Pis'ma v ZhETF, vol.68, iss.2, pp.131 - 135

ELECTRONS AND PHOTONS IN MESOSCOPIC STRUCTURES: QUANTUM DOTS IN A PHOTONIC CRYSTAL

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Submitted 15 June 1998

We report on synthesis and properties of a photonic crystal doped with quantum dots. The structure exhibits a two-stage self-organization of silica nanoparticles along with quantum confinement effects in semiconductor colloids. The interplay of electron and photon confinement results in controllable spontaneous emission of the mesoscopic structure.

PACS: 42.70.Qs, 78.66.-w, 81.05.Zx

Mesoscopic structures with a characteristic size either of the order of an electron de Broglie wavelength in semiconductors (1-10 nm) or close to the optical photon wavelength (100-1000 nm) exhibit non-trivial properties due to the modified electron or photon density of states. Three-dimensional spatial confinement of electrons in nanocrystals ("quantum dots") results in size-dependent energies and probabilities of optical transitions [1 – 3]. The photon density of states can be modified in structures with strong modulation of the refractive index in three dimensions (photonic crystals) [4 – 6]. It can be performed by means of supermolecular crystallisation of matter resulting in colloidal crystals with submicron period [7 – 10]. Because of the essentially different electron and photon wavelengths, the electron and photon densities of states can be engineered separately within the same mesostructure. In this letter we report on synthesis and several properties of a photonic crystal doped with semiconductor quanum dots. The structure exhibits a two-stage self-organization of silica nanoparticles along with quantum confinement effects in semiconductor colloids.

Photonic crystals used in our studies were synthesized from a sol of monodisperse SiO_2 spherical globules by means of sedimentation and hydrothermal treatment. Closely packed silica globules are cemented together and form a solid face-centered cubic lattice, each globule consisting of nanometer-size silica particles (Fig.1). Therefore, the resulting crystals show two stages of self-organization: aggregation of nanoparticles in a globule and close-packing of globules in a three-dimensional lattice. Thus developed superstructures, called artificial opals, exhibit photonic pseudogap in the visible range [8, 11, 12] which manifests itself as a pronounced stop band in transmission/reflection spectra in the

spectral range determined by the globule size, refraction index of globules and of interglobule cavities, and crystallographic orientation of photonic crystal (Fig.2). The physical origin of a pseudogap in a three-dimensional colloidal crystal is multiple rescattering and interference of optical waves propagating throughout.

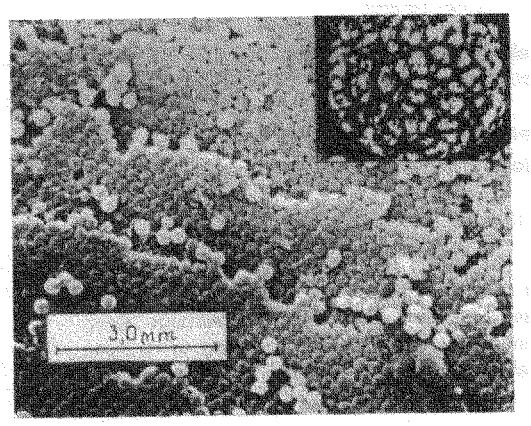

Fig.1. Electron microphotograph of the surface of a solid state silica-based colloidal crystal. Clearly seen are several successive layers consisting of close-packed spherical submicrometer-sized silica globules. Each globule in its turn consists of nanometer-sized silica particles (insert). The whole superstructure forms a three-dimensional face-centered cubic lattice. Because of coherent effects in multiple scattering of optical waves, these structures inhibit propagation of electromagnetic waves within a certain spectral range

Since interglobule cavities form a network, it is possible to embed therein desirable species (molecules, ions, or nanocrystals) exhibiting electron resonance in absorption or emission of light. To get overlapping size-dependent electron resonance in nanocrystals and structural optical resonance in a photonic crystal, the latter was doped with cadmium telluride nanoparticles. Semiconductor crystallites have been prepared through the addition of fresh oxygen-free NaHTe solution to N_2-saturated $Cd(ClO_4)_2 \cdot 6H_2O$ solution in the presence of thiols as stabilizing agents [13]. Well-defined CdTe nanocrystals were developed with predominant cubic crystalline structure possessing significant intrinsic emission in the visible spectral range (Fig.3). Due to the size restriction, the absorption spectrum shifts by more than 1 eV (from 827 nm in the bulk CdTe crystal to 460-500 nm in clusters). In the context of quantum-size effects, this is the typical strong confinement range when kinetic energies of electrons and holes are substantially larger than the energy of the electron-hole Coulomb interaction. Because of the pronounced size dependence, the emission spectrum can be tuned towards a photonic pseudogap of a photonic crystal. This was performed using 1-thioglycerol as stabilizer. The mean size of the CdTe crystallites in this case was about 2.4 nm. The intrinsic emission band peaking at 575 nm dominates in the luminescence spectrum. The spectrum shows a pronounced inhomogeneous broadening and strongly non-exponential decay with the mean lifetime of about 10^{-8} s.

Semiconductor quantum dots embedded in a photonic crystal exhibit a noticeable change of the luminescence spectrum when the latter overlaps with the photonic pseudogap (Fig.4). The modification of the spontaneous emission is due to a modified density of photon states in the pseudogap region. It is known that the spontaneous decay of an

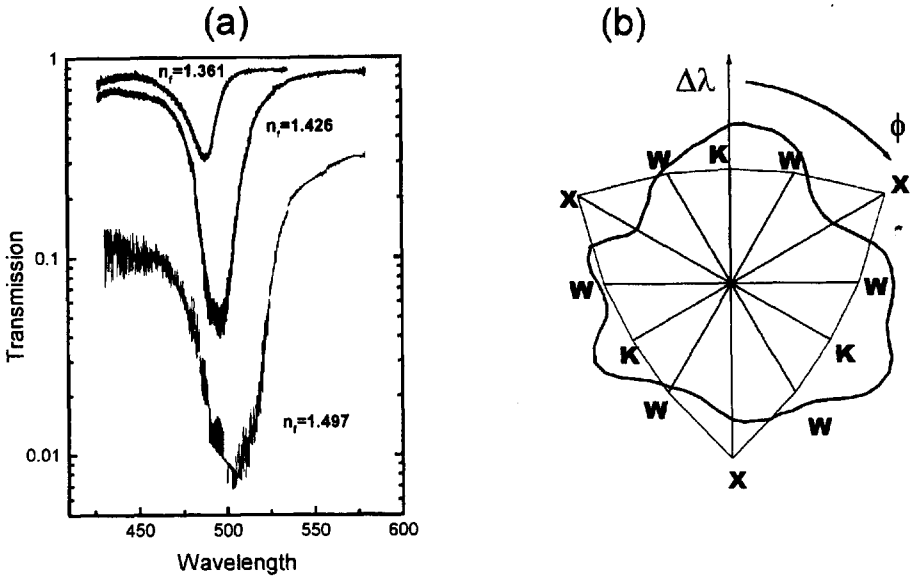

Fig.2. Photonic stop band in an opal-based photonic crystal. Presented in (a) are transmission spectra of an opal platelet sample impregnated with fillers possessing successively growing refraction index n_f. In the polar diagram (b) is depicted the angular dependence of the stop band. $\Delta\lambda$ is spectral shift of stop band as compared to $< 111 >$ direction, and φ is polar angle inside (111) plane. Deviation from $< 111 >$ was 20^0. Underlying triangle contour emphasizes special directions of Brillouin zone of a photonic crystal, lengths of radial lines are proportional to the angles between $< 111 >$ and directions to special points

excited state of every quantum system is not an intrinsic property of the system but a result of its interaction with the electromagnetic vacuum. The density of photon states redistributes in a photonic crystal as compared to free space. It vanishes within the gap and increases near the gap edges. Therefore, the spontaneous decay rate which is directly proportional to the photon density of states is expected to be inhibited within the gap and enhanced in the close vicinity outside the gap. Our experiments clearly show a dip in the emission spectrum (Fig.4) following the spectral position of the pseudogap (e. g., Fig.2). The appearance of the dip is indicative of the inhibited spontaneous emission. Although a modification of the emission spectrum also takes place at the edges of the pseudogap, additional studies are necessary to make an unambiguous conclusion on the enhanced emission at the gap edges. But to our knowlege[14], the rate of spontaneous emission splits into slowered and accelerated components, when dye molecules are located inside a photonic crystal with pseudogap. Unfortunatelly, unsufficiently high quantum yeald of fluorescence impedes analogous experiments with semiconductor nanocrystals.

The observed modification of the spontaneous emission spectrum of quantum dots in silica-based photonic crystals is much more significant than the modification reported for organic molecules in solid-state [8] and liquid-like[15] colloidal crystals. This is due to an intrinsically narrower emission spectrum of quantum dots as compared to organic molecules, which provides a stronger overlap of the emission spectrum and the gap. The homogeneous linewidth of a given nanocrystal emission spectrum is substantially narrower than the integral emission spectrum of a nanocrystal ensemble. Inhomogeneous

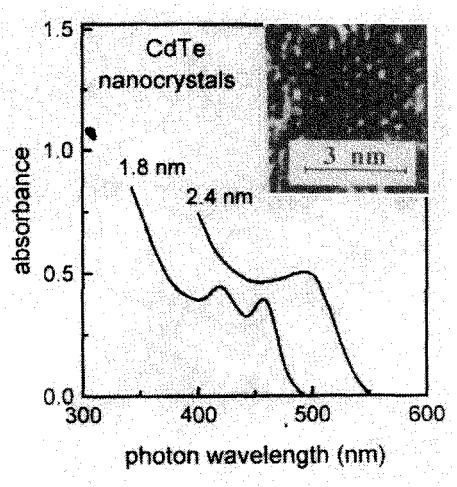

Fig.3. Absorption spectra of two representative colloidal solutions containing cadmium telluride crystallites of the mean size of 1.8 and 2.4 nm. Unlike bulk CdTe crystal whose fundamental absorption edge features onset at 827 nm, nanocrystals exhibit multiband absorption spectra with the first absorption feature tunable up to the near ultraviolet range. Within the framework of quantum-size effects, an evolution from a crystal to cluster can be interpreted in terms of the electron-hole confinement in a three-dimensional quantum box. The crystallites considered in this context correspond to the so-called strong confinement limit. The insert shows a single nanocrystal with pronounced crystallographic planes

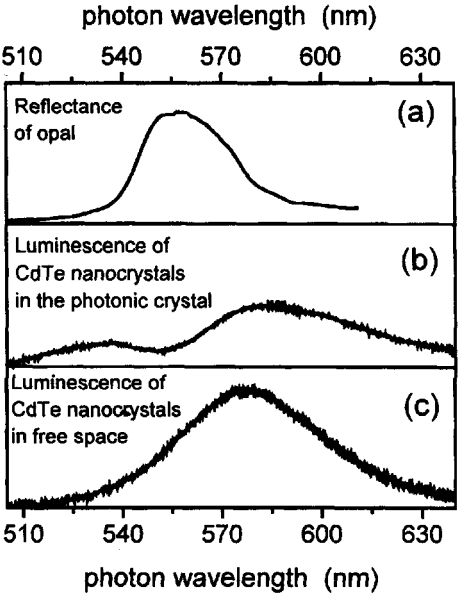

Fig.4. Photonic band gap effect on the spontaneous emission of CdTe nanocrystals. Panel (a) shows the reflection spectrum of the silica colloidal crystal doped with CdTe crystallites with the size of 2.4 nm. The pronounced peak in reflection is indicative of a dip in the spectral distribution of the photon density of states due to the periodic three-dimensional lattice of silica globules. In the spectral range relevant to the photonic pseudogap the luminescence spectrum has a minimum (panel b) which is indicative of an inhibited spontaneous emission. Panel (c) presents the reference emission spectrum of the same nanocrystals outside the photonic crystal

broadening is inherent in every ensemble of semiconductor clusters. It arises because of a distribution of transition energies and decay rates which in turn is related to distributions in cluster size, surface structure, local environments, and impurities. Therefore, each individual component within an inhomogeneously broadened spectrum reacts individually to the modified density of photon states. Thus, the total modification of the spontaneous emission enhances in the case of an inhomogeneously broadened spectrum as compared to a homogeneous band with the same total bandwidth. Under condition of an enhanced *modulation of the refraction index, silica-based photonic crystals doped with quantum* dots will offer a possibility to observe a noticeable slowing down of the spontaneous decay of a quantum system down to the emergence of "frozen" excited states predicted by the theory[16].

To summarize, we demonstrate a novel mesostructure with separately controllable densities of photon and electron states and show that the spontaneous emission of nanocrystals which is controlled at large by the quantum confinement effect, experiences strong

modification due to modified photon density of states in a photonic crystal with respect to free space.

Stimulating discussions with S.Ya. Kilin are greatly acknowledged. The work has been supported in part by INTAS Program of European Community and Volkswagen Foundation.

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