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# Influence of polar solvent on light-emitting property of $\mathrm{SiO_x}$ $(x = 1.2 - 1.6)$ nanoparticles irradiated by ultraviolet ozone

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**Abstract.** $\mathrm{SiO}_x$ $(x = 1.2 - 1.6)$ powder with nanoparticle sizes of 5−15 nm was irradiated by ultraviolet ozone (UVO), followed by immersion into polar solvent to form a sol-like sample for investigating the influence of a polar solvent on light-emitting property of $\mathrm{SiO}_x$ nanoparticles. Photoluminescence (PL) spectral examinations reveal that the intensity of a broad blue-emitting band peaked at around 420 nm strongly depends upon UVO irradiation and meanwhile relates with the solvent polarity. PL excitation spectral analysis and Fourier-transform infrared absorption measurements suggest that the blue PL band arise from optical transition in the –OH binding states (possibly H bonds to the interstitial oxygen) at the surfaces of $\mathrm{SiO}_x$ nanoparticles, which are induced by the interaction of polar solvent with $\mathrm{SiO}_x$ nanoparticles. This work clearly indicates that we cannot ignore the influence of solvent polarity on the light-emitting property of a composite of organic material and inorganic nanocrystals.

**PACS.** 81.07.Wx Nanopowders – 61.25.-f Studies of specific liquid structures – 78.55.Hx Other solid inorganic materials

## 1 Introduction

Since the integration of organic and inorganic materials at the nanometer scale into hybrid optoelectronic structures enables active devices that combine the diversity of organic materials with the high-performance electronic and optical properties of inorganic nanocrystals, a large number of experimental investigations have been carried out on the light-emitting properties of a composite of organic material and inorganic nanocrystals [1–4]. Some significant phenomena such as an improvement of luminescence efficiency have been observed and used in hybrid light-emitting diode [5,6]. However, the complexity of microscopic details in such an integrated structure makes it difficult to explain the light-emitting mechanism. Many light-emitting origins are still unclear so far. Therefore, much work is needed from experiments and theory to address this issue.

In organic and inorganic composite materials, inorganic nanocrystals are usually mixed into organic material through a kind of polar solvent to achieve uniform distribution of inorganic nanocrystals in organic material. However, a problem arises: Whether does the polar solvent affect the light-emitting properties of the composite system? In the previous investigations, this problem has unintentionally been ignored. So it is necessary to design some experiments to clarify this problem. Since $\mathrm{SiO}_x$ nanoparticles are of a feature of direct energy band and can provide a large number of defect/surface states as the luminescence centers [7,8], $\mathrm{SiO}_x$ powder as inorganic material is a suitable candidate to be mixed into the polar solvents. In this work, we investigate the photoluminescence (PL) spectra of ultraviolet ozone (UVO)-irradiated $\mathrm{SiO}_x$ $(x = 1.2 - 1.6)$ powder immersed in three kinds of different polar solvents. Our experimental results clearly show that the polar solvent changes the excitation and recombination processes of carriers and thus leads to the appearance of a strong PL band peaked at around 420 nm.

## 2 Samples and experiments

Commercial $\mathrm{SiO}_x$ powder was prepared through sol-gel synthesis, followed by low-temperature treatment and ball-milling [9]. The $\mathrm{SiO}_x$ powder with porous structure is oxygen-deficient with $x = 1.2 - 1.6$. The sizes of $\mathrm{SiO}_x$ nanoparticles by transmission electron microscope observations are in the range of 5−15 nm. The particle surfaces have a large number of dangling bonds and –OH bonds. Raman scattering results showed that the nanoparticles are amorphous. The specific surface areas are between 640−700 $\mathrm{m^2/g}$. Such large specific area makes the surface of $\mathrm{SiO}_x$ nanoparticle have more oxygen vacancies. The $\mathrm{SiO}_x$ powder was first irradiated in a UVO cleaner

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(Model No. 144A-220 equipped with Model 1000 ozone generator, Jelight Company, USA) with different times. Concentration of ozone is 3100 parts per million. The output intensity of low-pressure mercury vapor grid lamp in the UVO cleaner was 50 mW/cm$^2$. The distance between the SiO$_x$ powder and lamp was 2.54 cm. The UV emissions are in the wavelength range of 184~579 nm. When high-energy ultraviolet rays strike oxygen molecules (O$_2$), they split the molecule into two single oxygen atoms. The free oxygen atoms can then combine with oxygen molecules to form ozone (O$_3$) molecules:

$$\begin{gathered} \mathrm{O_2} + \mathrm{UV\ light} \rightarrow 2\,\mathrm{O}, \\ \mathrm{O} + \mathrm{O_2} + M \rightarrow \mathrm{O_3} + M, \end{gathered}$$

where $M$ indicates conservation of energy and momentum. Since the UVO irradiation is a photo-sensitized oxidation process in which atomic oxygen is simultaneously generated when molecular oxygen is dissociated by the 184.9 nm radiation and ozone by the 253.7 nm radiation. When both wavelengths are present, atomic oxygen is continuously generated, and ozone is continually formed and destroyed. As a result, SiO$_x$ powder is oxidized gradually and oxygen vacancies at the surfaces of SiO$_x$ nanoparticles are then decreased. With increasing the irradiation time, oxygen interstitials (Si-O-O-Si) come into being to form some oxygen-excess luminescence centers at the surfaces of nanoparticles. Combining with original oxygen-deficient defect centers mainly inside the SiO$_x$ nanoparticles, the SiO$_x$ powder can be expected to possess various oxygen-related luminescence defects and therefore show new light-emitting properties. The Raman scattering investigation shows that the irradiated powder is still amorphous and no crystallization occurs. Afterwards, to investigate the influence of different polar solvent on light-emitting property of SiO$_x$ nanoparticles irradiated by ultraviolet ozone, the powder was immersed in different polar solvents, H$_2$O, CHCl$_3$, and C$_8$H$_{10}$, to form sol-like samples. The SiO$_x$ powder immersed in a solvent usually exists in a form of cluster. This will produce many interfaces between the nanoparticles, which are not affected by solvent. As a result, it is impossible to obtain the information from the interaction of single nanoparticle and the solvent. Therefore, it is necessary to uniformly disperse the SiO$_x$ nanoparticles in the solvent. To reach this purpose, the solution samples were sonicated for 20 min (operating power: 50 W, frequency: 40 kHz). In our experiments, PL and PL excitation (PLE) spectral measurements were carried out on a Hitachi 850 fluorescence spectrophotometer. Fourier-transform infrared (FTIR) absorption spectra were obtained on a Nicolet 170SX spectrometer. All the spectral measurements were performed at room temperature.

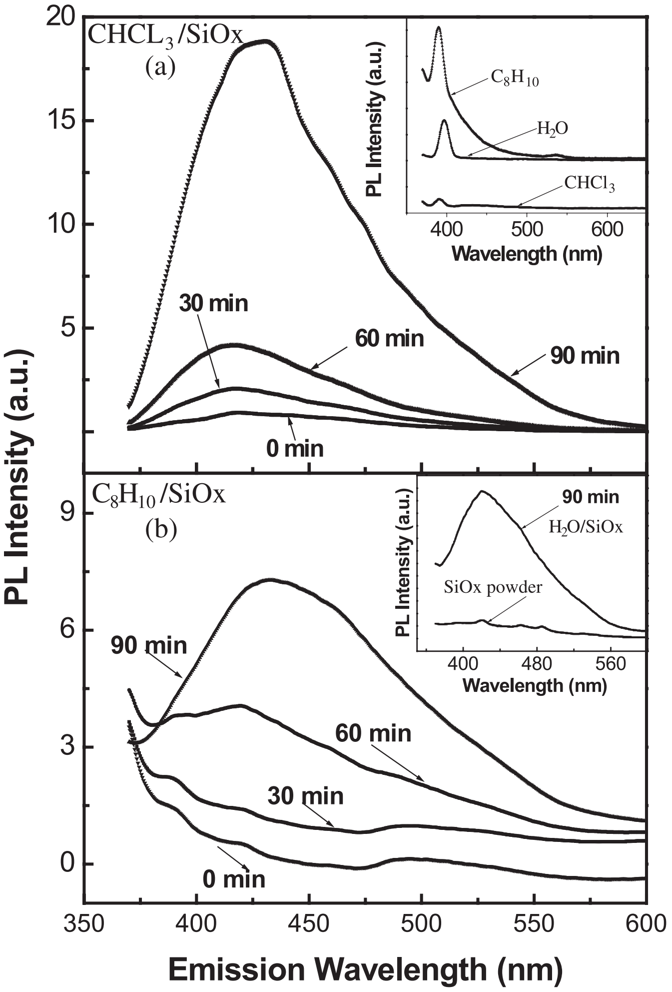

**Fig. 1.** PL spectra of (a) CHCl$_3$/SiO$_x$ and (b) C$_8$H$_{10}$/SiO$_x$ solution samples with UVO irradiation times of SiO$_x$ powder for 0, 30, 60, and 90 min, taken under excitation with the 350 nm line of a Xe lamp. The insets show the PL spectra of CHCl$_3$, H$_2$O, C$_8$H$_{10}$ background solvents, SiO$_x$ powder without UVO irradiation, and the H$_2$O/SiO$_x$ solution sample with an irradiation time of SiO$_x$ powder for 90 min.

## 3 Results and discussions

Figure 1a shows the PL spectra of four CHCl$_3$/SiO$_x$ solution samples, taken under an excitation of the 350 nm line of a Xe lamp. One can see that a broad PL band appears at ~420 nm with asymmetrical spectral shape. The PL peak shows a slight shift (<10 nm) with increasing the irradiation time of SiO$_x$ powder. Its intensity is far larger in the sample with an irradiation time of SiO$_x$ powder for 90 min than those in the samples with irradiation times less than 60 min. If we further increase the irradiation time, the blue PL intensity slightly increases. When the irradiation time reaches about 120 min, we found that the blue PL intensity trends to saturation. This result indicates that the blue PL is closely related to some kinds of defects or defect groups. Similar PL results can be observed in Figure 1b, which shows the PL spectra of four C$_8$H$_{10}$/SiO$_x$ solution samples. However, we note that the PL intensities from the C$_8$H$_{10}$/SiO$_x$ solution samples are reduced about 3 times compared to those from the CHCl$_3$/SiO$_x$ samples. For the H$_2$O/SiO$_x$ solution samples (note that the polarity of H$_2$O is more than that of CHCl$_3$), we found that the blue PL intensities are much stronger than those from the C$_8$H$_{10}$/SiO$_x$ solution samples and close to those from the $CHCl_3/SiO_x$ samples. Since no similar PL band was observed from the background solutions and initial SiO$_x$ powder samples with the same UVO irradiation time [see the insets in (a) and (b)], we infer that the blue PL band strongly depends upon UVO irradiation and relates with the solvent property. At the same time, strong polarity of the solvent may be beneficial to enhancement of the PL intensity. Here, we would like to mention that we have tested the influence of ultrasonic treatment on the PL intensity. We found that the PL intensity initially increases with ultrasonic treatment time and almost keep unchanged after the ultrasonic treatment of 20 min. This indicates that a uniform distribution of nanoparticles in the solvent is beneficial to the improvement of the PL intensity. This result also implies that the solvent has a large effect on the PL intensity.

To identify the origin of the blue PL band, we examined the PLE spectra of all solution samples by monitoring at ~420 nm. Figure 2a presents some typical results from four $H_2O/SiO_x$ solution samples. For the solution samples with an irradiation time of SiO$_x$ powder shorter than 60 min, the 350 nm PLE band has a weak intensity. However, the band greatly gains its intensity in the solution sample with an irradiation time of SiO$_x$ powder for 90 min. This behavior is the same as that of the 420 nm PL band. Shown in Figure 2b are the PLE spectra from the $H_2O/SiO_x$, $CHCl_3/SiO_x$, and $C_8H_{10}/SiO_x$ solution samples with an irradiation time of SiO$_x$ powder for 90 min. One can see that the 350 nm PLE band has a high intensity in the three samples, indicating that the 420 nm PL band is intimately related to the 350 nm excitation band. For the three background solutions, we found that only $CHCl_3$ solvent has a broad PLE band at ~350 nm [see the inset in Fig. 2a], indicating that $H_2O$ and $C_8H_{10}$ solvents themselves do not provide the photoexcited carriers but $CHCl_3$ solvent. Since there do not exist the luminescence centers in the three background solvents, the 420 nm PL band should originate at the interfaces of the solvent/SiO$_x$ nanoparticles and be induced by the existence of the solvent.

What happened for the irradiated SiO$_x$ powder? To clarify this point, we examined the FTIR spectra of the SiO$_x$ powder samples with irradiation times of 0, 30, 60, and 90 min [10]. The obtained results showed an increased absorption in the 1100−1200 cm$^{-1}$ range at the side of the 1070 cm$^{-1}$ peak, which is characteristic of interstitial Si-O-Si vibration [11]. Thus, UVO irradiation leads to increase and decrease of oxygen interstitials and oxygen vacancies mainly at the surfaces of SiO$_x$ nanoparticles, respectively. The largest density of oxygen interstitials exists in the powder sample with an irradiation time of 90 min. Our energy-dispersive X-ray fluorescence measurements support this conclusion [10]. So the blue PL may be related to the interstitial oxygen.

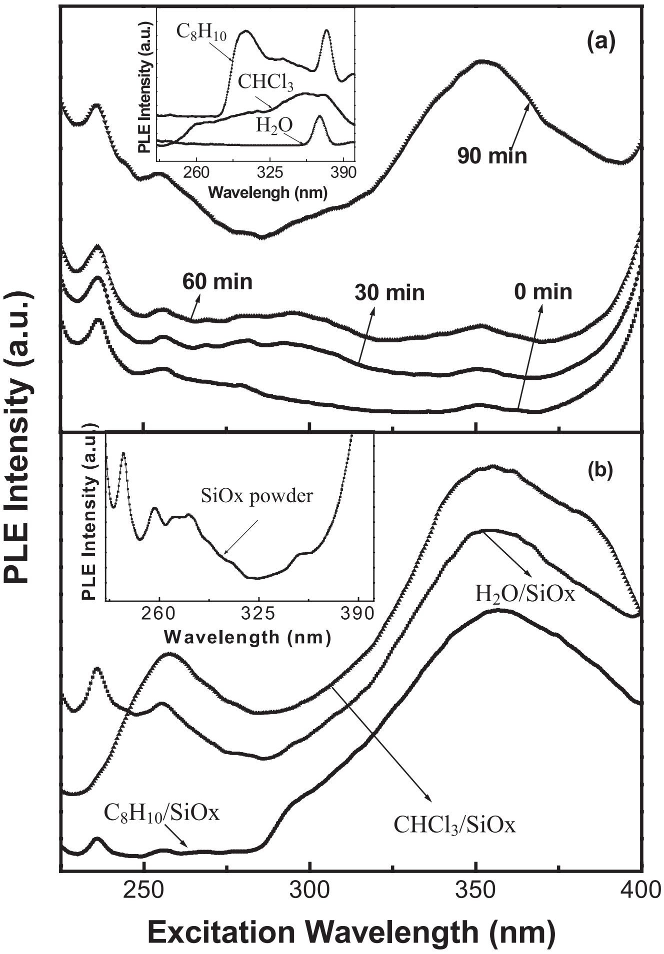

**Fig. 2.** (a) PLE spectra of $H_2O/SiO_x$ solution samples with UVO irradiation times of SiO$_x$ powder for 0, 30, 60, and 90 min, taken by monitoring at 420 nm. The inset in (a) shows the PLE spectra of $CHCl_3$, $H_2O$, and $C_8H_{10}$background solvents. (b) PLE spectra of $CHCl_3/SiO_x$, $H_2O/SiO_x$, and $C_8H_{10}/SiO_x$ solution samples with an irradiation time of SiO$_x$ powder for 90 min. The inset in (b) shows the PLE spectrum of SiO$_x$ powder without UVO irradiation.

Figures 3a–3c show the FTIR spectra of the $CHCl_3/SiO_x$, $H_2O/SiO_x$, and $C_8H_{10}/SiO_x$ solution samples with an irradiation time of SiO$_x$ powder for 90 min, respectively. A sharp feature of these spectra is that the intensity of the vibration band at ~3040 cm$^{-1}$ is greatly enhanced in comparison with that of the background solvent. In addition, we further found that the ~3040 cm$^{-1}$ vibration band intensity increases with the irradiation time of SiO$_x$ powder [see the inset of Fig. 3a].This result implies that the bonding state connected with the vibration band acts as the luminescence centers responsible for the radiation at 420 nm. Since $H_2O$ solvent only contains two elements, H and O, we can infer that the ~3040 cm$^{-1}$ band should be from H/O-related vibration [12–14]. In view of this inference, we believe that the luminescence centers with the 420 nm radiation should be related to OH bonding states, possibly H bonding to the interstitial oxygen at the surface of SiO$_x$ nanoparticle. The fact that the solvent/SiO$_x$ solution samples with an irradiation time of SiO$_x$ powder for 90 min have the largest density of oxygen interstitials is consistent with this conclusion. From the obtained FTIR spectra (Fig. 3), we can also see that the ~3040 cm$^{-1}$ vibration band has the greatest

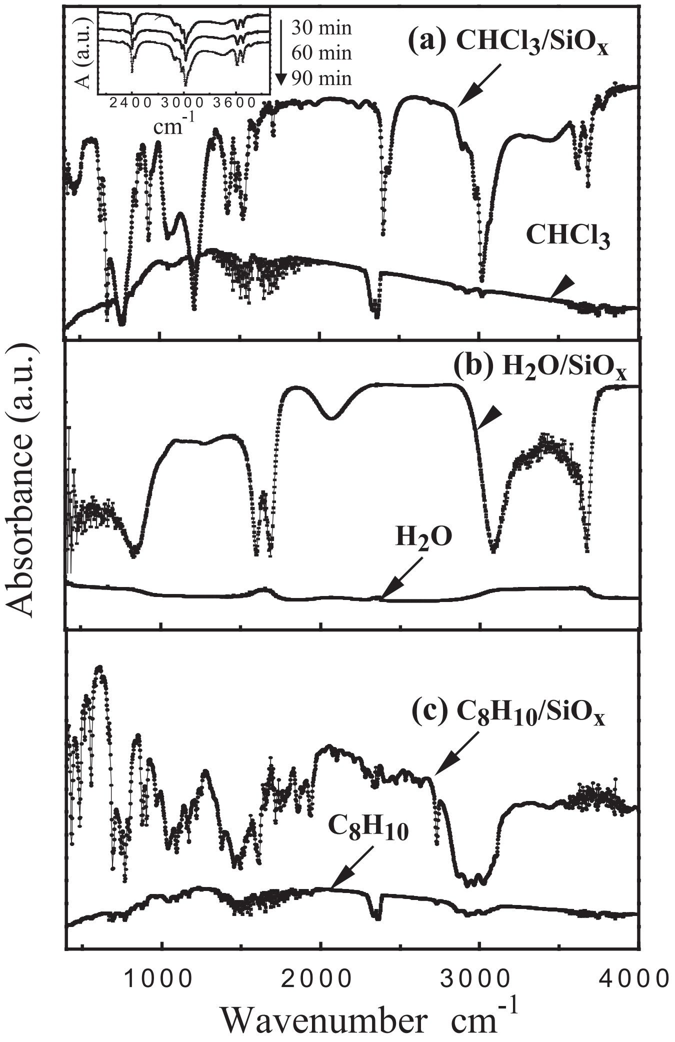

**Fig. 3.** FTIR absorption spectra of (a) $CHCl_3/SiO_x$, (b) $H_2O/SiO_x$, and (c) $C_8H_{10}/SiO_x$ solution samples with an irradiation time of $SiO_x$ powder for 90 min. The FTIR spectra of the corresponding background solvents are also given for comparison. The inset in (a) shows the FTIR spectra of $CHCl_3/SiO_x$ solution samples with UVO irradiation times of $SiO_x$ powder for 30, 60, and 90 min.

absorption in the $CHCl_3/SiO_x$ solution sample. The absorption is slightly weaker in the $H_2O/SiO_x$ solution sample and the weakest in the $C_8H_{10}/SiO_x$ solution sample. These results indicate that the density of OH bonding states is the greatest in the $CHCl_3/SiO_x$ solution sample. Considering the PL behavior in different solution samples, we may obtain similar conclusion: the blue PL is mainly related to the OH bonding states in the interfaces between the solvent and $SiO_x$ nanoparticles.

Asymmetrical feature of the blue PL band is noteworthy. Our previous investigation on the light-emitting property of the irradiated $SiO_x$ powder samples showed that the 446, 456, and 535 nm PL bands exist in the samples with irradiation times of 30, 60 and 90 nm, respectively. The corresponding PLE spectrum showed a redshift with increasing the monitored emission wavelength. The energy of the highest absorption band is at 3.14 eV (395 nm). We attributed these PL and PLE results to such a process: The photoexcited carriers take place in a band with quantum confinement [15], whereas the radiative recombination occurs in a defect pair of an oxygen vacancy $V_0$ and an interstitial oxygen $I_0$ that also forms a peroxy linkage with lattice oxygen (optical transition of so called self-trapped excitons) [16]. Since the present solution samples also contain the irradiated $SiO_x$ nanoparticles and the energy of the excitation band (PLE band) is at 3.54 eV (350 nm) higher than 3.14 eV (395 nm), the excitation and recombination processes in the irradiated $SiO_x$ powder samples should also exist in the current solution samples. The presence of these excitation and recombination processes may be responsible for asymmetrical and broad features of the current PL and PLE bands. Thus, the broad PL spectrum does not only originate from optical transition in a single type of defect. However, we can see from the obtained results that the 420 nm radiation is a result of interaction of the irradiated $SiO_x$ nanoparticles with the polar solvents. Now, we may easily understand the fact that the ~420 nm PL band has a maximal intensity in the $CHCl_3/SiO_x$ solution samples, because the $CHCl_3$ solvent and $SiO_x$ powder both provide carriers to radiatively recombine in the OH bonding states. This also accounts for why the PL intensity from the $H_2O/SiO_x$ system is close to that from the $CHCl_3/SiO_x$ system, although solvent $H_2O$ has the strongest polarity.

Finally, we should further mention the role of the solvent polarity in the light-emitting process. We know that the electric field induced by the solvent polarity only exists at the molecular scale. Therefore, it may affect the excitation, transport, and recombination processes of carriers, especially around the defect centers. The molecule-scaled electric field may increase the excitation and emission efficiencies of carriers in the defect centers through resonant electronic energy transfer from the solvent to the defect centers at the surface of $SiO_x$ nanoparticle and thus lead to an enhanced PL [17]. The electronic transfer efficiency should be related to the electric field. The stronger the electric field (i.e. the solvent polarity), the higher the PL intensity. In fact, this influence has been shown in the systems of porous silicon when in contact with acetone or $NH_3$ [18,19]. Contact between porous silicon and polar liquid causes the increase of the electrical conductivity of porous silicon. The increase can only be explained to be due to the influence of absorbed polar solvent. From the viewpoint of energy band theory, the existence of polar solvent around the $SiO_x$ nanoparticle will form a series of almost continuously energy levels in the band gap of $SiO_x$. These levels will resonantly mix with those from the −OH bonding states at the surfaces of $SiO_x$ nanoparticles and therefore lead to the widening of the energy levels and the increase of the transition probability. This corresponds to both the broad PL character and strong PL intensity. Currently, due to the complexity of the energy bands of solution, exact nature of the polar solvent-$SiO_2$ nanoparticle interaction is unclear and more work is needed to address this issue.

## 4 Conclusions

We have investigated the light-emitting property of the solvent ($\mathrm{CHCl_3}$, $\mathrm{H_2O}$, and $\mathrm{C_8H_{10}}$)/$\mathrm{SiO}_x$ solution samples with different UVO irradiation times of $\mathrm{SiO}_x$ powder. A strong PL band was observed at ∼420 nm with broad line shape. Its intensity strongly depends upon UVO irradiation and meantime relates with the solvent polarity. Proper irradiation time and strong polarity solvent can lead to a high PL intensity. PLE spectral analysis and FTIR absorption results suggest that the blue PL arises from optical transition in the −OH bonding states (possibly H bonds to the interstitial oxygen) at the surfaces of $\mathrm{SiO}_x$ nanoparticles. This work demonstrates that when we fabricate a composite of organic material and inorganic nanocrystals, we cannot ignore the influence of the polar solvent on the light-emitting property of the composite.

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## References

1. C.B. Murray, D.J. Norris, M.G. Bawendi, J. Am. Chem. Soc. **115**, 8706 (1993)
2. V. Colvin, M. Schlamp, A.P. Alivisatos, Nature **370**, 354 (1994)
3. C.R. Kagan, D.B. Mitzi, C.D. Dimitrakopoulos, Science **286**, 945 (1999)
4. W.U. Huynh, J.J. Dittmer, A.P. Alivisatos, Science **295**, 2425 (2002)
5. S. Coe, W.K. Woo, M. Bawendi, V. Bulovic, Nature **420**, 800 (2002)
6. M.C. Schlamp, X.G. Peng, A.P. Alivisatos, J. Appl. Phys. **82**, 5837 (1997)
7. H.Z. Song, X.M. Bao, Phys. Rev. B **55**, 6988 (1997)
8. L. Pavesi, L.D. Negro, C. Mazzoleni, G. Franzo, F. Priolo, Nature (London) **408**, 440 (2000)
9. A.J. Lecloux, J.P. Pirard, J. Non-Cryst. Solids **225**, 146 (1998)
10. D. Lu, X.L. Wu, J. Appl. Phys. **94**, 7288 (2003)
11. H.Z. Song, X.M. Bao, N.S. Li, X.L. Wu, Appl. Phys. Lett. **72**, 356 (1998)
12. X.L. Wu, X.M. Bao, S.S. Jiang, D. Feng, S. Tong, Appl. Phys. Lett. **70**, 2401 (1997)
13. A.L. Smith, Spectrochim. Acta **16**, 87 (1960)
14. L.J. Bellamy, *The Infrared-Red Spectra of Complex Molecules*, 3rd edn. (Chapman and Hall, London, 1975), Chap. 20
15. Y.H. Xie, W.L. Wilson, F.M. Ross, J.A. Mucha, E.A. Fitzgerald, J.M. Macaulay, T.D. Harris, J. Appl. Phys. **71**, 2403 (1992)
16. W. Hayes, M.J. Kane, O. Salminen, R.L. Wood, S.P. Doherty, J. Phys. C **17**, 2943 (1983)
17. B. Valeur, *in Molecular Fluorescence: principles and applications* (Wiley-VCH Verlag GmbH, Weinheim, 2001) p. 200
18. C.F. Young, E.H. Poindexter, G.J. Gerardi, J. Appl. Phys. **81**, 7468 (1997)
19. M. Chiesa, G. Amato, L. Boarino, E. Garrone, F. Geobaldo, E. Giamello, Angew. Chem. Int. Ed. **42**, 1 (2003)