions is the lowest, real sulphurizing agent are the ions HS^{-}, whose concentration increases with pH. At low HS^{-} concentrations the rate of CdS seeds grown is low while at highest HS^{-} concentrations the growth rate increases and, as a result, the average diameter of nanoparticles increases as well.

iii) An effect of pH on the solubility of nanoparticles. An equation that describes the dependence of molar solubility S_{CdS} on pH, derived on the basis of the theory of heteroge-
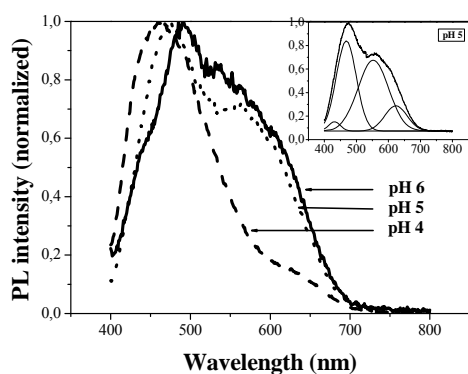
Figure 1 Photoluminescence spectra of composite PVA/CdS:Mn nanoparticles synthesized at different pH values (Na_2S concentration is $0.5 \cdot 10^{-2}$ mol·l^{-1}).
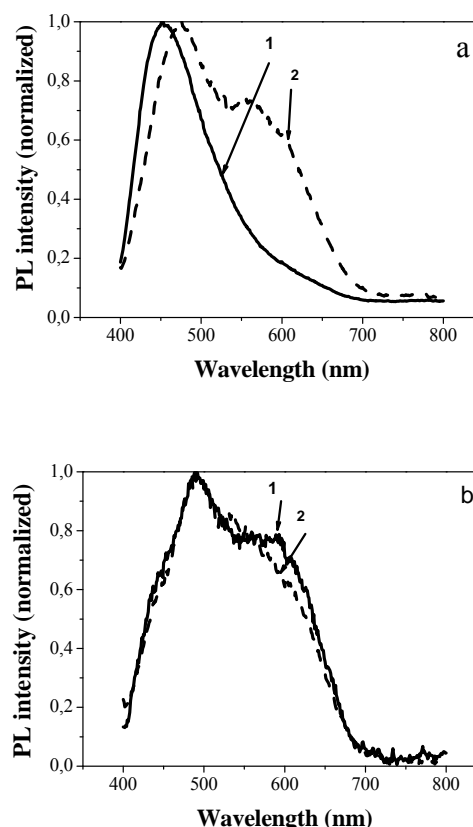
Figure 2 Photoluminescence spectra of composite PVA/CdS:Mn nanoparticles synthesized at pH = 5 (a) and pH = 6 (b). Curves 1, 2 correspond to Na_2S concentrations of $0.5 \cdot 10^{-3}$ mol·l^{-1} and $0.5 \cdot 10^{-2}$ mol·l^{-1}, respectively.

neous equilibria using the product of solubility of cadmium sulfide, assumes the form:

$$lgS_{CdS}=-4{,}105\text{-}pH, \qquad (1)$$

i.e., the higher the pH the lower the solubility.

The effect of Na_2S precursor concentration on the PL properties of CdS:Mn nanoparticles is shown in Fig. 2(a,b). It is seen that the increase of Na_2S concentration influences the size and surface states of the particles differently, depending on pH of the colloidal solution. Indeed, at pH=5 the increase of Na_2S concentration leads to the increase of both average particles size and surface states density; at pH=6 the spectral position of the band at 470 nm in the PL spectrum does not change with the growth of the Na_2S concentration, although all the conditions for their enlargement (elevated concentrations of ions HS^- and OH^-) are fulfilled. The observed stabilization of the sizes of CdS:Mn nanoparticles at pH=6 may be due to the decrease of the concentration of Cd^{2+} ions owing to a formation of hydroxocomplexes $[Cd(OH)]^+$ and $[Cd(OH)_2]^0$ which are less reactively capable and are characterized by considerably lower coefficients of diffusion.

The influence of US irradiation is shown in Fig. 3. It is seen that in the US-treated samples the particles size and surface states density do not depend on the pH value (see Fig.3) contrary to the behavior of the untreated samples (Fig.1). The effect of US derives primarily from acoustic cavitation. It is known that cavitation in the fluid-solid system is a source of highly energetic phenomena [13]. Cavitation in fluids may exert a considerable effect on the surface of nanoparticles. The effect of microcurrents, shock waves and interparticle collisions on the chemical composition and physical morphology of nanoparticles may considerably enhance the chemical reactive activity of the inorganic phase and the absorptive capacity of a polymer.

For pH = 5 and pH = 6 US-treated samples, the PL band edge emission position (Fig. 3), located at lower wavelength compared to the untreated sample ones (Fig. 1) and then corresponding to nanoparticles of smaller size, can be explained by the following: i) Destruction of the ab-

sorptive layer around the nanoparticles caused by the desorption of OH^- ions from the surface of nanoparticles by ultrasonic treatment; ii) Change of nanoparticles dissolution depending on pH (see Eq. (1)) and stimulation by the action of US vibrations.

Note, that the action of two external factors (decrease of the pH value and US treatment) on the characteristics of nanoparticles is correlated.

An analysis of the findings obtained and their comparison with the available data indicate that the effect of US treatment on the properties of PVA/CdS:Mn nanoparticles composites is a result of mechanical action of ultrasonic waves that changes the structure of the adsorptive layer around the nanoparticles, whereas the effect of pH is implemented via the change of OH^- and HS^- ions concentrations in the reactive medium.

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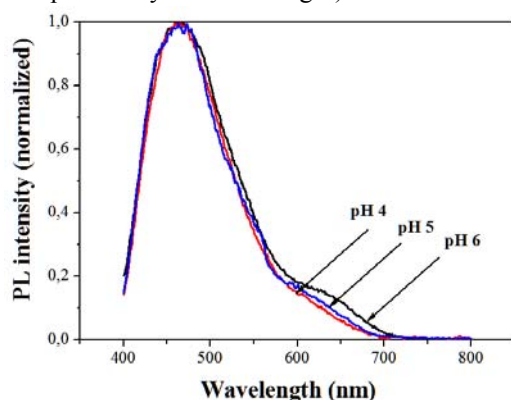
Figure 3 Photoluminescence spectra of composite PVA/CdS:Mn nanoparticles after US irradiation. Na_2S concentration is $0.5 \cdot 10^{-2}$ mol·l^{-1}.