CHIN.PHYS.LETT. Vol. 18, No. 10 (2001) 1350

Photoluminescence Study of $CdSe_xS_{1-x}$ Quantum Dots in a Glass Spherical Microcavity *

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(Received 2 April 2001)

The photoluminescence (PL) of $CdSe_xS_{1-x}$ semiconductor quantum dots (QDs) in a glass spherical microcavity is investigated. The $CdSe_xS_{1-x}$ semiconductor clusters embedded in a glass matrix are fabricated by using the heat treatment method. Periodical structures consisting of sharp spectral lines are observed in the PL spectra of $CdSe_xS_{1-x}$ QDs, which can be well explained by the coupling with the whispering gallery modes of the spherical microcavity based on Mie scattering theory.

PACS: 42. 55. Sa, 78. 66. Hf

Recently, the fabrication and optical properties of different kinds of planar microcavities which contain semiconductor nanoclusters or quantum dots (QDs) have attracted much research,[1−6] while studies of spherical or cylindrical microcavities embedded with semiconductor QDs are scarce. A spherical three-dimensional optical microcavity can be made of a non-absorbing microsphere with a higher refractive index than the surrounding medium and a diameter comparable with or slightly larger than the light wavelength, i.e. a few micrometres. In such microcavities, a number of discrete resonant optical modes exist, the so-called whispering gallery modes (WGMs).[7,8] It is well known that II-VI semiconductor compound QDs can be grown in different matrices, such as glasses, solid solutions, polymers or even cavities of zeolites by different manufacturing processes.[9,10] When semiconductor QDs are embedded in the spherical microcavity, the quantum dot luminescence can couple with the WGMs, and a lower threshold of stimulated emission or lasing modes of QDs may be realized. Artemyev and Woggon[8] prepared spherical microcavities using a chemical method. They embedded CdSe semiconductor QDs in the poly methyl methacrylate (PMMA) microsphere and realized the coupling of electronic and photonic states.

Glass provides an ideal matrix to accommodate semiconductor nanoclusters as the bonds in amorphous glass are flexible, being easy to prepare and compatible with the optical fibre. However, until now there has been no report on the embedding of semiconductor QDs into glass spherical microcavities and their optical properties. We have used a new approach to prepare glass microspheres embedded with $CdSe_xS_{1-x}$ semiconductor QDs. These have a better optical stability than the polymer microspheres prepared by the usual chemical approaches, because the latter are often degraded under strong illumination due to the photosensitive surface reactions. The resonant WGMs are observed in the glass microspheres with QDs for the luminescence of both excitonic transitions and from surface defect states of the embedded QDs. High-quality factor Q values are realized for WGMs.

To prepare the optical microspheres containing semiconductor QDs, we have used commercially available glass ingots as source materials for making optical filter glasses, for example, RG645 or other types in the same series. The glass has a refractive index of 1.5 or more, being suitable to use as the microcavity media surrounded by air (refractive index n equals 1). The glass ingots contain several oxides, including CdO, CdS, and elemental sulphur (S^{2-}) or selenium (Se^{2+}),[9] in their composition. They were first pulverized into small glass pieces with the size of a few micrometres and sifted by sieves. Then a specially-designed gas burner was used to heat and blow off micrometre-sized glass pieces. In this heating process the glass pieces were melted at a temperature higher than the softening point and they formed into microspheres due to the surface tension. Spheres of a size of tens of micrometres could be obtained using such a preparation method. The obtained microspheres were annealed at a certain temperature for several hours in order to precipitate and grow $CdSe_xS_{1-x}$ nanoclusters in the microspheres. The typical heat treatment was done in a furnace, for example, at 590° C for 10 h. The colour of the microspheres changes from transparent to red after the annealing, corresponding to a variation of the effective energy gap and absorption edge of the $CdSe_xS_{1-x}$ semiconductor QDs formed in the glass matrix. The precipitation and growth of nanoclusters were controlled by the nucleation and the solid phase diffusion dynamics. The size of the $CdSe_xS_{1-x}$

*Supported by the National Natural Science Foundation of China under Grant Nos. 29890217 and 69876037.

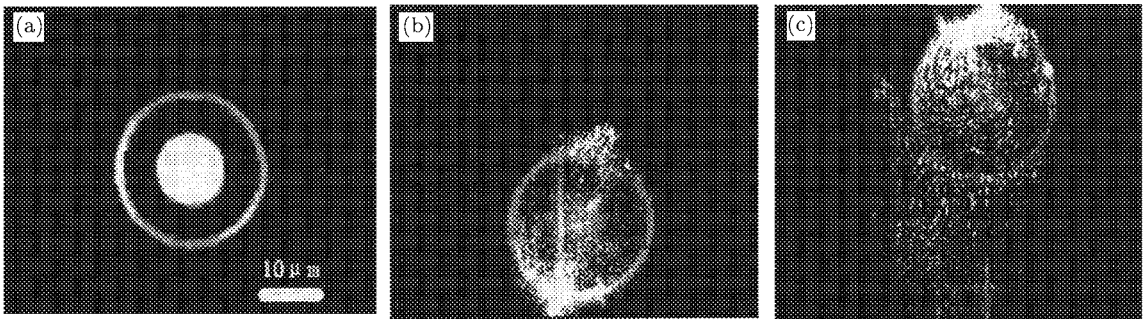

Fig. 1. (a) Optical image of the single annealed microsphere with the diameter of 22.9 μm. (b) Image of the microsphere illuminated by an Ar^+ laser along its upper side; a bright laser spot appears on the lower side. (c) Image of the microsphere illuminated by an Ar^+ laser along its lower side; a bright laser spot appears on the upper side.

semiconductor nanocrystals depends on the annealing temperature and time.[9,10]

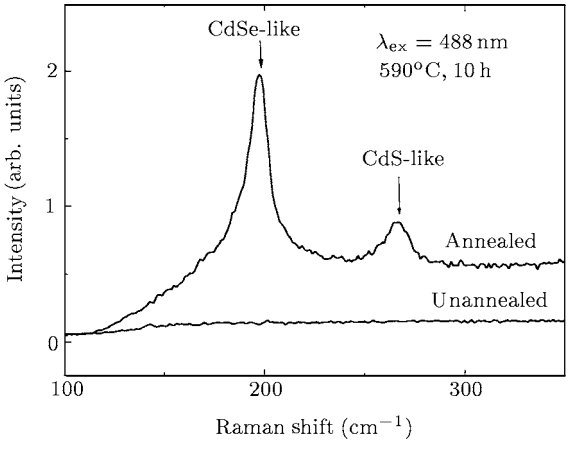

Fig. 2. Raman spectra of the single annealed and unannealed glass microspheres measured at room temperature and in a backscattering configuration.

The Raman scattering and photoluminescence (PL) spectra of the glass microspheres embedded with $CdSe_xS_{1-x}$ QDs are measured in the backscattering geometry using a Dilor Super Labram Microraman system, with a typical spectral resolution of 1 cm^{-1}. A spatial resolution of less than 2 μm is achieved using a microscope with a 100× objective lens. The excitation light wavelength is 488.0 nm from an Ar^+ laser. The scattered or emitted light is passed through a monochromator equipped with a nitrogen-cooled charge coupled device (CCD) camera. Annealed microspheres are put on a quartz glass plate during the measurements in order to reduce the substrate's influence on the measuring results. During the measurements each time only one microsphere was selected under the focused light. The images of the annealed microspheres can be examined under lamp or laser illumination, as shown in Fig. 1. There are three CCD

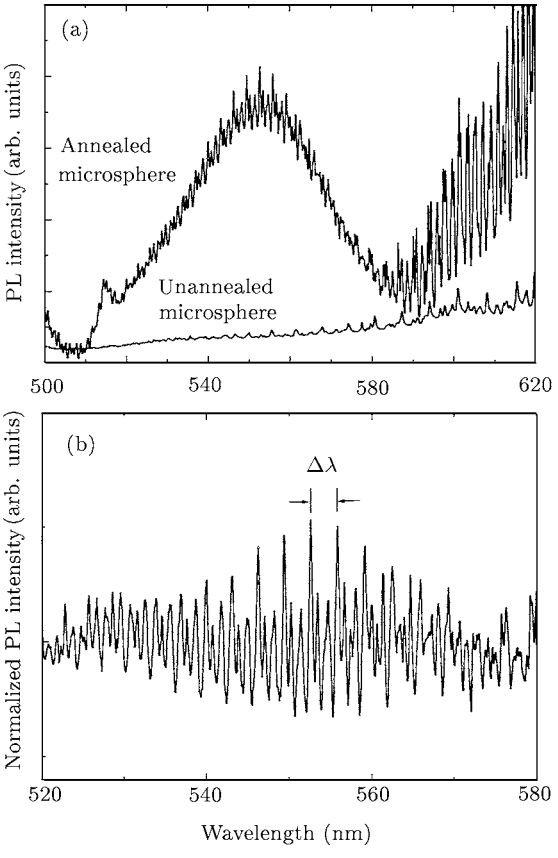

Fig. 3. (a) The upper curve shows the room temperature PL spectrum of a single microsphere with $CdSe_xS_{1-x}$ QDs annealed at 590°C (shown in Fig. 1). The lower curve represents the PL spectrum of an unannealed microsphere. The excitation wavelength is 488.0 nm. (b) Normalized PL spectrum of the upper curve in Fig. 3(a) after subtracting the Gaussian luminescence background of QDs, showing clearer WGMs. The separations between the adjacent peak wavelengths of the resonant WGMs, $\Delta\lambda$, is shown by arrows.

images in Fig. 1. We can clearly see the image of the microsphere illuminated by lamp, as shown in Fig. 1 (a), with a diameter of 22.9 μm. Because the measurement of the CCD images was done with the backscattering geometry method, when the Ar^+ laser

line excites the microsphere along its upper (or lower) side, a bright Ar^+ laser spot appears on the opposite side for the reflection of Ar^+ laser light along the inner surface, which is the lower (or upper) side, as shown in Figs. 1(b) and 1(c). These clearly prove that the prepared micrometre-sized glass microspheres have a perfect surface, which guarantees that the microsphere is a high-quality spherical microcavity.

Raman spectra of the unannealed and annealed microspheres were measured as shown in Fig. 2. The Raman signals from the microsphere sample annealed at 590°C for 10 h are strong for both CdSe-like longitudinal optical (LO) phonon and CdS-like LO phonon modes, located at 197.2 and 266.3 cm,[1] respectively, in agreement with the results expected by the two-mode behaviour of the lattice vibrations in the $CdSe_xS_{1-x}$ alloy.[11,12] However, there is no remarkable Raman signal in this spectral region for the unannealed microspheres. This confirms that the $CdSe_xS_{1-x}$ clusters or QDs are formed after the annealing process.

The optical properties of unannealed and annealed microspheres are also investigated by room temperature PL spectra. It is found that the annealed microsphere samples with a diameter of 22.9 μm exhibit periodic sharp peaks superimposed on PL bands when the excitation light is focused on the microsphere near the inner surface. The upper curve of Fig. 3(a) shows the emission spectrum of the annealed microsphere excited by a 488.0 nm laser line. Many regularly spaced sharp peaks were observed which superimpose on the PL bands. These sharp peaks can be ascribed to the resonant microspherical cavity modes. In addition, the intensity of resonance peaks is different in different wavelength regions. The lower curve of Fig. 3(a) is the PL spectrum of an unannealed microsphere. We cannot find any peak similar to the upper curve arising from $CdSe_xS_{1-x}$ QDs, for there are no QDs in the unannealed microsphere. Details of the WGM peak structure of the QD intrinsic peak position (~550 nm) are shown in Fig. 3(b) after subtracting the Gaussian background lineshape of the upper line curve in Fig. 3(a). Based on the Mie scattering theory,[13] the separation between the adjacent peak wavelengths of the WGM resonance modes, $\Delta\lambda$, is approximately given by

$$\Delta\lambda = \frac{\lambda^2 \arctan\left\{(n_1/n_2)-1\right\}^{1/2}}{\pi n_2 d\left\{(n_1/n_2)-1\right\}^{1/2}}, \qquad (1)$$

where λ and d (~22.9 μm) are the emission wavelength and the diameter of the measured microsphere, respectively, and n_1 and n_2 represent the refractive indices of the sphere ($n_1 \sim 1.523$) and the surrounding air ($n_2 \sim 1.0$), respectively. The calculated value for $\Delta\lambda$ at the intrinsic spectral range of 552 nm is 3.16 nm, which agrees well with the observed mode spacing 3.23 nm, as shown in Fig. 3(b). The small peaks between the regular-spaced peaks are ascribed to the different resonance mode and order numbers in the microsphere, which will not be discussed here. We have also calculated the value of the quality factor Q. The Q value can be given by[13]

$$Q = \frac{\hbar\omega_0}{2\hbar\nu}, \qquad (2)$$

where $2\hbar\nu$ is the Lorentzian fit of the linewidth of the cavity modes and $\hbar\omega_0$ is the photon energy. At the wavelength of $\lambda = 552$ nm ($\hbar\omega = 2.24$ eV) the Lorentzian fit of the linewidth of the resonance mode is about $2\hbar\nu = 0.0024$ eV. From formula (2), we find that the quality factor Q at the intrinsic PL band (~ 552 nm) is about 933. From the above results, we can conclude that by embedding the nanocrystals in the glass spherical cavity a strong coupling between photonic and electronic states has occurred.

In summary, we have successfully embedded the $CdSe_xS_{1-x}$ QDs in a glass microsphere and observed the resonance modes with high Q-factors. This way of preparing a microsphere has unique advantages and is controllable. The microsphere combined with the optical fibre is expected to be used as a stable near-field scanning optical microscope (NSOM) optical probe with high sensitivity and high spatial resolutions, or used for photo storage device applications.[14]

We are grateful for the illuminating discussion with Professor U. Woggon, and are very grateful to Professor LU Kun-Quan, Institute of Physics, CAS, for his help.

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