# Letters to the Editor

## Template synthesis of nanocomposite CdS with nonlinear optical properties

*I. M. Nassar,[a] I. G. Galyaviev,[b] G. M. Safiullin,[b] V. G. Nikiforov,[b] V. S. Lobkov,[b] and Yu. G. Galyametdinov[a,b]**

*[a]Kazan State Technological University,*
*68 ul. Karla Marksa, 420015 Kazan, Russian Federation.*
*Fax: +7 (843) 231 4177. E-mail: yugal2002@mail.ru*
*[b]E. K. Zavoisky Kazan Physicotechnical Institute, Kazan Research Center of the Russian Academy of Sciences,*
*10/7 ul. Sibirskii trakt, 420111 Kazan, Russian Federation*

Nanocomposite materials based on semiconductor nanoparticles, such as CdS, are of special interest for many areas of science and technology: optics, electrochemistry, and optoelectronics.[1,2] This is due to the fact that nanoparticles are endowed with unusual chemical and electronic properties needed for the application in these areas.[3] The nonlinear optical properties of composite materials containing semiconductor nanoparticles depend on their size, shape, and procedures used to prepare nanoparticles.[4] The method of preparation of CdS nanoparticles in the presence of thiophenol is commonly described in the literature.[5—7] We used the method of CdS preparation by mixing of two lamellar lyotropic mesophases based on the nonionogenic surfactant, monododecyl tetraethylene glycol $C_{12}H_{25}O(CH_2CH_2O)_4H(C_{12}EO_4)$, one of which contained 0.1 *M* cadmium nitrate, and the second mesophase contained an equivalent amount of sodium sulfide

$$C_{12}EO_4/Cd(NO_3)_2 + C_{12}EO_4/Na_2S \longrightarrow$$
$$\longrightarrow CdS + 2\,NaNO_3 + 2\,C_{12}EO_4.$$

The corresponding mesophases were obtained and monitored by the methods similar to those described for the lanthanide-containing lyotropic mesophases.[9] Nanoparticles of CdS were isolated by the treatment of the reaction mixture followed by the precipitation of CdS in a centrifuge, and the precipitate was washed with ether. Nanoparticles of CdS in pyridine were mixed in an ultrasonic stirrer with poly(methyl methacrylate) (PMMA) in an amount of 7% of the polymer weight. Then the suspension obtained was poured on a quartz support and dried at 60 °C. The resultant sample was a film 0.3 mm thick. The absorption spectrum of the nanocomposite CdS—PMMA exhibits a shift to the blue region compared to that of a single crystal of CdS. This shift is due to the quantum-dimensional effect characteristic of nanoparticles of semiconductor crystals.[10] The size of the CdS nanoparticles is 2.5±0.2 nm as determined from the X-ray diffraction and UV spectroscopic data.[10,11]

The photoluminescence (PL) spectra of the obtained nanocomposite were studied on an automated optical spectrometer based on an MDR-12 monochromator. An LGI-21 pulse nitrogen laser (radiation wavelength 337 nm, pulse frequency 50 Hz, pulse duration 12 ns) and a femtosecond titanium—sapphire laser (Avesta-proekt) equipped with an amplifier (radiation wavelength 790 nm, pulse frequency 3 KHz, pulse duration 50 fs) were used for PL excitation.

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The PL spectra excited at the wavelengths 337 and 790 nm have a narrow intense band with a maximum at 529 nm. In addition, the second harmonic at 395 nm is generated in both samples when excited at 790 nm (Fig. 1, *a*). The band maximum of the second harmonic lies at 405 nm, which is due to re-absorption because of the great thickness of the samples. Figure 1, *b* shows the plot of the luminescence intensity ($I_{lum}$) at the wavelengths 400 and 529 nm *vs* excitation energy density *P* at the wavelength 790 nm. These dependences correspond to the power function $I_{lum} \sim P^n$, where *n* reflects the power of the multiphoton process.[12] The value of $n = 1.2$ for the band at 400 nm indicates the two-photon absorption process. We believe that the difference of the value of *n* from 2 is caused by a considerable effect of re-absorption at 400 nm. For the band with a maximum at 529 nm, $n = 3.4$, which indicates the processes of two- (395 nm), three- (263 nm), and four-photon (197 nm) absorption upon excitation at the wavelength 790 nm. Figure 1, *c* shows that the region below 250 nm is a fundamental absorption band for the nanocomposite CdS—PMMA. Accordingly, the probability of absorption in this region exceeds the probability of absorption in regions of 264 and 395 nm by at least an order of magnitude. Note that PMMA absorbs in the same region (see inset in Fig. 1, *c*); however, there is no PL of PMMA at 300—600 nm. Probably, this peculiarity, as well as a higher peak excitation intensity of a femtosecond laser result in multiphoton processes of absorption of CdS—PMMA. A possible explanation of the three- and four-photon processes is the multiphoton excitation of PMMA in the region of fundamental absorption and the energy transfer to CdS nanoparticles followed by luminescence. The probability of direct excitation of the CdS nanoparticles due to the three- and four-photon absorption processes can be considered negligible compared to the two-photon absorption. Note that the mechanisms of the processes considered need further detailed studies.

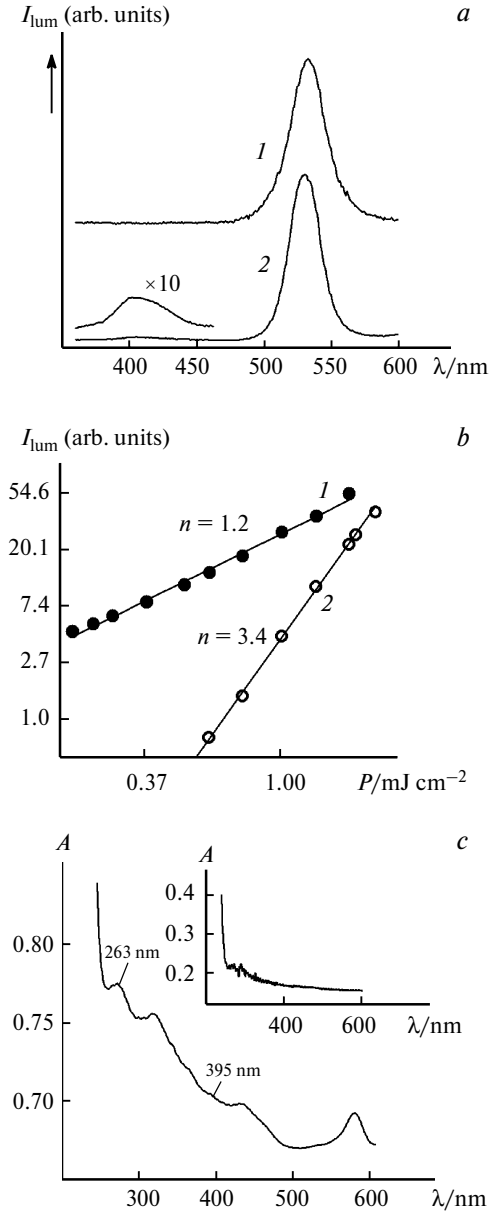


**Fig. 1.** *a.* Luminescence spectra of CdS—PMMA upon laser excitation at the wavelength $\lambda_{exc}$ = 337 (*1*) and 790 nm (*2*). *b.* Luminescence intensity at 400 (*1*) and 529 nm (*2*) *vs* excitation energy density. *c.* Absorption spectrum of CdS—PMMA; the absorption spectrum of PMMA is shown in inset (all data were obtained at 300 K).

Thus, we assert that nonlinear processes of second harmonic generation, multiphoton absorption, and luminescence at 529 nm were observed in the nanocomposite CdS—PMMA upon excitation by femtosecond pulses at the wavelength 790 nm.

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