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Journal of Colloid and Interface Science 284 (2005) 516–520
Journal of Colloid and Interface Science
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Effect of layer thickness on the luminescence properties of ZnS/CdS/ZnS quantum dot quantum well

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Received 21 May 2004; accepted 27 October 2004

Abstract

ZnS/CdS/ZnS quantum dot quantum well was prepared. The optical properties of ZnS/CdS/ZnS QDQW with different thickness of CdS well and ZnS shell were studied. Absorption spectra, emission spectra, and luminescence lifetimes were measured. The observed luminescence was assigned to the bulk donor–acceptor pair recombination of CdS and can be enhanced by increasing the thickness of the CdS well or coating an appropriate thickness of ZnS shell on the surface of the CdS well. The luminescence enhancement was caused by the relative reduce in the surface effect. The luminescence lifetimes were influenced strongly by the surface state.

Keywords: Quantum dot quantum well; ZnS; CdS

1. Introduction

With different properties from the bulk materials, semiconductor quantum dots have drawn considerable interest. Research in this field has been active for several decades. The study followed three directions. The first is preparing quantum dots of new materials. Up to now, a wide variety of II–VI [1–3], III–V [4–6], and even IV–IV [7–9] semiconductor quantum dots have been prepared. The second is preparing quantum dots of usual materials by novel methods. The inverse micelles method [10,11] is one of the best methods by which small nanoparticles with narrow size distributions can be obtained. The third is building up complex heterostructures such as core–shell structures [12–17] and quantum dot quantum well structures [18–23]. At low temperatures, some core–shell structures have displayed a quantum yield of 80%. Luminescence in the entire visible light region has been obtained by tuning the thickness of various layers in the CdS/HgS/CdS quantum dot quantum well.

We have prepared a ZnS/CdS/ZnS quantum dot quantum well in inverted micelles [24]. The optical properties were not just the superposition of the properties of separated ZnS and CdS nanoparticles. Recently, Little et al. [25] reported the chemical characteristics of the same sample structure, ZnS/CdS/ZnS QDQWs, and the electronic states obtained by absorption spectra. In this paper, we reported the effect of layer thickness on the absorption spectra, the emission spectra, and the luminescence lifetime. In particular, we fitted the decay curves with hyperbolic functions.

2. Experimental

The ZnS/CdS/ZnS quantum dot quantum well was prepared in three steps by a method described elsewhere [24]. First, the ZnS core was prepared in AOT (dioctylsulfosuccinate sodium salt) in heptane with water-to-surfactant mole ratio $W = 4$, which led to the diameter of the ZnS core being 3 nm. Second, a calculated amount of Cd^{2+} ions

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doi:10.1016/j.jcis.2004.10.066

was added to displace the Zn^{2+} ions in the Zn–S bond to form a Cd–S bond on the surface of the ZnS core, resulting in the formation of a CdS well. This was chemically reasonable because the solubility of CdS was at least five orders of magnitude smaller than that of ZnS. Third, the ZnS shell was formed by the slow introduction of H_2S and then appropriate amounts of Zn^{2+} ions. Thickness of the ZnS shell can be controlled by changing the amount of Zn^{2+} ions addition. Repeating steps two and three will lead to the thickening of the CdS well. The ZnS/CdS/ZnS quantum dot quantum well was characterized elsewhere [24]. In this paper, the ZnS/CdS/ZnS QDQW was represented by $ZnS(CdS)_m(ZnS)_n$, where m and n are the numbers of monolayers of CdS and ZnS. The thickness of the well and the shell layer can easily be calculated by taking into account the mole volumes of CdS and ZnS and the initial molar ratio of Zn^{2+} to Cd^{2+} ions. According to the calculation, the thickness of a monolayer of CdS was 0.46 nm and that of ZnS was 0.42 nm.

Absorption spectra were measured with a Shimadzu recording spectrophotometer. Fluorescence spectra were taken by a HITACHI F-4500 fluorescence spectrophotometer. The emission lifetime measurements were performed by a SP-70 nanosecond fluorescence spectrometer.

3. Results and discussion

Fig. 1 gives the absorption spectra of ZnS/CdS/ZnS QDQW of a 1-monolayer CdS well with different thicknesses of ZnS shell. It can be seen that for the sample with a 0-monolayer ZnS shell, an absorption onset at 355 nm and a large shoulder at 325 nm were observed. When the particles are covered by a 1.4-monolayer ZnS shell, the onset and the shoulder shifted to 375 and 345 nm, respectively. The positions of the absorption onset and shoulder change little while the thickness of the ZnS shell increases from 1.4 to 3.4 monolayers. We assign the absorption onset and shoulder to an electronic transition within the CdS well. It is blue-shifted from 495 nm for the bulk CdS because of the quantum confinement effect [26]. In the sample with a 0-monolayer ZnS shell, the barrier between the CdS conduction band and the surroundings is so high that the electrons in CdS can tunnel only slightly into the surrounding organic matrix (AOT and heptane) and hence they are well restricted within the CdS monolayer. When a shell of ZnS surrounds the CdS well, the barrier height gets lower and the electrons in the CdS layer may tunnel into the ZnS shell. The increased delocalization of the electron lowers its confinement energy and results in a red shift of the absorption onset and shoulder. Beyond a certain thickness of the ZnS shell the electrons cannot spread out further, and the confinement energies remain constant [14]. So we can say that the coupling between well and barriers determined the position of the absorption band. When there is only one layer of CdS well, both the ZnS core and shell make important contributions to the absorption. But, as the thickness of the CdS well increased, the well had a more important influence on the absorption bands (shown in Fig. 5).

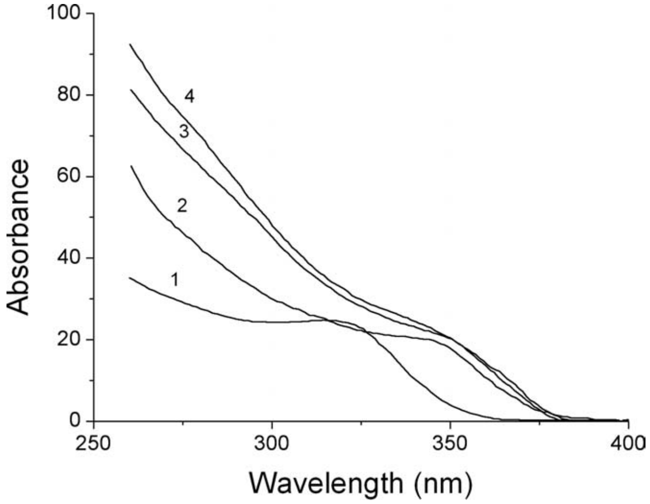

Fig. 1. Absorption spectra of ZnS/CdS/ZnS QDQW of a 1-monolayer CdS well with different thicknesses of ZnS shell. (1) $ZnS(CdS)_{1.0}(ZnS)_0$; (2) $ZnS(CdS)_{1.0}(ZnS)_{1.4}$; (3) $ZnS(CdS)_{1.0}(ZnS)_{2.7}$; (4) $ZnS(CdS)_{1.0}(ZnS)_{3.4}$.

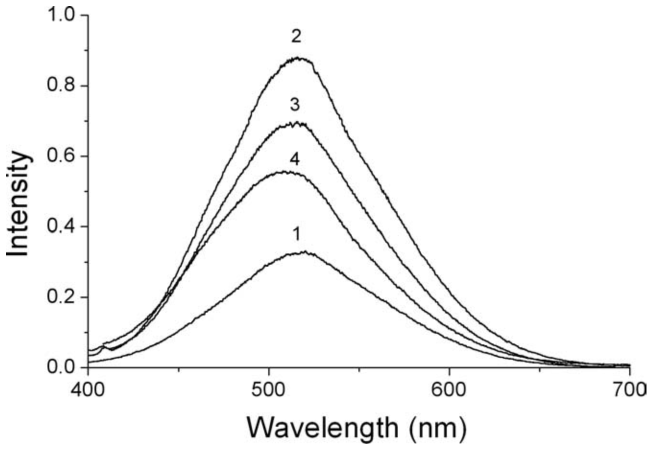

Fig. 2. Emission spectra of ZnS/CdS/ZnS QDQW of a 1-monolayer CdS well with different thicknesses of ZnS shell excited at 356 nm. (1) $ZnS(CdS)_{1.0}(ZnS)_0$; (2) $ZnS(CdS)_{1.0}(ZnS)_{1.4}$; (3) $ZnS(CdS)_{1.0}(ZnS)_{2.7}$; (4) $ZnS(CdS)_{1.0}(ZnS)_{3.4}$.

The emission spectra of ZnS/CdS/ZnS QDQW of a 1-monolayer CdS well with different thicknesses of ZnS shell are presented in Fig. 2. A broad emission band for CdS with maximum at 520 nm is observed. It is also shifted to blue in comparison with the bulk CdS. When a 1.4-monolayer ZnS shell overcoats the CdS well, the luminescent intensity increases. As the thickness of the ZnS shell further increases, the luminescent intensity decreases to a small degree. The emission corresponds to the bulk donor–acceptor recombination of CdS. Surface states usually act as radiationless recombination centers. The ZnS shell compensates for most of the vacancies on the surface of the CdS well and the nonradiative recombination sites are passivated. These are respon-

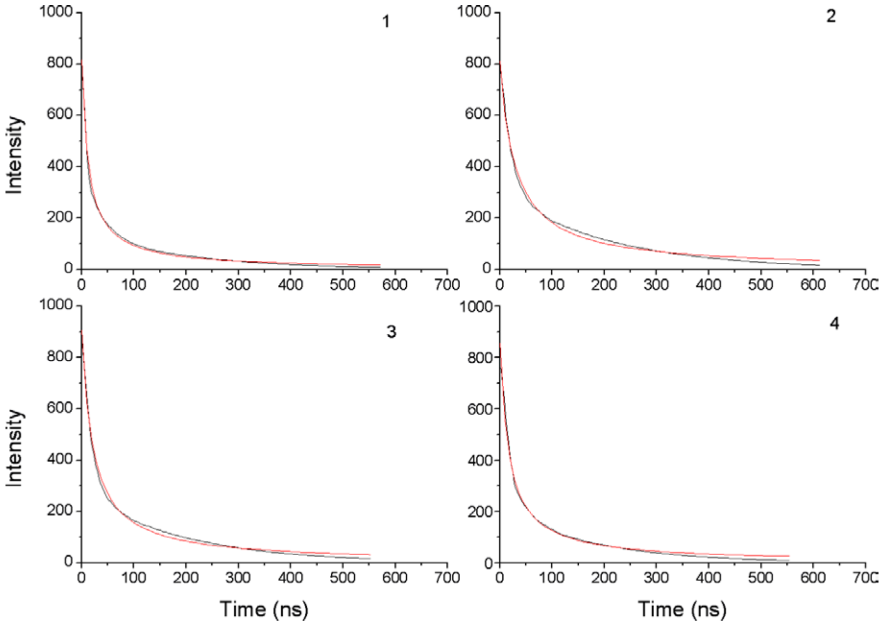

Fig. 3. Luminescence decay curves of ZnS/CdS/ZnS QDQW of a 1-monolayer CdS well with different thicknesses of ZnS shell at 520 nm excited by 337 nm. Experimental curves (black); fitting curves (red). (1) $ZnS(CdS)_{1.0}(ZnS)_0$; (2) $ZnS(CdS)_{1.0}(ZnS)_{1.4}$; (3) $ZnS(CdS)_{1.0}(ZnS)_{2.7}$; (4) $ZnS(CdS)_{1.0}(ZnS)_{3.4}$.

Table 1
Emission lifetime data of ZnS/CdS/ZnS QDQW with different thicknesses of ZnS shell

No.	a	b (ns^{-1})
1. $ZnS(CdS)_{1.0}(ZnS)_0$	817.7 ± 6.7	0.075 ± 0.0011
2. $ZnS(CdS)_{1.0}(ZnS)_{1.4}$	812.7 ± 7.5	0.033 ± 0.0006
3. $ZnS(CdS)_{1.0}(ZnS)_{2.7}$	905.5 ± 8.0	0.046 ± 0.0008
4. $ZnS(CdS)_{1.0}(ZnS)_{3.4}$	858.0 ± 9.5	0.056 ± 0.0012

Note. $c = 1.02$.

sible for the luminescence enhancement. The lattice parameters of CdS differ from that of ZnS by 7%. About one-unit-cell-thick coating layers can accommodate the lattice misfit between CdS and ZnS by elastic strain exclusively [13]. But as the shell is thickened further, the increasing strain due to the lattice mismatch could lead to the formation of dislocations. Some reduction in the luminescent intensity is attributed to the generation of misfit dislocations, which act as centers for radiationless recombination when the thickness of the shell increases [14]. On the other hand, with the amounts of ZnS increasing, the concentration of the CdS luminescence centers decreases which results in some of the reduction in the luminescence intensity.

Fig. 3 (black) exhibits the luminescent decay curves of ZnS/CdS/ZnS QDQW of 1-monolayer CdS with different thicknesses of ZnS shell. Due to the pair feature of the emission, we fit the decay curves with a hyperbolic function:

$$F(t) = a\big(1/(1+bt)\big)^{c}.$$

We chose a single c (c is a parameter that is proportional to the velocity of donor-accepted recombination) for all the decay curves; thus b or $1/b$ (with $t = 1/b$ the intensities decays to 2^{-c} of its original intensity) can be compared. $1/b$ was the time constant. The fitting curves are exhibited in Fig. 3 (red) too. The decay parameters derived from this analysis are summarized in Table 1.

As presented in Table 1, the time constant $1/b$ increases when a 1.4-monolayer ZnS shell surrounds the CdS well. When the thickness of the ZnS shell increases further, $1/b$ decreases again gradually. This indicates that the ZnS shell or the surface plays an important role in the luminescence. Usually, radiationless recombination is a fast process and the radiationless recombination route decreasing would lead to the luminescent decay slow. That the luminescent decay was slowed down by a ZnS shell indicates that the surface vacancies, which act as nonradiative recombination centers, are passivated by the ZnS shell. When the ZnS shell is thickened further, the increased dislocations lead to the surface vacancies increasing, resulting in a shorter luminescent lifetime.

The luminescent lifetimes of ZnS/CdS/ZnS QDQW at various monitoring emission wavelengths are also measured (Fig. 4). They exhibit a range of wavelength-dependent emission lifetimes. The luminescent decays are found to be slower at longer wavelengths. This is one of the characteristic properties of pair recombination. As shown earlier, the wavelength dependence of the emission lifetime in a semiconductor crystallite arises from the contribution of the coulombic energy of interaction between the electron–hole pair to the total energy of the emitted photon [27].

We also studied the properties of ZnS/CdS/ZnS QDQW of a 1-monolayer ZnS shell with different thicknesses of CdS well. Fig. 5 presents the absorption spectra. It can be seen that the absorption onset at 375 nm and the shoulder at 345 nm shift red to 410 and 375 nm when the thickness of CdS well increases to 4 monolayers from 1 monolayer. The red shift is attributed to the size increase of nanoparti-

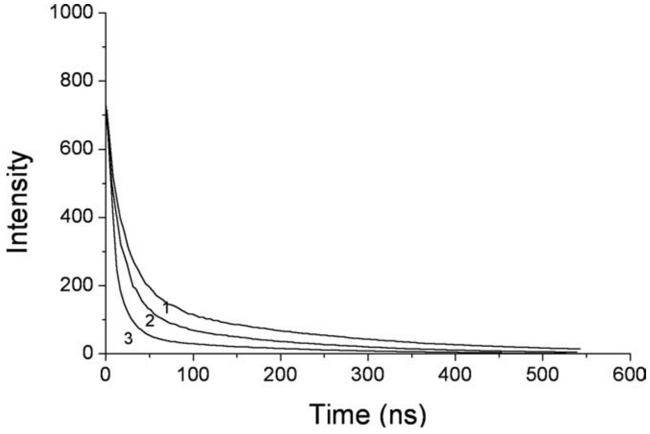

Fig. 4. Luminescent decay curves of $ZnS(CdS)_{1.0}(ZnS)_{3.4}$ monitored at different wavelengths excited by 337 nm. (1) 550 nm; (2) 510 nm; (3) 470 nm.

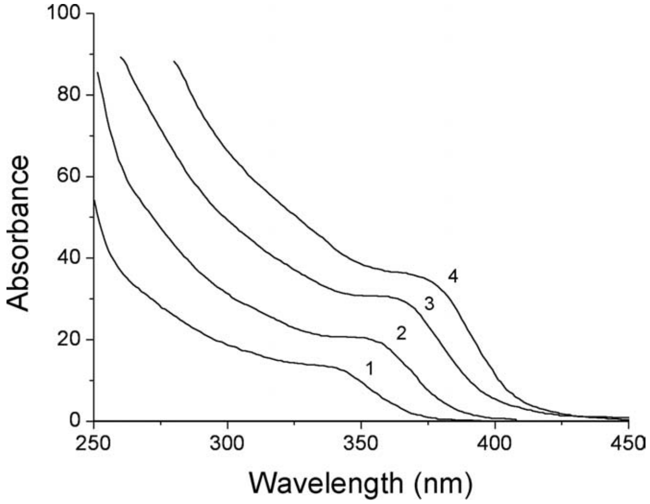

Fig. 5. Absorption spectra of ZnS/CdS/ZnS QDQW of a 1-monolayer ZnS shell with different thicknesses of CdS well. (1) $ZnS(CdS)_{1.0}(ZnS)_{1.0}$; (2) $ZnS(CdS)_{2.0}(ZnS)_{1.0}$; (3) $ZnS(CdS)_{3.0}(ZnS)_{1.0}$; (4) $ZnS(CdS)_{4.0}(ZnS)_{1.0}$.

cles. With increasing thickness of the CdS well, red shift of emission maximum and increase of emission intensity are observed (Fig. 6). The luminescent enhancement is assigned to the contribution of the increased amount of CdS in one particle.

The luminescence decays of the ZnS/CdS/ZnS QDQW with 1-monolayer ZnS shell and various thicknesses of CdS well were also measured (Fig. 7, black). The CdS molecules can be divided into two kinds. One is closely related to the vacancies (nonradiative recombination centers) on the interface, whose luminescence decay should be faster. The other is far from those vacancies, which should have longer lifetimes. So the luminescence decay should have two hyperbolic components. These decay curves were fitted by a hyperbolic function, given as

$$F(t) = a_1\left(1/(1+b_1 t)\right)^{c_1} + a_2\left(1/(1+b_2 t)\right)^{c_2},$$

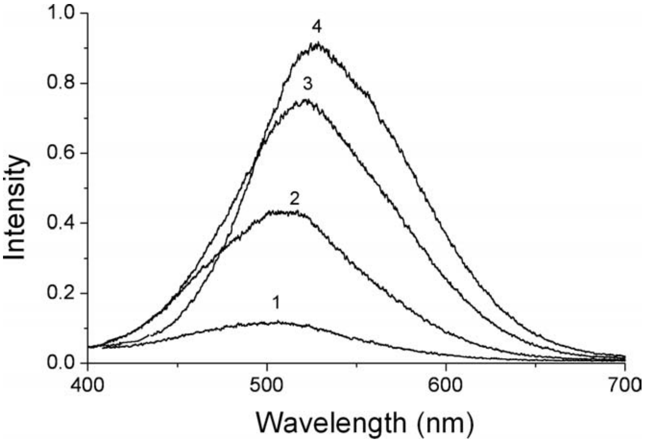

Fig. 6. Emission spectra of ZnS/CdS/ZnS QDQW of a 1-monolayer ZnS shell with different thicknesses of CdS well excited at 370 nm. (1) $ZnS(CdS)_{1.0}(ZnS)_{1.0}$; (2) $ZnS(CdS)_{2.0}(ZnS)_{1.0}$; (3) $ZnS(CdS)_{3.0}(ZnS)_{1.0}$; (4) $ZnS(CdS)_{4.0}(ZnS)_{1.0}$.

Table 2
Emission lifetime data of ZnS/CdS/ZnS QDQW with different thicknesses of CdS well

No.	a_1/a_2
1. $ZnS(CdS)_{1.0}(ZnS)_{1.0}$	10.10
2. $ZnS(CdS)_{2.0}(ZnS)_{1.0}$	3.45
3. $ZnS(CdS)_{3.0}(ZnS)_{1.0}$	2.74
4. $ZnS(CdS)_{4.0}(ZnS)_{1.0}$	2.52
5. $ZnS(CdS)_{4.0}(ZnS)_{1.3}$	2.39

Note. b_1: 0.013; b_2: 0.0013; c_1: 5.46; c_2: 5.39.

where the subscript 1 denotes type 1 CdS, which has faster decay, while 2 denotes type 2 CdS, which has slower decay. Keeping b_1, b_2, c_1, c_2 as constants for all curves, the ratio of a_1/a_2, which gave the relative contributions of the fast decay process and the slow one to the overall emission could be compared. The fitting curves are presented in Fig. 7 (red) and the decay parameters from the fitting analysis are presented in Table 2.

Table 2 indicates that the ratio of a_1 to a_2 decreases gradually with CdS well thickening. This indicates that the relative contribution of the fast process to the overall emission is decreasing and that of the slow process is increasing. In other words, the ratio of the nonradiative recombination to the overall emission, viz., the surface effect is reduced. Table 2 also gives parameters of the sample $ZnS(CdS)_{4.0}(ZnS)_{1.3}$. Compared to the sample $ZnS(CdS)_{4.0}(ZnS)_{1.0}$, the ratio of a_1 to a_2 is smaller. This also indicates that the surface strongly influences the luminescent properties of nanoparticles and the surface modification of the ZnS shell enhances the luminescence.

4. Conclusions

The optical properties of ZnS/CdS/ZnS QDQW with different thicknesses of CdS well and ZnS shell were studied. Luminescence at 520 nm can be assigned to the bulk donor–

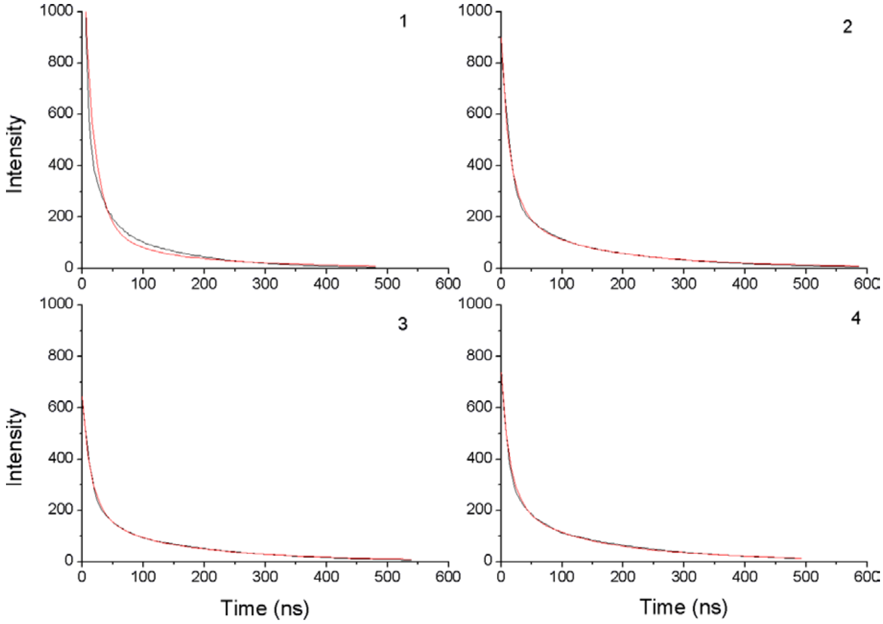

Fig. 7. Luminescent decay curves of ZnS/CdS/ZnS QDQW of a 1-monolayer ZnS shell with different thicknesses of CdS well at 520 nm excited by 337 nm. Experimental curves (black); fitting curves (red). (1) $ZnS(CdS)_{1.0}(ZnS)_{1.0}$; (2) $ZnS(CdS)_{2.0}(ZnS)_{1.0}$; (3) $ZnS(CdS)_{3.0}(ZnS)_{1.0}$; (4) $ZnS(CdS)_{4.0}(ZnS)_{1.0}$.

acceptor recombination of the CdS. Increasing the thickness of the CdS well could lead to the enhancement of the luminescence. The luminescent intensity first increases and then decreases slightly with the ZnS shell thickening. Whether the luminescence is enhanced or reduced has a relation to the contribution of the surface relative to the overall emission. The luminescent decay curves were fitted well with hyperbolic functions.

Acknowledgments

We thank the Natural Science Foundation of Shandong Province (Q2002B01), the Excellent Young Teachers Program of MDE, People's Republic of China ([2003]355), and the State Key Project of Basic Research (Grant 973. G19981309) for financial support.

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