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КВАНТОВО-ЭЛЕКТРОДИНАМИЧЕСКИЕ ПРОЦЕССЫ ВБЛИЗИ ПОВЕРХНОСТИ

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MODIFICATION OF PHOTON STATES IN PHOTONIC MOLECULES WITH SEMICONDUCTOR NANOCRYSTALS

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Abstract—We report on the coherent coupling of whispering gallery modes (WGM) in a photonic molecule formed from two melamine-formaldehyde spherical microcavities coated with a thin shell of CdTe nanocrystals (NCs). Utilizing different excitation conditions the splitting of the WGM resonances originating from bonding and anti-bonding branches of the photonic states is observed and fine structure consisting of very sharp peaks resulting from lifting of the WGM degeneracy has been detected. Observation of optical wavelength switching with controllable spectral position and separation is reported.

INTRODUCTION

In recent years the modification of electromagnetic modes in solid spherical microcavities has been of great interest both for studies of fundamental optical properties and for the potential applications [1, 2]. Extending the ideas of the linear combination of atomic orbitals approach to the classical wave case, it was shown that Mie resonances of single microspheres play the same role as the atomic orbitals in the electronic case [3]. Following the analogy with quantum mechanics, three integers, n, l and m, describing whispering gallery modes (WGMs), correspond to angular, radial and the azimuthal quantum numbers, respectively. The spatial distributions of WGMs can be described using the eigenfunctions of the vector wave equation for an electromagnetic field in the sphere [2], by direct analogy with the orbitals of the electron bound in the hydrogen atom as deduced from the Schrodinger equation. This approach has enabled small dielectric spheres to be considered as "photonic atoms" [3, 4]. It is well known that the resonant internal field of a spherical cavity is not completely confined to the interior of the microparticle. Depending on the size of the microsphere, the evanescent field can extend into the surroundings up to couple of micrometers. It was recently recognized that the partial delocalization of Mie resonance states is of great importance because it suggests a possibility for coherent coupling between WGMs of two adjacent spherical particles with closely matched sizes. Such a system of coherently coupled "photonic atoms" may be called a "photonic molecule "PM" [5] and can be employed in order to manipulate photons in the micrometer length scale. In analogy to the formation of molecular electronic orbits, the tight binding approximation provides two combinations for the electromagnetic field in a system of interacting microspheres: bonding (BN) and antibonding (ABN) states [5–8]. Experimentally, the coupling of the photon modes of individual microspheres in the PM can cause a narrow resonance of a "photonic atom" to split into two modes of lower quality factor [6]. This phenomenon has been clearly demonstrated in a system of two square, photonic dots coupled by a narrow channel [5], in a dye-stained bisphere system [7, 9, 10] and in chains of polymer-blend microparticles [11].

Detailed consideration of coherent mode coupling also reveals the possibility of lifting the degeneracy in the PM with respect to m indices [8]. For the case of off-axis incidence the modes originating from coupling of WGMs with different m numbers contribute differently to the measured signal, resulting in a number of small peaks (m-resonances) between the upper and lower peaks of $m = \pm 1$. Although theoretically predicted, this phenomenon has not been experimentally observed thus far.

In this paper we have studied the WGM structure in interacting spherical microcavities formed from melamine formaldehyde (MF) latex microspheres coated with a thin shell of CdTe NCs under different excitation conditions. We report on the observation of two major features, unique to strong coupling between the photonic states of the two spherical microcavities forming the PM. First, we have observed splitting of the WGM resonances originating from BN and ABN branches of the photonic states. Secondly, fine structure of very sharp peaks (FWHM = 0.3 ⟶ 0.5 nm)

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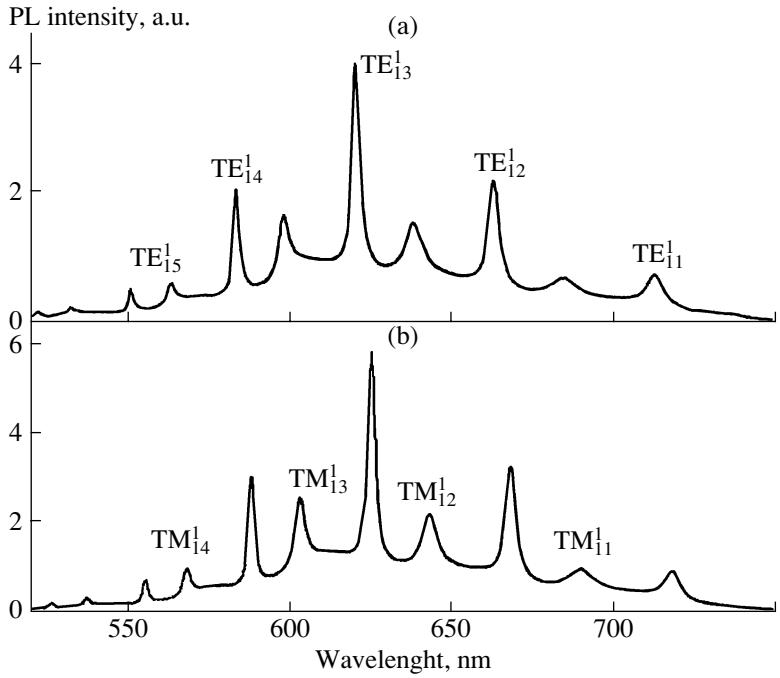

Fig. 1. Emission spectra of two single microspheres with diameters of 1.98 μm (a) and 1.99 μm (b).

was detected photoliminescence in (PL) spectra of the PM, which can be interpreted as a result of the removal of the WGM degeneracy with respect to *m* due to the difference in symmetry of the PM and the single microsphere.

EXPERIMENTAL

Aqueous dispersions of MF microspheres, of 2 μm in diameter with a size deviation of 0.1 μm (Microparticles GmbH, Berlin), were combined with luminescent CdTe NCs [12] using a layer-by-layer deposition technique, as described elsewhere [13, 14]. The relatively high refractive index (n_r = 1.68), high optical transparency and thermal and mechanical stability of MF make it ideal as a candidate for optical applications, while CdTe NCs produce size-dependent emission which can be tuned over a wide spectral region. In this work the colloidal solution of CdTe NCs, with a PL maximum at 620 nm (2.4 nm radius) and a PL quantum efficiency of ~25% at room temperature, was used for coating MF microspheres. The small size of the MF spheres was dictated by specific requirements for the optimal excitation conditions such as matching the laser wavelength to one of the WGM frequencies and achieving good correlation between the WGM and the laser linewidths [2, 13]. Wide separation of WGMs in spheres of this size [13] avoids intricate band mixing in a PM. Moreover, the moderate quality factor of small spherical particles forming the PM ($Q \sim 10^2$ for 2 μm diameter spheres [13]) provides better mode coupling than would be the case for larger microspheres ($Q \sim 10^3$ for a 5 μm diameter [7, 15]). To perform an experimental study of fine structure of coupled WGMs, we proceed from the assumption that a stronger coupling parameter can be of crucial importance governing the interaction between electromagnetic fields of two adjacent spheres.

The micro-PL spectra from microspheres were recorded in a backscattering geometry using a RENISHAW micro-Raman system (1800 mm^{-1} grating, >1 cm^{-1} spectral resolution) equipped with a notch and a plasma filters and a CCD camera. The spatial resolution, of less than 1 μm, was provided using a microscope with a 100× objective lens and a positioning stage. An Ar^+ laser (λ = 488 nm, 1 mW power) was used to provide excitation. For all measurements, a polystyrene/glass substrate was used and two spheres were in contact in order to provide the maximum possible coupling.

RESULTS

In order to analyze the spectral features of a PM, it is first necessary to examine the PL spectra of single microspheres. Two PL spectra of single microspheres, with slightly different sizes, are shown in Figure 1. The spectra are essentially identical except for the slight overall shift of the resonances. The observed spectral structure originates from coupling of electronic transitions in NCs to the photon modes of microsphere, with PL peaks corresponding to the resonant frequencies of WGMs with transverse electric (TE) and transverse magnetic (TM) polarizations. Due to the high PL quantum efficiency of NCs, the peaks in the PL spectra are

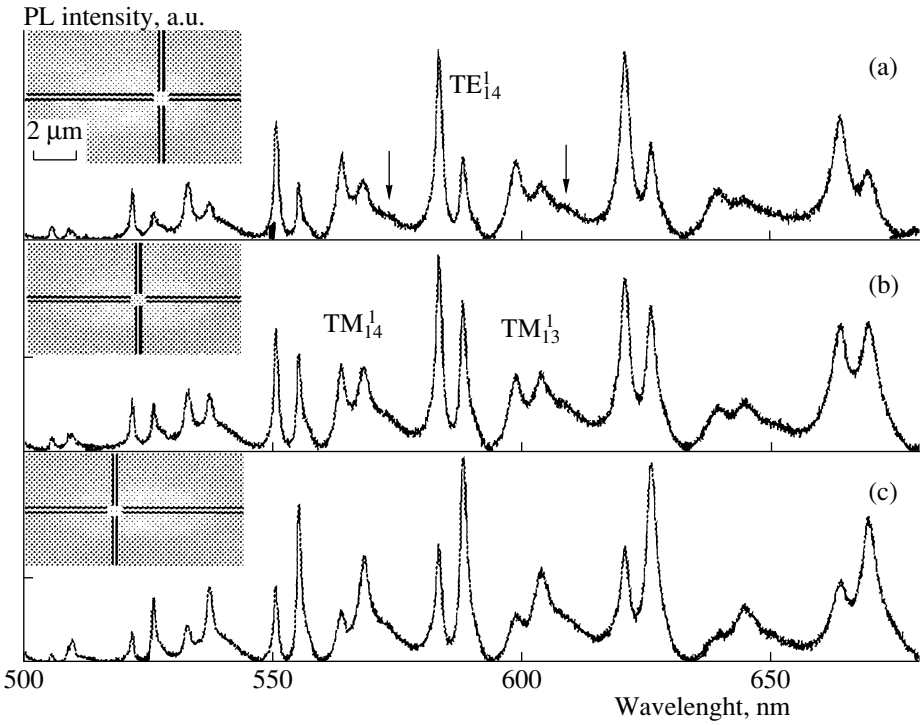

Fig. 2. Micro-PL spectra of a PM comprising two interacting spheres, with excitation and detection at three different positions along its longitudinal axis. Insets show microscope images of the PM, with the cross-hairs indicating the excitation-detection position. Background PL has been subtracted in all spectra presented, in order to show more clearly the WGM structure.

superimposed on a broad background signal arising from part of the NC emission, which does not match any WGM of the microsphere.

In the absence of gain, the WGM resonances can be characterized by a mode number (angular quantum number) n, the mode order l (radial quantum number) and azimuthal mode number m (azimuthal quantum number). The value of n is proportional to the circumference divided by the wavelength of the light propagating within the microsphere, the mode order l indicates the number of maxima in the radial distribution of the internal electric field, and the azimuthal mode number m gives the orientation of the WGMs orbital plane. WGMs are degenerate with respect to m because of the spherical symmetry of the sphere.

According to the Lorenz-Mie theory, mathematical conditions for WGM resonances can be given as [16]

$$n_r\psi_n(x)\psi_n'(n_r x) - \psi_n(n_r x)\psi_n'(x) = 0 \text{ (TM modes)} \quad (1)$$

and

$$n_r\chi_n(x)\psi_n'(n_r x) - \psi_n(n_r x)\chi_n'(x) = 0 \text{ (TE modes)}, \quad (2)$$

where $x = \dfrac{2\pi n_r R}{\lambda}$ is the size parameter, R is the radius of microsphere, $\psi_n(x)$ and $\chi_n(x)$ are the spherical Ricatti-Bessel functions of the first and second kind, respectively.

Solving equations (1) and (2) and comparing results with the spectral positions of the WGMs in the experimental PL spectra we can identify the indexes n and l (Fig. 1) for each mode and estimate the relative size of the sphere. Note that a shift in positions of WGMs can be clearly seen between the spectra in Fig. 1. from our calculations we have determined that this shift is a result of a difference in size of only 14 nm between the two microspheres.

To investigate the propagation modes in interacting spherical microcavities we have measured PL spectra scanning a sample along the longitudinal axis of the PM. For a given excitation and detection configuration we did not observe any new peaks in PL spectra of the PM (Fig. 2) as compared to that of single spheres (Fig. 1) except for weak broad features on the long-wavelength wings of the TM_{13}^{1} and TM_{14}^{1} modes (indicated by arrows in Fig. 2b). These peaks are weak evidence of intermode coupling in PM. The pronounced double structure, with the intensity distribution dependent on the excitation position (Fig. 2), is just a result of superposition of the uncoupled WGMs of individual microspheres. In this case the scattered or emitted field from one microsphere is the additional incident field for another microsphere with intensity decreasing as the excitation spot moves farther away from the contact point. The lack of strong intermode coupling in this configuration is not surprising because the coupling between electromagnetic fields of the spheres is expected

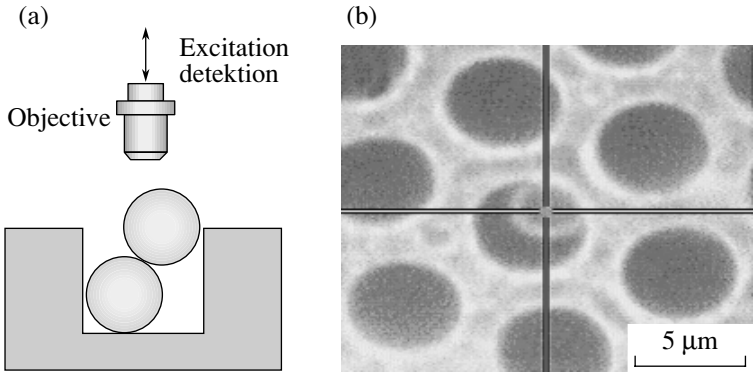

Fig. 3. Excitation and detection geometry (a) and microscope image of the PM in the microwell (b). The cross indicates the excitation position.

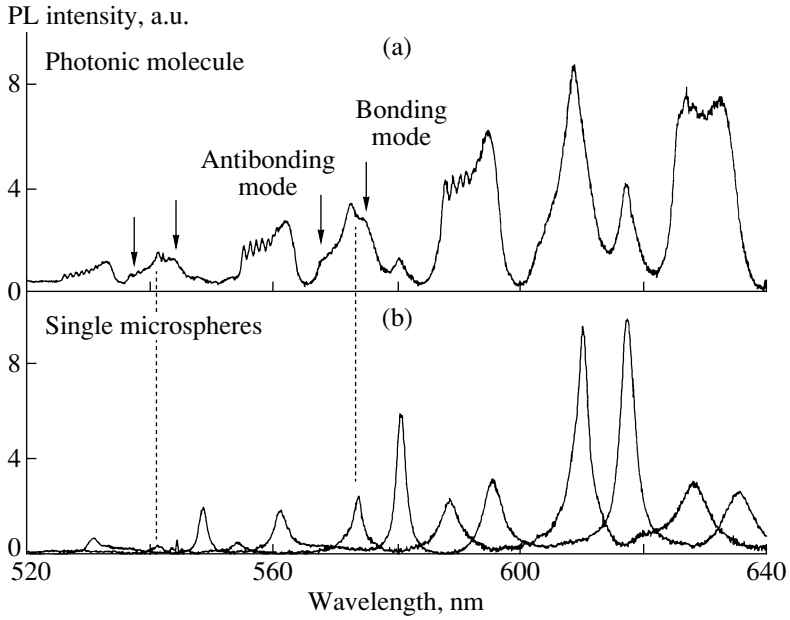

Fig. 4. Comparison of PL spectra of a PM accommodated in a microwell (a) and PL spectra of noninteracting microspheres (b). Arrows indicate the coupled modes.

to be maximum in the direction parallel to the PM axis, when some of WGM orbitals lie in the same plane [7]. However, the observed redistribution of intensity between the components of WGM double structure clearly demonstrates the propagation of the light along the PM and possibility of wavelength switching in the PM, which can be used in optical interconnection devises. Clearly, the spectral position and the separation between components of the double PL structure (see for example, spectral region of TE_{14}^{1} modes in Fig. 2) can be easily controlled selecting microspheres of appropriate size.

As predicted in Ref. [7], controllable alignment geometry of the PM is crucial in order to observe the strong coupling between the spheres. The signal from the coupled microsphere modes is expected to be more pronounced when the incident light propagates parallel to the longitudinal axis of the PM. We employed a novel technique in order to control the alignment of the spheres constituting the PM. We utilized a polystyrene substrate containing a three-dimensionally ordered array of pores of ~5 μm in size prepared through a thermocapillary convection [17]. The surface layer of the substrate contains an array of open microwells of 3–5 μm depth. Only one pair of the 2 μm microspheres can be accommodated within each microwell, and the axis of the PM is close to the surface normal. In the experiments detailed here, MF/CdTe microspheres were deposited on top of the porous substrate and then manipulated into position with a tapered optical fiber tip attached to a mechanical translation stage. Schematic

excitation and detection geometry and microscope image of the PM in the well are presented in Fig. 3.

The WGM structure in the PL spectra of single microspheres was found to be practically unaffected by the microporous substrate, except for a very small broadening of the WGM resonance lines. This can be understood by taking into account the difference in size between the microspheres and the microwell, and the interaction between the microwell walls and the microsphere is sufficiently small that the Q value of the WGMs is essentially preserved.

Figures 4 show the PL spectrum of a PM accommodated in a microwell and the spectra of the individual microspheres prior to being manipulated into the microwell. The presented PL spectra clearly revealed two major features unique to strong coherent coupling between the photonic states of the two microspheres forming the PM. First, the appearance of the two satellites (indicated by arrows in Fig. 4) can be interpreted as a result of the formation of BN and ABN orbitals in the PM [5] with the "ABN" peak observed at a lower wavelength than the "BN" one. The high PL efficiency of CdTe NCs and coupling of the electronic transitions of NCs to the resonances of PM allows us to detect the BN and ABN branches in a wide spectral region (520–600 nm). Secondly, one can clearly see a number of narrow peaks (*m*-resonances) grouping in the spectrum for the PM on short wavelength side of the TE and TM resonances, which are due to the presence of $m \neq \pm 1$ components.

The deconvolution of the lineshape of the *m*-resonances of the PM using Lorentian functions reveals the most remarkable experimental fact: the *Q* factor of *m*-resonances in spectra of the PM (~2000) (and therefore lifetime of a photon in the resonant modes) exceeds the *Q* value (~800) and photon lifetime of individual spheres across the whole spectral region. This fact along with estimated value of BN/ABN splitting (~6–8 nm) implies a possibility for the development of new PM based photonic devices such as an optical delay line with controllable spectral and temporal tunability, which can be highly useful for a variety of applications in optical communication systems.

In summary, we have experimentally investigated the optical modes in a PM fabricated from two spherical microcavities coated with a thin shell of CdTe NCs. PL spectra clearly reveal two major features unique to strong coherent coupling between the photonic states of the two microspheres forming the PM: the splitting of the WGM resonances originating from the BN and ABN branches of the photonic states, and the fine structure of very sharp peaks resulting from lifting of the WGM degeneracy with respect to the azimuthal index. Our observation of coherently coupled modes in the PM accommodated in a microporous matrix shows the possibility of engineering new high-Q devices with strong photon confinement.

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