Electrons and photons in mesoscopic structures: quantum dots in a photonic crystal

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The synthesis and properties of a photonic crystal doped with quantum dots are reported. 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 from the mesoscopic structure. © *1998 American Institute of Physics.*
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Mesoscopic structures with a characteristic size either of the order of the electron de Broglie wavelength in a semiconductor (1–10 nm) or close to the optical photon wavelength (100–1000 nm) exhibit nontrivial 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 crystallization of matter, resulting in colloidal crystals with a submicron period.[7–10] Because of the substantially 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 the synthesis and several properties of a photonic crystal doped with semiconductor quantum dots. The structure exhibits a two-stage self-organization of silica nanoparticles along with quantum confinement effects in semiconductor colloids.

The photonic crystals used in our studies were synthesized from a sol of monodis-

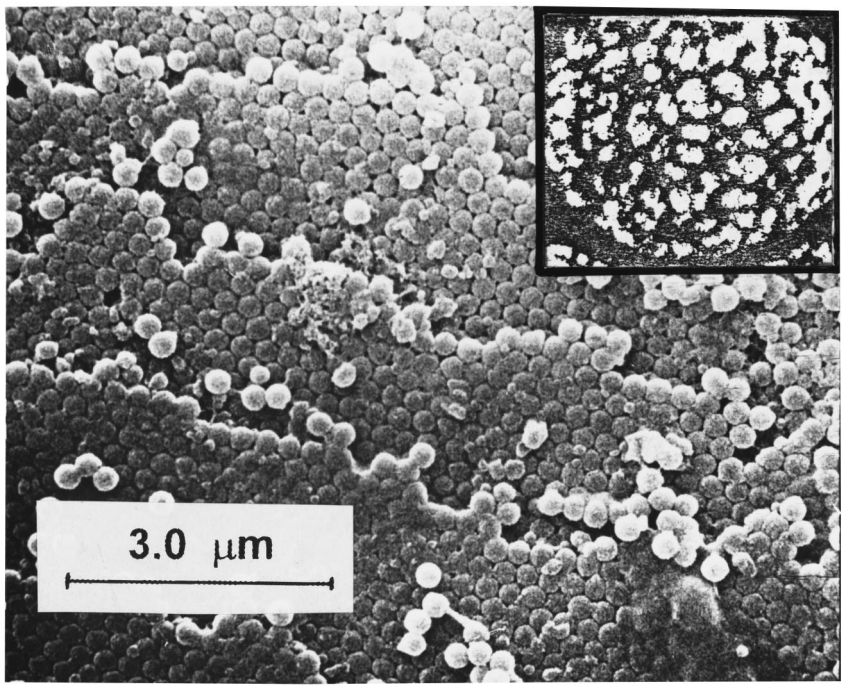

FIG. 1. Electron micrograph of the surface of a solid state silica-based colloidal crystal. Clearly seen are several successive layers consisting of close-packed spherical submicron-sized silica globules. Each globule in its turn consists of nanometer-sized silica particles (inset). The whole superstructure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

perse SiO_2 spherical globules by means of sedimentation and hydrothermal treatment. Close-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. The superstructures thus developed, which are called artificial opals, exhibit a photonic pseudogap in the visible range[8,11,12] which manifests itself as a pronounced stop band in transmission/reflection spectra in a spectral range determined by the globule size, the refractive index of the globules and interglobule cavities, and the crystallographic orientation of the 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.

Since the 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

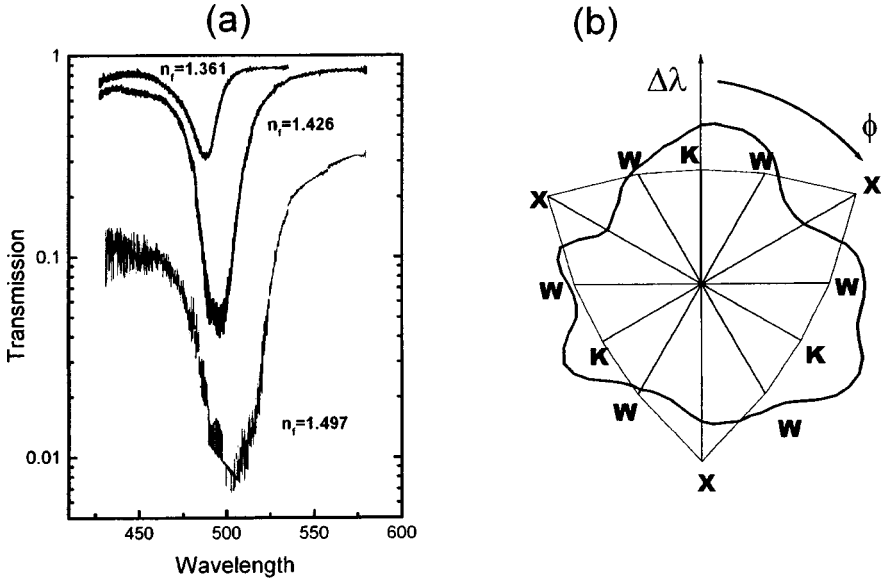

FIG. 2. Photonic stop band in an opal-based photonic crystal. Presented in (a) are transmission spectra of an opal platelet sample impregnated with fillers possessing successively growing refraction index n_f. The polar diagram (b) shows the angular dependence of the stop band. $\Delta\lambda$ is the spectral shift of the stop band as compared to the $\langle 111 \rangle$ direction, and φ is the polar angle inside the (111) plane. The deviation from $\langle 111 \rangle$ was 20°. The underlying triangular contour emphasizes the special directions of the Brillouin zone of a photonic crystal; the lengths of the radial lines are proportional to the angles between $\langle 111 \rangle$ and the directions to the special points.

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 the clusters). In the context of quantum size effects, this is the typical strong confinement range, when the kinetic energies of the 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 a 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 nonexponential decay with a 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 excited state of any 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 is redistributed 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

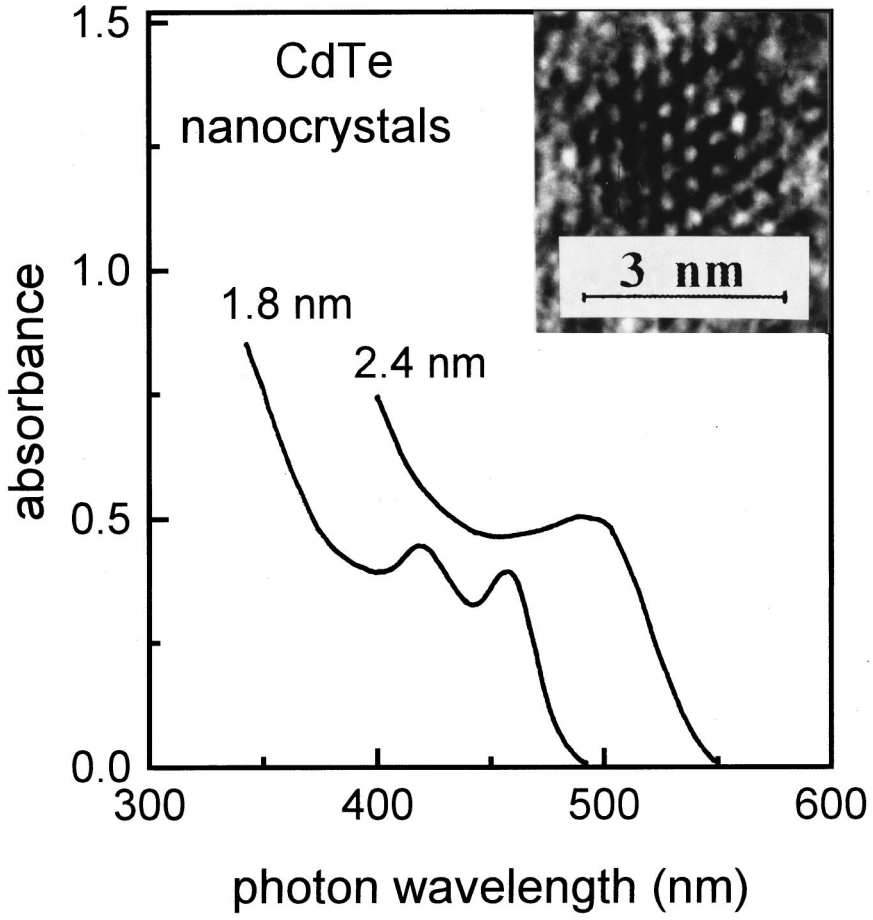

FIG. 3. Absorption spectra of two representative colloidal solutions containing cadmium telluride crystallites of mean size of 1.8 and 2.4 nm. Unlike the bulk CdTe crystal, whose fundamental absorption edge rises at 827 nm, nanocrystals exhibit multiband absorption spectra with the first absorption feature 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. Considered in this context, the crystallites correspond to the so-called strong confinement limit. The inset shows a single nanocrystal with pronounced crystallographic planes.

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 reach an unambiguous conclusion about enhanced emission at the gap edges. To our knowlege,[14] however, when dye molecules are located inside a photonic crystal with a pseudogap, the rate of spontaneous emission splits into slowed and accelerated components. Unfortunatelly, the insufficiently high quantum

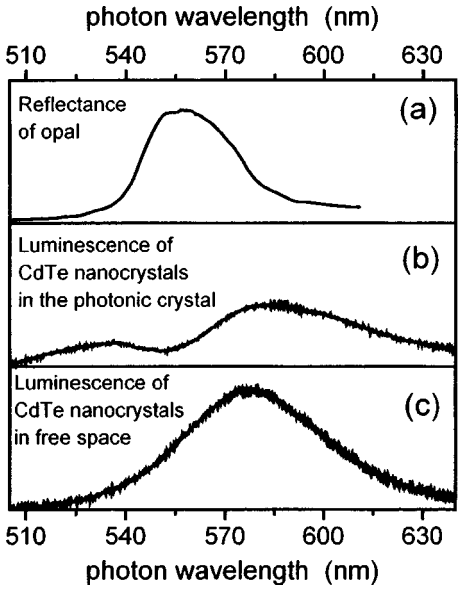

FIG. 4. Effect of the photonic band gap on the spontaneous emission of CdTe nanocrystals. Panel (a) shows the reflection spectrum of a silica colloidal crystal doped with CdTe crystallites with a size of 2.4 nm. The pronounced peak in reflection is indicative of a dip in the spectral distribution of 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) shows the reference emission spectrum of the same nanocrystals outside the photonic crystal.

yield of fluorescence is an impediment to 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 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 the 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 is enhanced in the case of an inhomogeneously broadened spectrum as compared to a homogeneous band with the same total bandwidth. Under conditions of enhanced modulation of the refraction index, silica-based photonic crystals doped with quantum dots will afford a possibility of observing a noticeable slowing down of the spontaneous decay of a quantum system, down to the emergence of the ''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 in a photonic crystal as compared to free space on account of the modified photon density of states.

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