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Optical properties of CdS nanoparticles embedded in polymeric microspheres

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ABSTRACT

Mesoporous microspheres of styrene-divinylbenzene (Sty-DVB) copolymer have been used as template for encapsulation of CdS nanocrystal-quantum-dots (NQDs). Raman, micro-photoluminescence and optical absorption were used to investigate the optical properties of the nanocomposites containing CdS NQDs. When a single microsphere nanocomposite is excited by a laser beam at room temperature, very strong and sharp whispering-gallery mode (WGM) is shown on the background of CdS NQD PL spectra, which confirms that coupling between the optical emission of the encapsulated NQDs and spherical cavity modes was realized. The results show that the microspheres loaded with CdS nanoparticles work as an optical microcavity allowing the observation of WGM. The lasing behavior is achieved at relatively low laser excitation intensity (~1 mW) at room temperature. High-optical stability and low-threshold value make this optical system promising in visible microlaser applications.

1. Introduction

Semiconductor nanocrystal-quantum-dot (NQD) has attracted a great deal of attention since they can provide a superior performance and can be used in a broad range of applications such as optoelectronics, telecommunications, sensors, and artificial photosynthesis. The design and synthesis of nanometer-scaled particles (specifically, semiconductor nanocrystal-quantum-dot based) have been the focus of intense fundamental and applied research, with special emphasis on their size-dependent properties [1–12]. From fundamentals to lasing applications several types of microcavities structures have been used [4–10]. A spherical three-dimensional optical microcavity can be made of a non-absorbing microsphere with a higher refractive index than the surrounding medium, having a diameter comparable to or slightly larger than the light wavelength, i.e. a few microns [13,14]. In such microcavities there exist a number of discrete resonant optical modes, the so-called whispering-gallery modes (WGM). WGM is a resonance of light wave trapped inside dielectric spheres or disks by total internal reflection. Glass and polymeric microspheres are suitable for optical devices with WGM resonators. Efficient lasing from dye-doped polystyrene microspheres has been observed [8,11]. When a single microspherical cavity is excited by a laser beam, at room temperature, very strong and sharp resonance peaks appear on the PL spectra, which can be well explained by the coupling of the QD luminescence with the WGM of the spherical microcavity based on the Mie scattering theory.

This study reports on the optical characterization of CdS semiconductor quantum dots encapsulated into microspheres of mesoporous styrene-divinylbenzene (Sty-DVB) copolymer template. We found that the luminescence from the NQD (CdS) can couple with the WGMs of the polymeric hosting template while a lower threshold of stimulated emission or lasing modes of the NQD can be realized. We emphasize the simplicity and flexibility in fabricating polymeric Sty-DVB-based microspheres ranging in diameter from 10 to 100 μm. The ion-exchange method used here to prepare the semiconductor nanocomposite provides full control of the density of NQDs encapsulated into the polymeric micron-sized spheres.

2. Sample description and experimental details

The Sty-DVB copolymer used in this study was synthesized by suspension polymerisation in the presence of inert diluents [15,16]. Apparent density (0.44 g/cm^3), surface area (140 m^2/g), average pore diameter (13 nm), toluene regain (1.52 cm^3/g), heptane regain (1.24 cm^3/g), percentage of volume swelling in toluene (100%), and percentage of volume swelling in heptane (58%) were parameters used to characterize the spherical, micrometer-sized polymeric template. Sulphonation of the Sty-DVB spheres were performed using concentrated sulphuric acid (2 g of polymer/30 mL of sulphuric acid). The reaction was carried out in the presence of dichloroethane (40% in volume with respect to sulphuric acid). The Sty-DVB spheres were first suspended in dichloroethane for a few minutes. Then, sulphuric acid was added slowly while the temperature was maintained at 70 °C for 4 h. The Sty-DVB polymer microspheres were separated by filtration, washed thoroughly with deionized water, and dried at 60 °C for 24 h. The ion-exchange capacity (4.8 mmol of H^+/g) was determined as described in the literature [17]. CdS nanoparticles were embedded into the microspheres by ion exchange as described in the literature [18]. The

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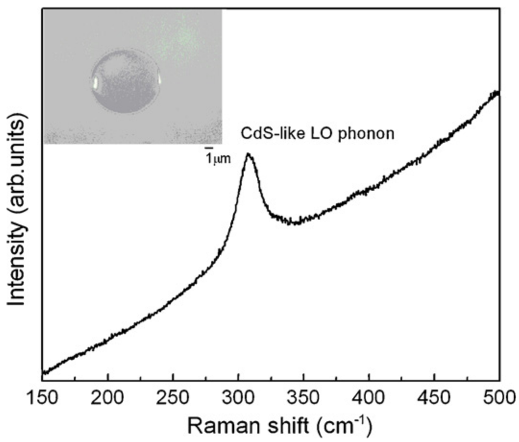

Fig. 1. Raman spectrum of CdS nanoparticle hosted in mesoporous microspheres of styrene-divinylbenzene (Sty-DVB) recorded at room temperature. The wavelength of excitation laser line was 514 nm. The inset shows a picture of a single polymer microsphere.

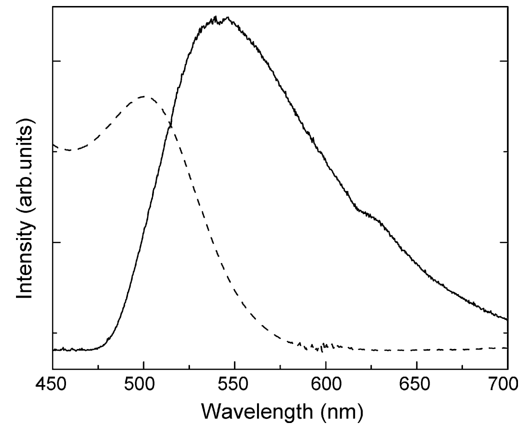

Fig. 2. Photoluminescence (solid line) and absorption (dashed line) spectra of CdS NQD embedded in mesoporous microspheres of styrene-divinylbenzene (Sty-DVB) recorded at room temperature. The wavelength of excitation was 514 nm, and the laser power was set at 50 mW.

microsphere used in the PL experiments showed a perfect surface with diameter ranging from 10 to 100 μm.

Optical characterization of the CdS NQD encapsulated into the polymeric microspheres was realized by Raman spectroscopy, micro-photoluminescence (μ-PL), and optical absorption. Raman scattering spectra of the micrometer-sized polymeric microspheres loaded with CdS NQD were recorded in a backscattering geometry by using a Jobin Yvon triple micro-Raman system. CW argon-ion laser was used operating at the wavelength 488.0 nm and power of 50 mW. The scattered light was detected by a CCD camera. A 50× objective focused the laser light onto the microspheres. To reduce auto-focalisation inside the sample that may damage it, we had to work at lower laser power. In the μ-PL experiment a CW argon-ion laser beam working at the excitation wavelength 514 nm and excitation power at 10 mW is focused onto a spot of about 3 μm on the sample surface using a microscope objective (10×), but due to the spherical shape, the beam becomes tightly focused inside the sample, providing a spot as low as 1 μm wide [19]. The incident laser beam hits the surface and excites electrons in the NQDs. Electrons return to the ground state by emitting photons. Emission from the excited microsphere is collected through the same microscope objective. A beam-splitting prism is used to reflect the light back from the sample towards the scanning monochromator. A Spex 750 M was used to determine the microlaser emission wavelength whereas a CCD camera operating at 140 K was used to measure the PL intensity. The optical absorption data were obtained at room temperature using a spectrophotometer operating between 250 and 1000 nm.

3. Results and discussion

A typical Raman spectrum of the nanocomposite sample is shown in Fig. 1, using the 488 nm excitation line of an argon-ion laser. The Raman signal from the microsphere sample is strong for the CdS-like longitudinal optical (LO) phonon located at 308 cm^{-1}, in agreement with what is expected from the two-mode behavior of the lattice vibrations in CdS alloy. The large background accounts for the luminescence due to the polymeric template.

Fig. 2 demonstrates the PL emission and the optical absorption obtained by exciting an ensemble of semiconductor nanocomposite microspheres. The spectral distribution demonstrates low size dispersion related to the CdS nanoparticle. The CdS nanoparticle exhibit band-to-band absorption centred at 2.48 eV (500 nm). Using this information the average nanoparticle size was determined from the absorption onset by the effective mass model approximation [2]:

$$E \cong E_{\text{bulk}} + \frac{\hbar^2\pi^2}{2eR^2}\left(\frac{1}{m_e m_0} + \frac{1}{m_h m_0}\right) \quad (1)$$

where E is the NQD band gap, E_{bulk} is the band gap of the bulk material, R is the particle radius, m_0 is the free electron mass, and m_e/m_h is the effective mass of electron/hole. With the effective masses of electrons ($m_e = 0.21m_0$) and holes ($m_h = 0.80m_0$), we have obtained 14 nm (average diameter) for the CdS NQD. However, the PL emission changes significantly when we measure a single microsphere (diameter of 40 μm) using the μ-PL setup, as shown in Fig. 3. The spectral measurements typically indicate multimode laser operation over a narrow portion of the PL spectrum. The spectrometer resolution was set at 0.01 nm, allowing visualization of individual lasing WGM. Then, resonances due to the WGM are observed in the emission spectrum and demonstrate effectively the optical properties of the polymeric cavity. Details of the WGM structure are shown separately in Fig. 4, after subtracting the Gaussian background curve from the PL spectrum. There is a clear periodical modulation, which we assign to selected optical modes of the spherical microcavity. It is found that the intensity of the resonance modes is strong enough to emerge from the background emission and the intensities of the resonance modes increase with increasing excitation power, while the background emission intensity does not follow this trend; it became saturated at higher excitation power. This makes lasing behavior easy to achieve even at room temperature. Microlaser output power is shown in the inset of Fig. 4 as a function of absorbed pump power.

One of the reasons to observe this phenomenon is due to the large interlevel energy-spacing in NQDs; "quantum-confined" excitons are more robust than bulk excitons, allowing one to excite amplified spontaneous emission (ASE) at lower pump levels. Due to the discrete structure of optical transitions in NQDs thermal depopulation of the lowest "emitting" states is inhibited. Therefore, NQDs are predicted to provide superior performance in lasing applications in comparison with bulk and other low-dimensional

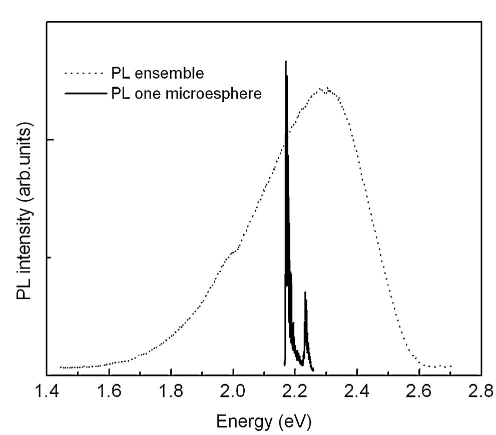

Fig. 3. Room-temperature PL spectra of a single polymer microsphere (solid line) compared to the PL of an ensemble of microspheres (dot line).

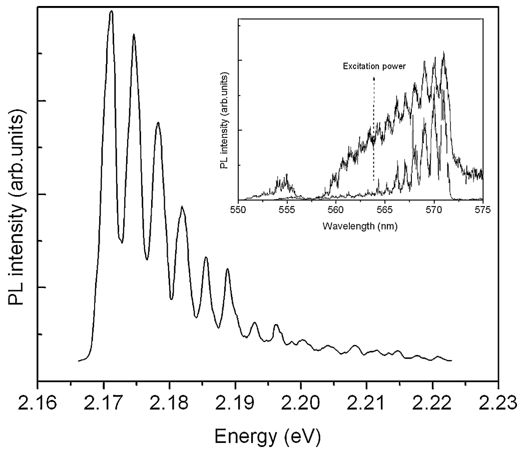

Fig. 4. Normalized PL spectrum shows the whispering-gallery modes. The inset shows room-temperature PL spectra of a single polymer microsphere at two excitation powers (2 mW and 23 mW).

semiconductors. Also, the NQD gain medium was combined with an optical cavity that provided efficient positive feedback. Note that the Q-factor of a resonator mode is defined as the ratio of resonance frequency to mode linewidth, so high Q values imply narrow linewidths and long cavity lifetimes. We have calculated the value of the optical microcavity quality factor (Q) using the following expression [20]:

$$Q = \frac{\hbar\omega_0}{2\hbar\gamma} \quad (2)$$

where $2\hbar\gamma$ is the Gaussian fitting to the linewidth of the cavity modes and $\hbar\omega_0$ is the photon energy. At the wavelength of 571.1 nm ($\hbar\omega = 2.17$ eV), the Gaussian fit is about $2\hbar\gamma = 0.0019$ eV. Then, the quality factor is about Q = 1, 142. From these findings we can conclude that by encapsulating the CdS nanocrystals in the polymeric microsphere cavity a strong coupling between photonic and electronic states indeed occurs.

4. Conclusion

In summary, mesoporous microspheres of styrene-divinylbenzene (Sty-DVB) copolymer have been used as a template to synthesize and to host CdS nanocrystal-quantum-dots. This system was used to study the optical properties of the polymeric cavity and the gain medium, allowing the observation of the resonances modes of whispering-gallery mode laser. The lasing behavior is realized at relatively low-threshold value. Thus, the high-optical stability of this system makes it very promising in visible microlaser applications such as telecommunication and chemical sensing.

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