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Whispering gallery mode emission from a composite system of CdTe nanocrystals and a spherical microcavity

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Abstract
We have studied the optical properties of a novel quantum dot–microcavity system consisting of CdTe nanocrystals attached to a melamine formaldehyde latex microsphere. The spheres were studied using conventional and confocal microscopy, the confocal system revealed defects in some spheres. The coupling between the emission of the nanocrystals and the spherical cavity modes was realized. Periodic very narrow peaks of the emission spectra corresponding to the whispering gallery modes were detected with strong emission into selected modes at a high pump intensity.

1. Introduction

Whispering gallery mode (WGM) oscillations within a single spherical microcavity doped by semiconductor nanocrystals (NCs) have been a subject of intense theoretical and experimental study for the last five years [1–5]. The combination of the high quality factor (Q) and the small mode volume of glass microspheres with tunable emission properties of CdSe NCs has made it possible to observe extremely narrow resonant structure in the emission spectra at room temperature, to develop techniques for the identification of transverse electric and magnetic modes [2], to observe the modification of photoluminescence (PL) decay lifetime [5, 6] and lasing [3, 6]. These unique optical properties and material compatibility with telecommunication optical fibres make spherical microcavities attractive and novel building blocks for fibre optics and photonic devices. However, presently whispering gallery modes have only been demonstrated for glass microspheres doped or covered by CdSe NCs with photoluminescence in the region of high fibre absorption (530–600 nm). In order to overcome this technological disadvantage we have developed the new composite system consisting of CdTe NCs and a melamine formaldehyde (MF) latex microsphere. The high optical transparency, thermal and mechanical stability of MF, make it interesting as a potential candidate in optical applications. The refractive index of MF in the visible region ($n_r = 1.68$) is greater than that of polymethylmethacrylate ($n_r = 1.48$), silica ($n_r = 1.47$) or other glass materials ($n_r = 1.5$). On the other hand, the spectral region of CdTe NC emission (600–770 nm) [7] corresponds to a local absorption minimum of plastic optical fibres [8], which are widely used in short-range communication systems.

In the present work, photoluminescence spectra of MF microspheres covered by a thin shell of CdTe NCs were studied in order to examine the emission intensity as a function of excitation power. The three-dimensional imaging of microspheres by using confocal scanning allows us to control the optical quality of the samples to be studied in PL. We aimed to take advantage of WGM by placing the emitter (shell of NCs) just outside the high refractive index microsphere. It is well known that the resonant internal field of a spherical cavity is not completely confined to the interior of the microparticle. Decaying exponentially, the evanescent field extends a couple of micrometres into the surrounding. By this method, efficient coupling of NC emission with WGM of microsphere was provided. Moreover, with the quantum-confinement effect we can provide the tunable coupling of

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cavity modes to the transition frequency of NCs across a wide spectral region. This matching is a critical requirement for low-threshold lasing in microspherical structures [9].

2. Experimental details

CdTe nanocrystals capped with thioglycolic acid and, thus, carrying a negative charge were synthesized in aqueous medium as described elsewhere [10]. Two aqueous colloidal solutions of nanocrystals with photoluminescence (PL) maximum at 595 and 635 nm and PL quantum efficiency of 25% at room temperature were used for modification of MF microspheres. The average size of the nanocrystals was estimated to be 4.4 and 5.1 nm respectively. Instead of the commonly accepted chemical bonding of nanocrystals to the surface of microspheres via mercaptosilanes, we have used an approach based on layer-by-layer (LbL) assembly of ultrathin films [11], which provides better quality for optoelectronic applications than films fabricated with other techniques [12]. Aqueous dispersions of MF microspheres of 5.2 mm in diameter (Microparticles GmbH, Berlin) were modified with luminescent CdTe NCs by this LbL deposition technique. The procedure was as follows. The particles originally possessing slightly positive surface charge were modified with monolayers of negatively charged polyelectrolyte, polystyrenesulfonate sodium salt (PSS), and positively charged polyelectrolyte, poly(allylamine hydrochloride) (PAH). This pretreatment allows us to increase the positive surface charge of the particles. In the next step the CdTe NCs, being negatively charged due to the carboxylic groups of stabilizer (thioglycolic acid), were assembled on the surface of MF particles. Thus, MF particles modified with only one layer of CdTe were prepared. Between all the steps of preparation, particles were carefully washed three times in water (by centrifugation) to remove the excess of non-binding polyelectrolyte molecules or nanocrystals. After preparation the modified and washed particles were separated from water by centrifugation and transferred to absolute ethanol.

Absorption and PL spectra of colloidal NCs were measured using a Shimadzu-3101 and Spex Fluorolog spectrometers, respectively. The PL spectra from a single microsphere were recorded using a RENISHAW micro-Raman system (1800 mm^{-1} grating, >1 cm^{-1} resolution) equipped with a microscope objective (×100), a notch and plasma filters and a CCD camera. An Ar^{+} laser (wavelength $\lambda = 514.5$ nm, 25 mW power) was used in the micro-PL measurements. Also a linearly polarized HeNe laser ($\lambda = 632.8$ nm, extinction ratio $>500 : 1$) was used as a light source for the confocal imaging system (figure 1). In the microscopy system, the expanded collimated light was focused on the sample through an infinity corrected objective lens with a numerical aperture (NA) of 0.9 (Leitz, Germany). The backscattered light from the sample was collected by the objective lens, then focused onto a 30 mm diameter pinhole by a tube lens. The signal was detected by a photomultiplier tube (PMT) and analysed using a computer. The computer also controlled a motorized stage moving in the x and y directions and a piezoelectric actuator driving the objective lens in z direction. When the pinhole is removed, considering the size of the detector and objective lens as infinitely large, the sectioning property of the system is removed and the system works as a conventional scanning microscope.

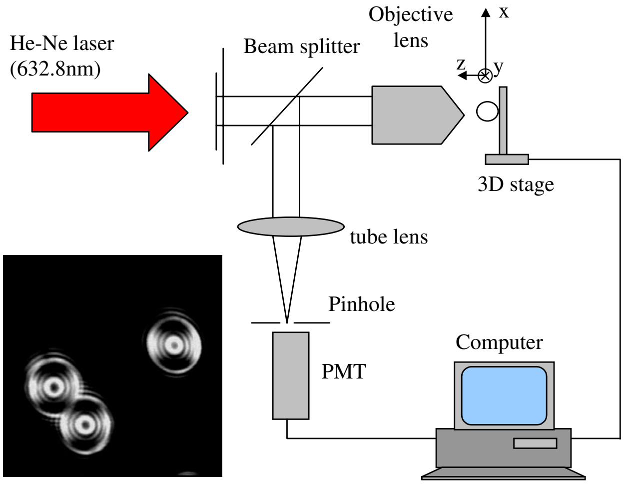

Figure 1. Diagram of the confocal scanning or conventional microscope (when the pinhole is removed). Inset: normalized images of the microspheres, 5.2 μm in diameter taken by conventional microscope.

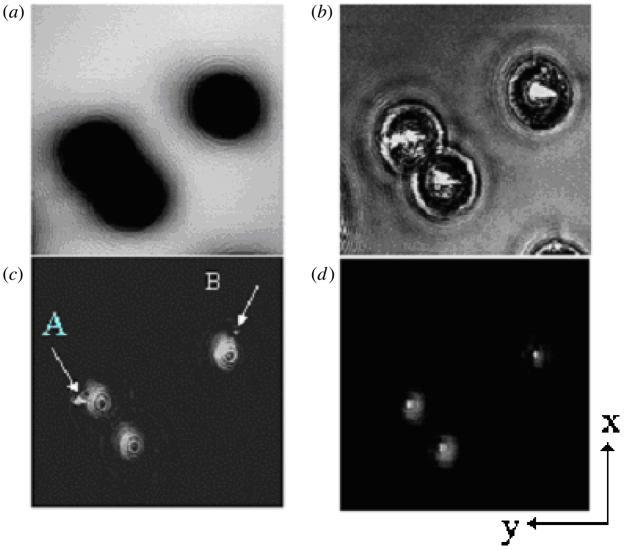

Figure 2. Normalized confocal scanning images of microsphere, 5.2 mm in diameter, with different axial locations. From (*a*)–(*f*): $z = -a$, 0, $a/2$ and a, respectively. Two defects A and B are inside the sphere.

3. Results and discussion

3.1. The three-dimensional imaging of microspheres

In order to control the optical quality of the samples we utilize the sectioning property of the confocal scanning microscope. The images are shown in figure 2. An isolated sphere and a pair of touching spheres are observed. The light was first focused on the surface of the substrate ($z = -a$) (near the back surface of the sphere) and only the shadow of the sphere can be seen in figure 2(*a*). When the focal plane is moved

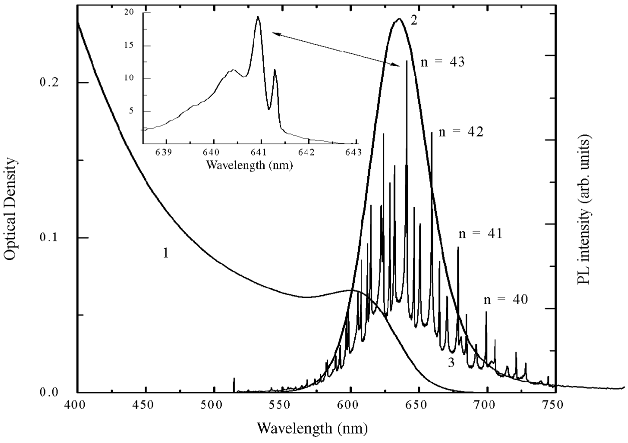

Figure 3. Room temperature absorption (1) and PL spectra of CdTe NCs in water (2) and PL spectra from single MF microsphere covered by one monolayer shell of CdTe NCs (3). Inset shows fine structure of the peak with $n = 43$.

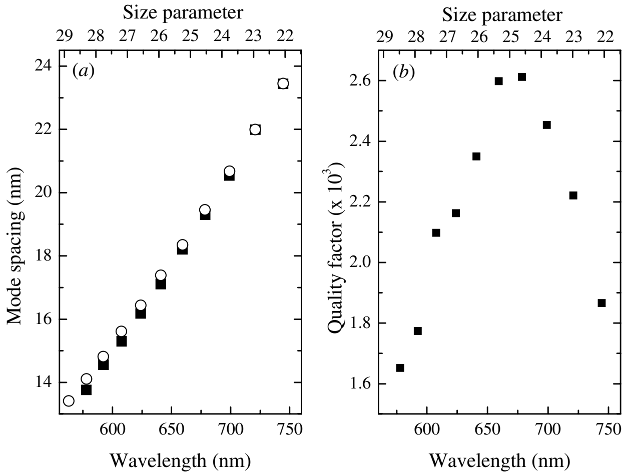

Figure 4. Experimental (squares) and calculated (circles) spacing between adjacent modes. (*b*) Calculated quality factor.

towards the equatorial plane of the sphere ($z = 0$), bright rings appear in the periphery of the sphere (figure 2(*b*)). Since the distance from the plane $z = 0$ to the substrate is about 2.6 mm and the FWHM of the system axial response of 0.8 mm is considerably less than this, light from the off-focused substrate will be blocked by the pinhole. In addition, other light scattering away from the focus will also be blocked by the pinhole. Hence bright rings can only be due to the light backscattered from the focused point of the sphere surface.

The bright centre in figure 2(*b*) can be explained in terms of geometrical optics: when the light is focused on the centre of the sphere, rays propagate along radial directions and reflect back. In order to see the rings around the sphere surface, we increased the gain of the detector, and as a result, the centre of the sphere is saturated in figure 2(*b*). Figures 2(*c*)–(*d*) show the images near $z = a/2$ and a, respectively, with the same gain of the detector which is comparatively lower than that in figure 2(*b*). Two point-like defects A and B can be clearly seen inside the sphere near the region between $z = a/2$, which cannot be observed by conventional microscopy (figure 1, inset) due to the poor sectioning property. The confocal imaging technique allows us to control the quality of the spherical microcavity, locate any defects, and then select the spheres of highest quality, although, due to the high refractive index of the sphere, the exact location of the defects needs to be calculated.

3.2. Spectral properties of emitting microspheres

The optical spectra of colloidal CdTe NCs in water are presented in figure 3, the pronounced peak in absorption and the single PL band demonstrating the excellent optical quality. The blue shift of the NC absorption band by 570 meV with respect to bulk CdTe indicates a strong electronic quantum-confinement effect.

In contrast to the broad, featureless PL band in the spectra of colloidal NCs, the emission spectra of a single MF/CdTe microsphere exhibit very sharp periodic structure (figure 3). The observed peak structure is a result of coupling of electronic states in NCs and photon states of microsphere. As one can see from figure 3, the WGM peaks with different n are superimposed on a background signal arising from part of NC emission, which does not match any WGM of the microsphere. The placement and spacing between WGM peaks are determined by the size and refractive index of the microsphere while spectral intensity distribution depends on the parameters of NCs and can be easily modified by using NCs of different size.

In the absence of gain, the placement of the WGM resonances can be characterized by a mode number (angular quantum number) n, which is equal to the circumference divided by the wavelength of the light propagating within the microsphere. Although the use of a ray interpretation in spherical microcavities of small size is controversial [13, 14], the geometric optics point of view often provides a useful and simple way for rough identification of WGM structure [1, 6].

For the WGM peaks shown in figure 3 the value of the angular quantum number n is much higher than the size parameter $x = \pi d/\lambda$ throughout the whole spectral region (d is the diameter of the microsphere). In this case, the approximate distance between two resonances of successive modes with the same order and polarization can be obtained from the expression [15]

$$\Delta\lambda = \frac{\lambda_n^2 \tan^{-1}\{n_r - 1\}^{1/2}}{\pi d\{n_r - 1\}^{1/2}} \qquad (1)$$

where λ_n is the emission wavelength of the WGM peaks with different n. According to (1), the mode spacing decreases with increasing mode number n. The calculated and experimentally observed $\Delta\lambda$ values for modes, which differ by one unit of angular momentum, are shown in figure 4(*a*), demonstrating good agreement and indicating that the monolayer of semiconductor material with a high refractive index does not influence the dielectric constant of the microcavity.

The high resolution of measurement system allows us to detect the fine structure of each WGM peak. For example, the inset in figure 3 shows that WGM peak with $n = 43$ ($\lambda_{43} = 640.9$ nm, $\hbar\omega_{43} = 1.93$ eV) consists of at least three superimposed peaks, with a separation of about 0.3 nm. Although detailed analysis of mode structure in CdTe/MF microspheres is not considered here, we suggest that these modes correspond to different m azimuthal numbers. The Lorentzian fit of the lineshape of PL peaks allows us to estimate the quality factor (Q) of WGM across whole spectral region (figure 4(*b*)). For example, at the wavelength of $\lambda_{41} = 678.3$ nm ($\hbar\omega_{43} = 1.83$ eV) the linewidth for the resonance mode is $\gamma = 2\hbar\Delta\omega = 0.0007$ eV. The $Q = \hbar\omega_{43}/2\hbar\Delta\omega$ value is then 2600.

Nonlinear behaviour of Q can be seen in figure 4(*b*): the initial growth of Q value with size parameter is followed by rapid decrease in the short-wavelength spectral region. We suggest that the observed reduction of the Q factors is due to absorption by NCs that are coupled to the relevant WGM. It is well known that absorption or gain or refractive index variations alter the Q value. Because of the significant Stokes shift (30 nm) between the intrinsic PL peak and absorption, the absorption coefficient is reduced at the long-wavelength part of the PL band, allowing a higher Q factor to be achieved in this spectral region. Note that the discrepancy between theoretical estimation of $\Delta\lambda$ values and experimental results can be seen again in spectral region where NC absorption is significant (figure 4(*a*)).

With knowledge of the quality factor, it is possible to estimate the average photon lifetime in the relevant mode: $\tau_n = Q_n/\omega_n$ [16]. For the WGM peak with $n = 43$ the τ value was estimated to be around 3.7 ps, whereas the average time for the peak with $n = 41$ increases up to 5.8 ps.

Because of the high quality factor of MF microspheres and the very narrow WGM peaks, spherical microcavities are very promising systems for the design of an optically pumped microlaser emitting at room temperature especially when coupled with the high quantum efficiency CdTe NCs [6]. In order to investigate the possibility of laser operation in this spectral region, we studied PL spectra of a single MF microsphere covered by a shell of NCs (average size of 4.4 nm, PL maximum at 595 nm) under optical excitation of various intensities (figure 5). A sharp peak with a Lorentzian lineshape and a full width at half-maximum of 2.3 nm emerges at 607 nm and grows to dominate the entire emission spectrum with increased excitation power. The intensity of this peak increases faster than the intensity of the background luminescence and nonlinear behaviour can be seen in the dependence of emission intensity on pump power. However, we cannot take this as clear evidence of lasing, as (i) we see enhanced scattering at 607 nm without NCs and (ii) we did not observe any mode narrowing in the spectral response with the NC layer present. Also, additional PL peaks (A and C) appear at the short-wavelength (peak A) and long-wavelength edges (peak C) as the pump energy increases. Neither of these showed a threshold behaviour in the $I_{PL} = f(I_{\text{pump}})$ dependence. Due to the lack of external high reflectivity mirrors in the spherical microcavity, threshold is not well established as in standard laser systems. Future studies will look at spheres of different diameters, of improved quality and with different thicknesses of NC layers to look for laser emission.

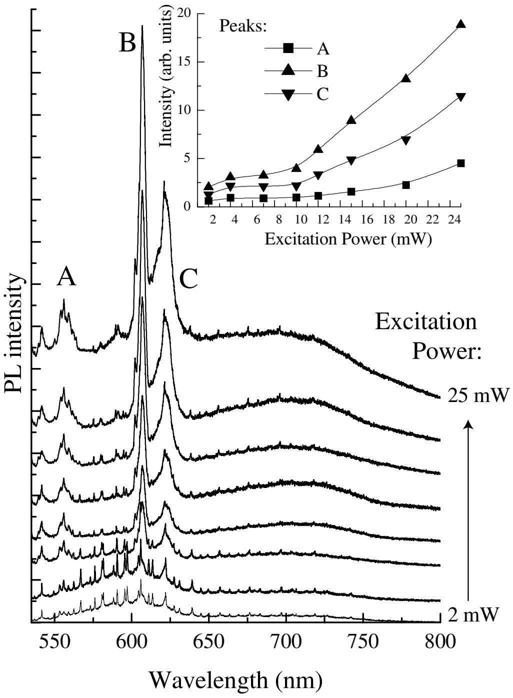

Figure 5. PL spectra of single MF/CdTe sphere at different pump energies. The inset shows the emitted intensity at 555 nm (peak A), 607 nm (peak B) and 621 nm (peak C).

4. Conclusion

We have demonstrated the resonance modes in a composite system consisting of a spherical microcavity and thin CdTe NC shell. The method of preparation of such structures has unique advantages. Confocal microscopy reveals that certain microspheres contain defects and thus allows us to pick the highest quality spheres for our studies. An increase in the photon storage time was obtained with a rise of the microcavity quality factor. Our results show that the MF/CdTe system is highly efficient in coupling out light from the NCs. Microspheres covered by CdTe NCs should therefore be useful for a variety of photonic applications.

Acknowledgment

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