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Role of the host polymer matrix in light emission processes in nano-CdS/poly vinyl alcohol composite

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ABSTRACT

Participation of a polymeric media in light-emitting processes of composite nano-CdS/polyvinyl alcohol is studied by probing different absorption-emission routes via adjustment of excitation wavelengths. It is shown that the polymeric constituent of the composite contributes chiefly to the photoluminescence excitation processes via absorption and excitation transfer to the embedded CdS nanoparticles while the composite emission occurs mostly within the nanoparticles.

1. Introduction

Polymer/nanoparticles composites are rapidly developing functional materials attractive for a large variety of applications in the fields of photonics, sensorics, biotechnologies, etc. [1]. Polymers, loaded with semiconductor nanoparticles (NPs), acquire additional features obtained from combining intrinsic advantages of polymers with size-dependent properties of NPs. In particular, nanocomposite CdS/polyvinyl alcohol (PVA) is the subject of increasing interest. PVA is a widely used polymer; its numerous applications range from textile and metallurgical industry to medicine and fine biotechnologies [2]. It is colorless, flexible, low-cost, and bio-degradable. This polymer provides a stable matrix to host nanocrystals and, being transparent in the visible range, is suitable for various optical studies and applications. As a part of the composite, CdS NPs allow wavelength tuning of visible light emission that makes the material a promising candidate for applications in light-emitting devices.

In view of the described attractive features, the system CdS/PVA has been extensively studied using photoluminescence (PL) spectroscopy that was proved to be one of the most convenient methods for this purpose; see, e.g. [3,4]. The majority of previous studies were focused on intrinsic PL of NPs while only few papers discussed the participation of the host polymer in the processes of light emission and excitation [5,6]. However, it should be noted that the PVA matrix is not a mere support for NPs. While the intrinsic highest occupied molecular orbital (HOMO)-lowest unoccupied molecular orbital (LUMO) gap of the pure PVA corresponds to the ultraviolet C range, commercially available materials always contain some amounts of radicals and chromophore groups. These imperfections can absorb and emit light in the long-wave ultraviolet A or even in the visible ranges [7–9] and, thus, can contribute to the overall optical properties of the composite.

In the present work we study the participation of the polymer matrix in the PL emission of the CdS/PVA nanocomposite as a whole. For this purpose we have chosen two excitation wavelengths which, on the one hand, provide excitation of either the lowest or very high excited states in NPs, and on the other hand, are absorbed by different chromophore groups in the polymer.

2. Experimental details

2.1. Synthesis of the CdS/PVA composite

Colloidal CdS NPs were synthesized in a water solution of PVA (with no more than 4 wt.% of acetate groups, pH 5–8) using $CdCl_2$ and Na_2S as precursors for particles growth. Molecules of PVA served as capping agents that restricted the size of NPs during the growth. Concentrations of $CdCl_2$ and Na_2S salts in the solution, its pH values, and sequences of synthesis steps can be found in [10]. All synthesis steps were performed under ambient conditions.

The method yielded colloidal solutions of CdS NPs that were further used to form solid nanocomposite films by drying in a pressure-tight vessel that contained an absorbent. The temperature of drying was 300 K.

2.2. Characterization techniques

Optical absorption measurements were carried out at 300 K using a deuterium lamp DDS-30 and a MDR-23 monochromator. PL emission

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was excited by a mode-locked Ti:sapphire pulsed laser that was operated at two wavelengths — 250 nm (4.96 eV) and 415 nm (2.98 eV). The pulse repetition rate was 80 MHz. Time-integrated PL spectra as well as luminescence decays were recorded at 200 K using a streak-camera system equipped with a 0.5 m monochromator. The response time of the system was about 20 ps. During the PL measurements the samples were kept in chemically inert helium atmosphere. The temperature of measurements was 200 K. This temperature was low enough to prevent temperature quenching of a red PL band of NPs [11].

Transmission electron micrographs (TEM) were recorded using a high resolution FEI Tecnai G2 200 keV FEG instrument. TEM samples were prepared by deposition of colloidal particles suspended in ethanol on 200 mesh copper grid.

3. Experimental results

3.1. Nanoparticles size

Fig. 1 shows, as an example, the representative transmission electron micrograph of CdS nanoparticles. It is seen that NP sizes are quite dispersed and that the NPs are not spherical. The average diameter of nanoparticles is equal to 5.4 ± 0.4 nm.

3.2. Absorption of PVA and CdS/PVA

Fig. 2 shows absorbance spectra measured within the ultraviolet–visible spectral range from the unloaded host polymer, nanocomposite CdS/PVA and single crystalline CdS. All structures have similar thicknesses of 100 ± 10 mkm. It is seen that the HOMO–LUMO absorption edge of PVA lies at much higher energies than the absorption edge of the composite. Keeping in mind that the absorption edge of the composite is predominantly determined by light absorption in CdS nanoparticles that are embedded in PVA one can state that the polymer matrix presents a confining potential for charge carriers within the CdS NPs (to be discussed below, see Fig. 5). This statement is further supported by the observation that the absorption edge of CdS/PVA lies at higher energies as compared with the one of bulk CdS. These point to the confinement-related increase of the band gap in the semiconductor NPs. Due to the wide dispersion and non-spherical shapes of NPs, no distinct absorption peaks from the CdS NPs can be resolved in the absorbance spectrum of CdS/PVA.

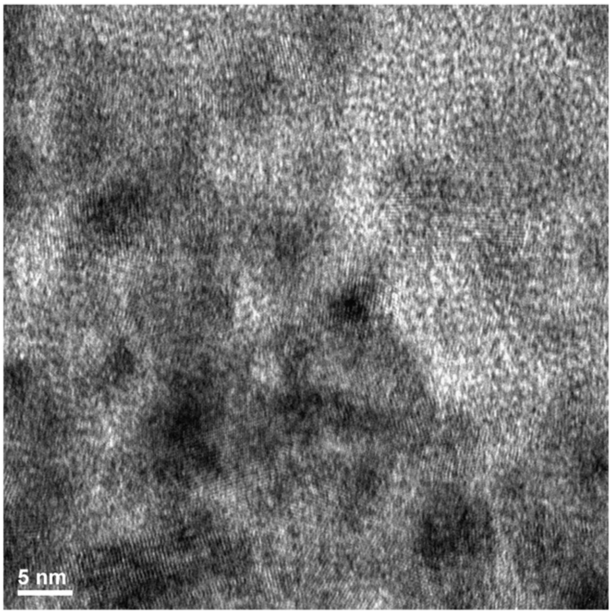

Fig. 1. Transmission electron micrograph of CdS nanoparticles.

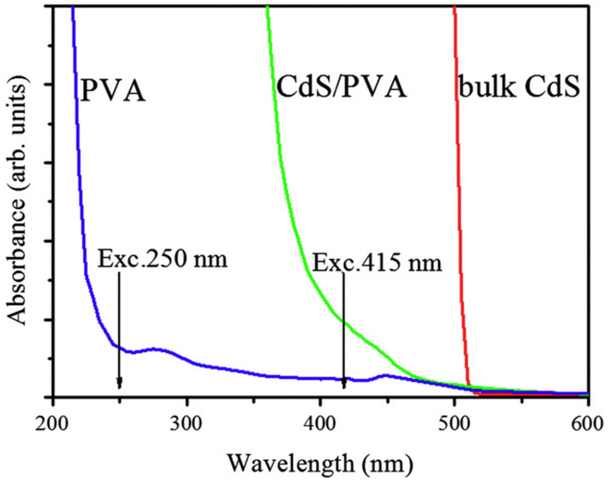

Fig. 2. Optical absorbance spectra of the unloaded PVA, nanocomposite CdS/PVA and bulk CdS crystal. The arrows indicate the wavelengths used for PL excitation.

Two wavelengths, i.e. 250 nm and 415 nm, were chosen for the PL excitation as marked by the arrows in Fig. 2. The former lies at the high-energy edge of the absorption band of carbonyl groups in the unloaded PVA (centered at ~280 nm [12]) and also corresponds to strong absorption into the higher laying excited states of the CdS NPs. The latter matches absorption transitions between the ground and low laying excited states of the CdS NPs and a weak absorption background of the unloaded PVA.

3.3. Time-integrated PL

Fig. 3 shows time-integrated PL spectra of PVA (a) and nanocomposite CdS/PVA (b) measured at two excitation wavelengths (415 and 250 nm). At both excitations, a single PL band is observed for the unloaded PVA matrix (Fig. 3a). The PL maximum position shifts, however, from 450 nm to 515 nm when the excitation wavelength (λ_{exc}) is changed from 250 nm to 415 nm. The spectrum of the nanocomposite, on the other hand, consists of two PL bands (Fig. 3b) in the green and red spectral ranges, and no traces of the polymer emission are seen. Spectral positions of both PL bands and their relative intensities do not depend on λ_{exc}, which implies that the same radiative centers are responsible for the emission observed at both excitations.

The observed spectrum is quite common for CdS nanocrystals [11,13–17] and has been observed for CdS NPs in various media, such as colloidal solutions, various polymer matrices (including PVA), and glass.

The “green” and “red” PL bands in colloidal nanoparticles are typically ascribed to the emission of shallow [18,19] and deep traps [15], although the exact origin of these bands remains unclear. Our time-decay results (see Fig. 4b, c) support the opinion that these PL bands have different origins because the characteristic PL decay times differ by orders of magnitude. Thus, in what follows we will regard these bands as being from two different sets of levels related to NPs.

3.4. PL decays

Fig. 4 shows experimentally measured decays of the PVA emission (a) as well as of the “green” (b) and “red” (c) PL bands in the nanocomposite CdS/PVA (the solid lines). It is seen that, in general, the change of the excitation wavelength causes opposite trends in the PL decays in two materials. Specifically, whereas an average decay rate increases in PVA when the excitation wavelength is changed from 250 to 415 nm, the decays become slower in the CdS/PVA under the same change of λ_{exc}. It should be noted that the shape of the PL bands both in PVA and CdS/PVA does not change during the decay.

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