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The formation of CdS nanocrystals in silica gels by gamma-irradiation and their optical properties

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Abstract

Silica gels dispersed with nanoscale CdS particles were prepared by the sol-gel process combined with γ -irradiation at room temperature and in ambient pressure. X-ray diffraction (XRD) and transmission electron microscopy have revealed the existence of CdS nanocrystals, as well as their structures and size distributions. The silica matrix affects the crystal structure of the CdS particles produced. A prominent quantum size effect was observed through the absorption and luminescence spectra of samples irradiated for different periods of time. The most interesting phenomenon is that on increasing the irradiation time, the surface-state emission disappears, and simultaneously band edge emission appears and becomes even stronger with longer irradiation: this is thought to be due to the passivation effect by the surrounding matrix through the interface electrostatic interactions around the particles.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Over the past decade, much attention has been paid to the nanoscale semiconductor structure and quantum dot materials from the viewpoints of scientific interest and their applications [1–5], since these materials exhibit many novel physical and chemical properties. In particular, II–VI semiconductor nanocrystals such as CdS and CdSe show potential applications in photoelectric, biological labelling and light emitting devices [6–9]. By incorporating semiconductor nanoparticles into polymer, glass, or ceramic matrix materials, their interesting optical properties including absorption, luminescence and nonlinearity as well as related applications [1, 5, 10–12] have been studied. In these systems, the very small particle size

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enhances their optical responses (quantum-confinement effect) while the matrix materials act to stabilize the particle size, limit the particle growth and confine the carriers. Because of the high activity of the surface atoms with the formation of surface states, nanoscale semiconductors often have poor luminescence efficiency. Passivation or encapsulation is critical to improve the surface properties of these particles [13–15]. Mesoporous SiO_2 or silica gel made by the well-known sol–gel method, with uniform nanoscale interconnected pores and high specific surface area, has recently been a new exotic kind of matrix for metal/semiconductor nanoparticle-doped materials, because of its good physical qualities and simplicity [10, 16–18]. Gamma-irradiation was extensively used to generate novel nanoscale materials with unusual properties a few years ago [16, 17, 19, 20], since it can help to prepare materials at room temperature and in ambient pressure, can be easily controlled, and induces no impurities into the matrix. But to the best of our knowledge, no work using gamma-irradiation to fabricate CdS nanoparticles in silica gel with good optical properties has been reported until now.

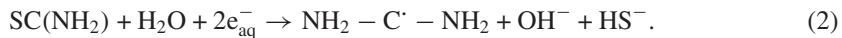
In this research, we used the sol–gel process to prepare mesoporous silica gels with $\text{Cd}(\text{CH}_3\text{COO})_2$ and thiourea in them. Gamma-irradiation was used to synthesize CdS nanocrystals dispersed in the silica gel matrix. The results showed that the silica gel matrix improved not only the dispersity and stability but also the emission responses of the well-dispersed CdS nanocrystals.

2. Experimental section

The CdS -doped silica gels were prepared in two steps. In the first step, the silica gels were made through the sol–gel process: analytical grade tetraethoxysilane (TEOS, 98%), alcohol, HNO_3 , deionized water, $\text{Cd}(\text{CH}_3\text{COO})_2$ and $\text{SC}(\text{NH}_2)_2$ (thiourea) were mixed in the molar rate 1:7:1:10:0.04:0.06. The mixture was stirred magnetically until a homogeneous solution was obtained. The resulting one-phase solution was then poured into a Teflon cylinder and sealed with a transparent glue tape for gelation at 60 °C. The wet silica gel formed after about four days. In the second step, the silica gel obtained was soaked in deionized water at room temperature. After sufficient soaking, the soaked silica gels together with the soaking solution were irradiated by a ^{60}Co γ -ray source (2.59×10^{15} Bq) with a dose rate 65.31 Gy min^{-1} at room temperature and under ambient pressure to induce the formation of CdS nanoparticles in the pores of the silica gels. Next, the irradiated samples were taken out of the soaking solutions and dried at 40 °C in a vacuum dryer, then ground to powder and washed with anhydrous alcohol to remove any by-product. The final powder samples were dried in vacuum again. The irradiated and dried gels were yellow or orange-yellow in colour. In contrast, a blank silica gel (without $\text{Cd}(\text{CH}_3\text{COO})_2$ and $\text{SC}(\text{NH}_2)_2$) and an aqueous CdS colloid were also prepared. The latter was also prepared through gamma-irradiation from a mixed solution of $\text{Cd}(\text{CH}_3\text{COO})_2$ and $\text{SC}(\text{NH}_2)_2$ with the same concentrations as those in the silica gels. The mechanism for the formation of the CdS particles could be described as follows, as indicated in the literature [20, 37]. Water irradiated with ionizing radiation produces the following molecules and radical species in solution:



To scavenge oxidative radicals H^\cdot and OH^\cdot , some isopropanol was added in the soaking water before irradiation. Then the reducing species e_{aq}^- may react with H_2O and thiourea:



Finally, CdS ion pairs form through the following reactions:



Table 1. The preparation conditions and the measurement results of the samples. (The gamma-irradiation dose rate was 65 Gy min⁻¹.)

Sample and number	Irradiation time (h)	Threshold peak		Emission peak (nm)	Particle size (nm)	Lattice structure
		nm	eV			
Blank Silica gel (1)	24	—	—	—	—	—
CdS/silica gel (2)	10	335	3.82	375 598	1.4	Hexagonal
CdS/silica gel (3)	16	394	3.17	424	1.8	Hexagonal
CdS/silica gel (4)	24	454	2.75	478	2.5 (2.7) ^a	Hexagonal
Colloidal CdS (5)	24	470	2.65	—	(4.2) ^a	Cubic

^a Sizes from the XRD measurements.

Then CdS ion pairs coalesce to form CdS clusters in solution:



Table 1 gives details of several samples and their preparation conditions. The samples obtained were characterized by x-ray powder diffraction (XRD) on a Japan Dmax- γ A x-ray diffractometer using graphite-monochromatized Cu K α radiation ($\lambda = 1.54178 \text{ \AA}$). The morphology and SAED of the CdS particles were performed on a JEOL 2010 high-resolution transmission electron microscope with an accelerating voltage of 200 kV. The camera length of the SAED experiment is 0.8 m. The optical absorption spectra were measured on UV-365 Spectrophotometer in the range from 200 to 650 nm at room temperature. Room-temperature luminescence spectra were recorded on a Hitachi 850 fluorescence spectrophotometer.

3. Results

Figure 1 shows the powder XRD patterns of the doped silica gels (sample 4) and the contrasting samples (1 and 5). The XRD pattern of the undoped silica gel (sample 1) shows a typical amorphous halo pattern around $2\theta = 23^\circ$ (a). However, some peaks appear for the CdS doped silica gel (sample 3) (b). The peaks at $2\theta = 24^\circ, 26.5^\circ, 28^\circ, 44^\circ, 48^\circ$ and 52.5° are assigned to the (100), (002), (101), (110), (103) and (112) diffractions of hexagonal wurtzite CdS, respectively [21]. This confirmed that the gamma-irradiation induced the formation of CdS nanocrystallites in the silica gel matrix. For the aqueous CdS colloid, peaks at $26^\circ, 44.5^\circ$ and 51.5° representing the (111), (220) and (311) diffractions of cubic cadmium sulfide appear [22].

Figure 2(a) is a TEM micrograph for the doped silica gel irradiated by γ -radiation for 24 h (sample 4), showing nearly spherical CdS particles uniformly dispersed in the gel matrix. The mean particle sizes were determined by measuring the size of 50 particles on an enlarged morphology micrograph, and are shown in table 1. The mean sizes of the dispersed particles increased with lengthening the irradiation time, which could be explained by the aggregation mechanism of Ostwald ripening [23]. The image inserted in figure 2(a) is the corresponding selected-area electron-diffraction pattern for the particles dispersed in sample 4. The values of interplanar spacing d_{hkl} calculated from the diameters of the diffraction rings are in good agreement with that of bulk hexagonal CdS. There are no other crystallites to be found in the examinations. Therefore, it is reasonably concluded that the microcrystallites dispersed in the

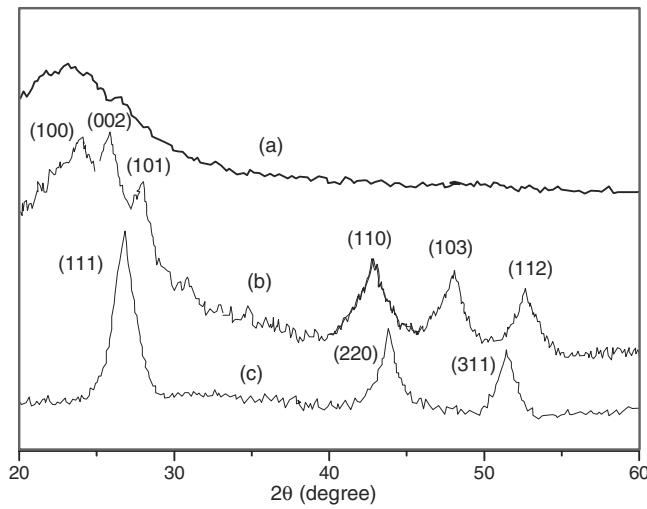


Figure 1. Curve (b) is the powder XRD pattern of a doped silica gel (sample 4), and curves (a) and (c) are of the contrasting samples (samples 1 and 5).

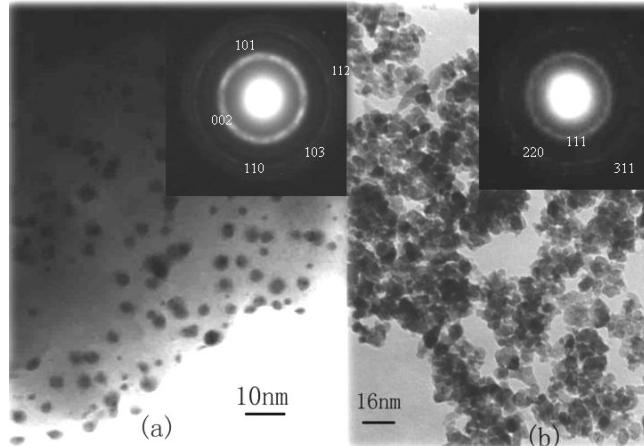


Figure 2. HRTEM morphology micrographs for the CdS/silica gel irradiated by gamma-rays for 24 h (sample 4) (a), and for the aqueous CdS colloid (sample 5) (b). The images in the top right-hand of (a) and (b) are the corresponding selected-area electron diffraction patterns.

networks of silica gels were all CdS particles. For comparison, the morphology micrograph and its corresponding electron diffraction pattern for the aqueous CdS colloid were also examined, and they are shown in figure 2(b). The mean sizes and the lattice structures of the particles in samples 2–5 agree well with those from the XRD measurements.

Figure 3 shows the optical absorption spectra of the samples. Curve (a) is for the reference blank silica gel (sample 1), and curves (b)–(d) with apparent and structured excitonic absorption are all for the CdS-doped silica gels (samples 2–4), showing an absorption threshold at 335 (3.82 eV), 394 (3.17 eV) and 454 (2.75 eV) nm, respectively. From the spectra, the band threshold of samples 2–4 has blueshifts of 177, 118, and 58 nm in wavelength as compared to 512 nm for bulk CdS [18], and the threshold of the doped sample shifts towards short wavelength

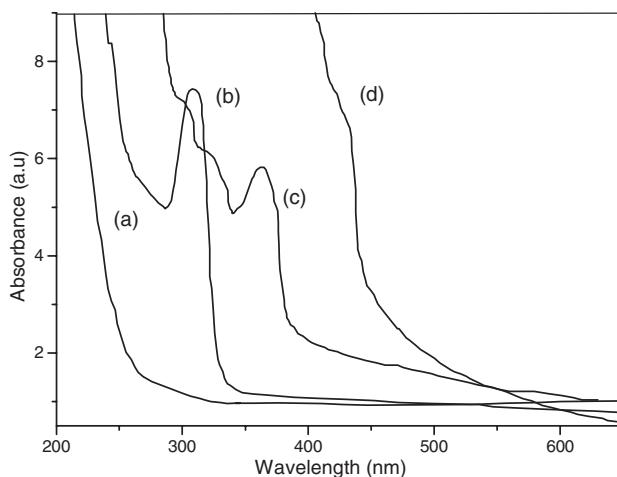


Figure 3. Optical absorption spectra: Curve (a) is for the reference undoped silica gel (sample 1), curves (b)–(d) are for the CdS-doped silica gels irradiated by gamma-rays for 10, 16 and 24 h, respectively (samples 2–4).

(i.e. high energy) with short gamma-irradiation time (or with decreasing the dispersed particle size).

Figure 5 shows the photoluminescence spectra of the CdS-doped silica gels (samples 2–4) with different irradiation times. Curve (a) (for sample 2) has two emission peaks at around 375 and 598 nm, but curve (b) and curve (c) (for samples 3 and 4) only exhibit one peak at about 424 and 478 nm, respectively. For the unrestrained colloidal CdS (sample 5), a very weak emission band at 598 nm was detected (curve (d)). This evolution gives interesting information on the nanocrystals and environments. The emission band at around 400 nm was related to the band edge emission coming from the direct recombination of the conduction band electrons and the valence band holes [31], and the emission peak at 598 nm was assigned to the luminescence of the surface trap, i.e., coming from the recombination of the electrons trapped inside a sulfur vacancy with the holes in the valence band of CdS nanoparticles [31–33]. From curves (a) to (c), we can observe that with increasing mean size of the dispersed CdS particles, the band edge emission exhibited a significant redshift accompanying the enhancement of the band edge emission intensity, whereas the surface state emission at 598 nm disappeared for samples 3 and 4 irradiated for a long time. The band edge emissions in samples 2–4 all show a large blueshift as compared to the band gap emission for bulk CdS (560 nm), which is due to the quantum confinement.

4. Discussion

From figure 2, it could be found that the silica gel matrix played an important role in controlling the size and the size distribution of the doped CdS particles, since an inevitable aggregation occurred in the unrestrained colloidal CdS particles due to their high surface energy [24]. The pores in the sol–gel silica matrix are small enough in size and highly separated [25], and the possible flow of the filling solution between the adjacent pores in the doped samples during γ -irradiation is avoided somewhat due to the viscosity of the gel and the surface tension; thus the CdS nanocrystals in the gels seldom aggregate, but are well dispersed.

From the XRD and HRTEM measurements, we could observe that the CdS microcrystals in the pores of the silica gels (samples 2–4) and the colloidal solution (sample 5) have,

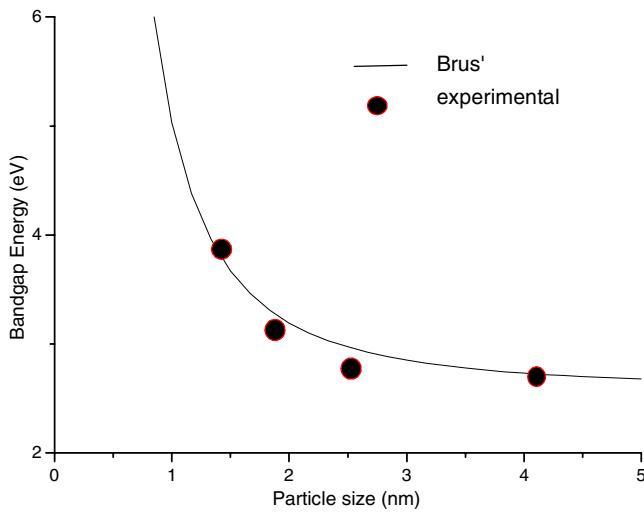


Figure 4. This figure shows the band gap energy $E(r)$ dependence of the particle size according to the Brus formula (solid curve) and the experiment results for samples 2–5, respectively (solid circle).

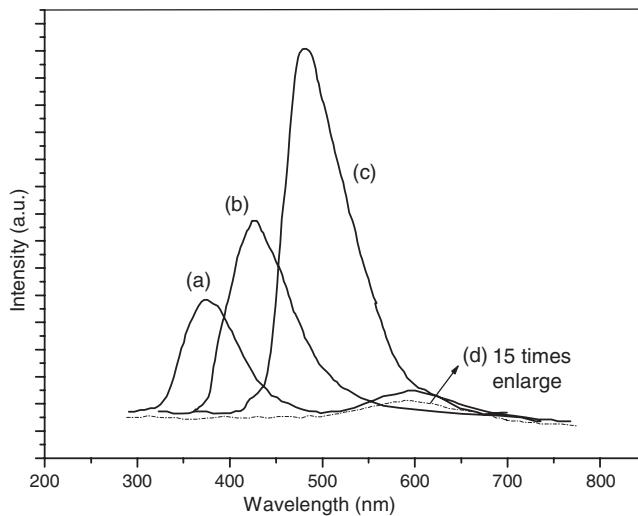


Figure 5. This figure shows the photoluminescence spectra of the CdS doped silica gels irradiated by gamma-rays for 10, 16 and 24 h, respectively (samples 2–4).

respectively, hexagonal and cubic structures. In our experiments, the CdS particles in the gels and the colloidal solution were prepared under a similar procedure, so the silica gel matrix should play an important role in determining the crystal structures of the as-prepared CdS particles. According to the publications [23, 25, 40], the cubic CdS crystallite is nonequilibrium metastable, while the hexagonal CdS crystallite is the stable phase. High temperature or particle growth usually leads to the stable hexagonal phase CdS [40, 41]. In our case, the large unrestrained particles in sample 5 are of the metastable cubic phase, but the small particles in the pores of the silica gels (samples 2–4) are of the stable hexagonal phase, so the size effect

would not be the decisive factor of the crystal phase, whereas the temperature effect might play the main role in the structure formation. During the gamma-irradiation, the induced chemical reaction in the pores of the silica gels should produce a large quantity of heat. The heat is hard to remove from the silica matrix over a short time, resulting in local high temperatures in the pores, since silica gel is a poor thermal-conductor because of its high porosity and composition [26]. As for the CdS particles in solution (sample 5), it is very easy for the heat to dissipate to the surroundings during the irradiation, then lead to a relatively low local temperature in the reaction system, and induce the formation of the metastable cubic phase of CdS particles. This preparation indicates the influence of microenvironments on the CdS structures. The silica matrix improved the dispersity and stability of the embedded CdS particles, which is similar to the situations in which the dispersity and stability of Pd nanoparticles were enhanced by growing in a graphite matrix [27, 28].

The large bandshifts with the particle size and the large blueshifts compared to the values for bulk CdS in the absorption and emission spectra should be caused by strong quantum confinement effect because of their very small sizes. The quantum size effect begins when the CdS crystallite size is smaller than Bohr's radius (6 nm), and there is a progressive increase in excitonic transition energy (band gap) with decreasing particle size [29]. The change of the band gap energy as a function of particle size can be described with the Brus formula [30]:

$$E(r) = E_g + \pi^2 \hbar^2 / 8r^2 [1/m_e + 1/m_h] - 1.8e^2 / \epsilon r, \quad (5)$$

where $E(r)$ is the absorption band gap of nano-semiconductor particles, E_g is the bulk semiconductor band gap energy, r is the radius of the particle, $u = 1/[1/m_e + 1/m_h]$ is the exciton reduced mass, where m_e and m_h are the effective masses of the electron and hole, and ϵ is the dielectric coefficient at optical frequencies. Generally, it is accepted that the effective masses of an electron and a hole expressed in free electron mass are 0.19 and 0.8, and the bulk band energy of hexagonal wurtzite CdS is 2.58 eV [30]. Figure 4 shows the band gap energy $E(r)$ dependence of the particle size according to the Brus formula as well as our experimental results. It can be seen that the results from samples 2 and 5 were in good agreement with that of the Brus theory. But for samples 3 and 4, some deviations exist. Combining the Brus formula and the relative deviations of the samples, we can find that the deviation of the theoretical and the experimental values should mainly come from the effective mass of the electron and the hole as well as the dielectric constant, which may be affected by the surrounding matrix of the particles. When the dispersed particles are much smaller than the sizes of the pores, they might be only partially bonded on the pore walls because of the large porosity at the cluster/matrix interface [17], and any effect from the stiff surrounding cannot take place, but when the size is large enough compared to the pore size, the silica matrix would exert a great effect on the properties of the enclosed particles, inducing large deviations of the band gap energy (samples 3–4). As for the very small particles in sample 2 and the unrestrained particles in sample 5, only small deviations of the band gap value occurred.

As regards the luminescence properties of semiconductor nanocrystals, even under the most favourable conditions, the light emission of CdS particles is not the most probable kind of recombination of the excited carriers, and radiationless recombination is dominant [34]. In particular, the surfaces of unrestrained or free CdS nanoparticles show many imperfections at which radiationless recombination of the trapped carriers would dominate [34], which usually lead to the competing radiative recombination being too weak to be detected. The surface properties of these particles could be improved by passivation or encapsulation of the surfaces to get high-quality luminescence [13–15, 31].

The appearance and enhancement of the emission bands from the doped silica gels with increasing particle size (from samples 2 to 4) and the disappearance of the surface-state

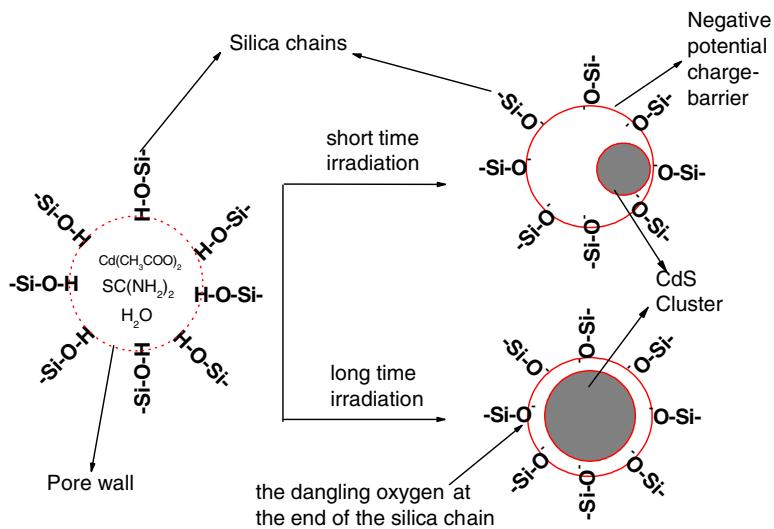


Figure 6. A model of passivation on the CdS surface by the silica chains.

emission in samples 3 and 4 indicate that the influence of the matrix or the surrounding medium on the surface properties is important. In these nanocomposites, the CdS particles are not free, but are uniformly dispersed within the nanoscale pores of the mesoporous silica matrix. Combining the structure of the porous silica gel and the luminescence mechanism of the nanoscale semiconductor, we need to propose a model to explain the different luminescence phenomena in these samples.

On the surfaces of the CdS particles and the internal pore walls in the mesoporous silica matrix, there exist a large number of dangling bonds (unsaturated bonds) at the end of the silica chains ($\text{Si}-\text{O}^-$) [35, 36] and interstitial sulfur atoms (surface state). When the silica matrix is soaked in the water solution, these $\text{Si}-\text{O}^-$ side-bonds combine with H^+ through electrostatic force to make the whole system electrically neutral. During gamma-irradiation, the H_2O molecules could be decomposed by the high-energy gamma-rays, so the H^+ bonded with $\text{Si}-\text{O}^-$ at the end of the silica chains would be sure to be broken by the gamma-rays like the water molecule. After the irradiation process, CdS particles or clusters formed in the pores, and a negative potential charge-barrier would occur around the internal pore walls. This picture is clearly shown in figure 6.

To some degree, the potential barrier will confine or shield the electrons from the core CdS nanocrystals through electrostatic repulsive interactions. Therefore, the surface imperfections responsible for the trapping of charged carriers from CdS particles would be partially blocked through these interactions. At the same time, some of the $-\text{Si}-\text{O}^-$ groups at the end of the silica chains on the pore walls might be fixed on the Cd^{2+} sites or the dangling bonds of the interstitial sulfurs at the interfaces of the dispersed nanocrystals to provide a positive passivation. Moreover, the overall electrostatic interaction would be stronger with larger particle size, because more interface interactions between the core particles and the silica matrix occurs. Hence the surrounding medium by $\text{Si}-\text{O}^-$ groups would make more passivations on the surfaces of CdS particles with energy and charge confinements, and induce higher band gap emission intensity and simultaneously lower the surface-state emission intensity, finally inducing the dominance of band edge emission and the disappearance of the surface-state luminescence band. Capoen *et al* have indicated that controlling surface states could play a

fundamental role in obtaining the well-structured exciton absorption peak of semiconductor nanocrystals [38], so the as-exhibited apparent and structured exciton absorption peaks in the doped silica gels also support a positive carrier confinement effect in this model, since the unrestrained or unblocked CdS clusters with the same size as ours also prepared by gamma-irradiation [22] and non-irradiation methods [39] showed no such strong exciton peaks due to their poor surface properties.

The silica matrix not only improved the dispersity and stability of the embedded particles, but also the emission responses of the dispersed CdS particles through the interface electrostatic interactions between the particle and the surrounding matrix. This effect has potential significance in the application of the materials.

5. Conclusions

We have successfully fabricated CdS/silica nanocomposites by combining the well-known sol-gel process and gamma-irradiation, and observed that the silica matrix not only helps to improve the particle dispersity and stability but also influences the crystal structure and band gap of the dispersed CdS particles. A prominent quantum confinement effect occurs for these particles as seen in optical measurements. Worth noting is that the embedding of CdS into the silica matrix has greatly improved the band edge emission responses of the particles, which is explained by the blocking of the imperfections on the particle surface by the surrounding matrix through the interface electrostatic interactions between the particle and the silica side-chain on the internal walls of the silica matrix pores.

Acknowledgments

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