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Effect of the Surface Chemical Modification on the Optical Properties of Polymer-stabilized PbS Nanoparticles

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PbS nanoparticles in the range 3.8–4.5 nm have been prepared in solution by H_2S treatment of a Pb^{2+}-containing copolymer (P-Pb). The variations of the P-Pb molecular weight before and after reacting with H_2S implied that there existed some chemical bonds between the surface of the PbS nanoparticles and the copolymer. IR results proved that the chemical bond was Pb—OOC. When the molar ratio (the ratio $H_2S : Pb^{2+}$) was $\leqslant 1$, there existed Pb—OOC bonds on the particle surface, while most of the Pb—OOC bonds were broken when the molar ratio increased to 2.5 : 1. Different surface bonding situations are represented by different absorption spectra, the higher the molar ratio, the larger the absorption coefficient. These effects prove that the surface defects relative to the Pb—OOC bonds on the particle surface, can trap the electron–hole pairs effectively and cause a decrease in the absorption coefficient. On the other hand, excess H_2S removed the Pb—OOC bonds and saturated the sulfur vacancies on the particle surface, where the radiation combination of the charge carriers occurred. As a result, the laser-induced luminescence bands appearing for the 0.75 : 1 and 1 : 1 colloids disappeared completely for the 2.5 : 1 colloid.

Semiconductor nanoparticles are representative of a state of matter intermediate between individual molecules and bulk species, the study of which has sparked increasing attention.[1–8] As the diameter of a semiconductor crystallite approaches its exciton Bohr diameter, the electronic properties of the semiconductor start to change. This is the so-called quantum size effect. The observation of quantum size effects for semiconductor nanoparticles was reported some time ago.[9–12] It is commonly observed that as the semiconductor particle size decreases, the optical absorption edge shifts to the blue end of the spectrum, and sometimes it is also accompanied by the appearance of discrete absorption bands.[13] Apart from the quantum size effect, surface chemical modifications also have a great effect on the optical properties of Q-particles.[5,14]

It is known that the surface : volume ratio increases as the particle size decreases, so a considerable number of atoms exist on the large surface area which form the surface defects. For the Q-particles, the charge carriers generated by the absorption of light can be easily trapped at these surface defect sites. The presence of the trapped carriers affects the absorption–fluorescence properties as well as the optical non-linearity of the Q-particles.[15] Exciton absorption bleaching experiments have proved that when one electron–hole pair is trapped by the surface defect, the exciton absorption of the whole cluster is bleached.[16,17] This result indicates that in the presence of trapped electron–hole pairs, the strong interaction between the trapped electron–hole pair and the exciton causes the reduction of spatial overlap of the electron and hole wavefunctions and the oscillator strength of the exciton,[15] which results in the bleaching of exciton absorption and gives rise to the optical non-linearity.

It has been proved by Henglein and co-workers that the fluorescence intensity of Q-size CdS particles may be drastically increased by certain surface modification procedures, such as covering the surface with cadmium hydroxide or silver sulfide.[5] This proved that the surface defect sites for the radiationless recombination of charge carriers can be destroyed chemically, which suggests that the surface modification is a good approach for controlling the optical properties of Q-particles.

In this paper, the optical properties of Q-size PbS were studied. A Pb^{2+}-containing copolymer was synthesized through copolymerization using styrene and lead methylacrylate. PbS nanoparticles in the range 3.8–4.5 nm were prepared in solution by treatment with H_2S of the Pb^{2+}-containing copolymer. It is known that bulk PbS has a direct gap at 0.41 eV at 300 K. The absorption edge is *ca.* 3200 nm, while the absorption edge of the above PbS nanoparticles was shifted to 700–800 nm. This proved the occurrence of the quantum size effect. As a result, the effect of the surface chemical modification on the optical properties becomes significant. Through controlling the molar ratio between H_2S and Pb^{2+} during the preparation of the PbS nanoparticles, different surface combinations between the PbS particles and the copolymer were controlled, which resulted in different optical properties of the PbS nanoparticles. This paper focusses on the effect of different surface combinations on the optical properties of the Q-size PbS particles.

Experimental

The styrene (St), lead oxide, methanol and tetrahydrofuran were all commercial products of the highest purity. The styrene and methylacrylic acid were both distilled at a pressure of 5 Torr.

Lead methylacrylate [$Pb(MA)_2$] was prepared from PbO and methylacrylic acid, and purified twice through recrystallization in water. The structure was identified by comparing its IR spectrum and melting point with that from the literature. It is known that there are two C=C bonds in each $Pb(MA)_2$ molecule, so in copolymerizing with St, it works as a cross-linking agent. The copolymerization reaction was performed in tetrahydrofuran solvent. First, 240 ml St and 3.964 g $Pb(MA)_2$ were dissolved into 450 ml of tetrahydrofuran in a tempered glass vessel. Then 1.52 g AIBN (azoisobutylnitrile) was dissolved in the mixture as an initiator. After being

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bubbled with nitrogen for 5 min, the solution was warmed to 60 °C and maintained at this temperature for 3 h using warm water. Finally, a light cross-linking Pb^{2+}-containing microgel (P-Pb) precipitation was obtained by pouring the above solution into a beaker containing 1500 ml methanol. The molecular weight of the microgel was measured as 6.5×10^4 by GPC methods. The weight percentage of lead in this composite microgel was found to be 2.5 by atomic absorption methods.

0.2 g of the P-Pb was dissolved into 4 ml of a mixed solvent (toluene : chloroform = 1 : 1) and then reacted with H_2S gas at different $H_2S : Pb^{2+}$ molar ratios (*i.e.* 0.75 : 1, 1 : 1 or 2.5 : 1) in a sealed container. After this procedure, it was found that using a low or a high molar ratio, the product turned the solution a brown or dark red colour, respectively, and no precipitation emerged during this process. The organosol solutions had a long-term stability, with no precipitation even after two years.

The diameter of the colloid particles in the mixed solvent with different molar ratios of 0.75 : 1, 1 : 1, and 2.5 : 1 were measured as 3.8, 3.9 and 4.5 nm, respectively, by small angle X-ray scattering (SAXS) methods.

Typically, the relationship between the scattering intensity and the scattering angle for round particles is given as follows:

$$\ln I = \ln(I_e N_n^2) - 4\pi R^2 \varepsilon^2 / 5\lambda^2$$

where I is scattering intensity, $\ln(I_e N_n^2)$ is a constant, ε is scattering angle and R is the radius of the particle. For ideal mono-distributed particles, $\ln I$ has a linear relationship *vs.* ε^2.

It was proved, from the relationships between $\ln I$ and ε^2, that the particle size was almost mono-distributed for 0.75 : 1 and 1 : 1 colloids and had a very narrow distribution for the 2.5 : 1 colloid (94.8% of the particles are 4.2 nm in size).

The UV–VIS absorption spectra of the organosol solutions with different $H_2S : Pb^{2+}$ molar ratios were measured in the mixed solvent using a Shimadzu 3100 spectrophotometer. After evaporating off the mixed solvent on KBr wafers, the IR spectra of the colloids were recorded by a Bruker IFS-66V IR spectrophotometer. The fluorescence spectra of the colloid solutions were recorded on a Hitachi 850 fluorescence spectrophotometer, and the laser-induced luminescence spectra on a JY-T800 laser Raman spectrophotometer, with an excitation wavelength of 4880 Å.

Results and Discussion

Fig. 1–3 present the IR spectra of MA, $Pb(MA)_2$, and the copolymer powder sample, respectively. When comparing the spectra of Fig. 1 and 2, it can be seen the C=O stretching vibration band of MA located at 1692 cm^{-1} in Fig. 1 disappears completely in Fig. 2 and the COO^- asymmetric stretching vibration band located between 1531 and 1551 cm^{-1}, which was absent in Fig. 1, appears in Fig. 2. The O—H stretching vibration band located at 1300 cm^{-1} in Fig. 1 also disappears in Fig. 2, which implies a combination between COO^- and Pb^{2+}. When comparing Fig. 2 and 3, it can be seen that the C—C vibration bands of the phenyl group located at 1600, 1492 and 1450 cm^{-1} appear in Fig. 3 after the copolymerization. The peak located at 1545 cm^{-1} in Fig. 3 indicated that lead ions were still covalently combined with the COO^- group after the copolymerization reaction.

As seen from the IR spectra of the colloids with different $H_2S : Pb^{2+}$ molar ratios (Fig. 4), as the molar ratio increases, the vibration band located at *ca.* 1693 cm^{-1} increases in intensity and becomes distinct, while the vibration band located at 1546 cm^{-1} decreases and becomes indistinct. This

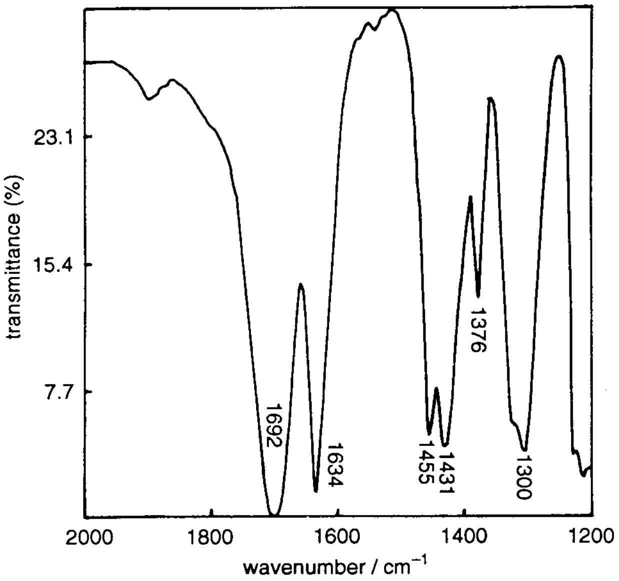

Fig. 1 IR spectrum of pure MA on the surface of a KBr wafer

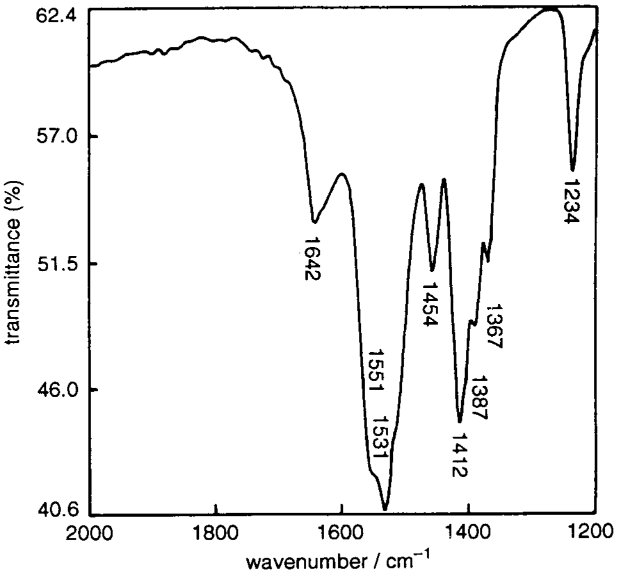

Fig. 2 IR spectrum of $Pb(MA)_2$ powder sample

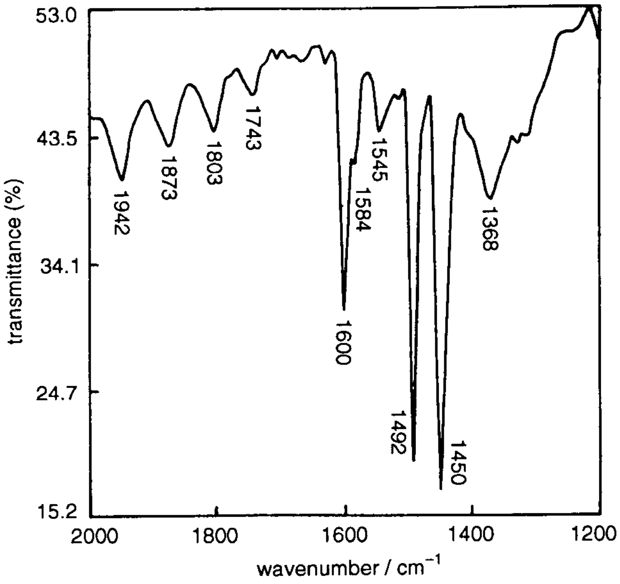

Fig. 3 IR spectrum of P-Pb copolymer powder sample

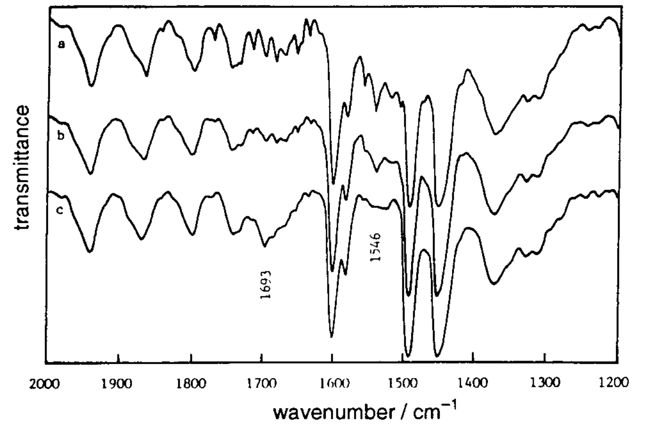

Fig. 4 IR spectra of the colloids prepared at different $H_2S : Pb^{2+}$ molar ratios; spectra (a), (b) and (c) correspond to colloids with 0.75 : 1, 1 : 1 and 2.5 : 1 molar ratios, respectively

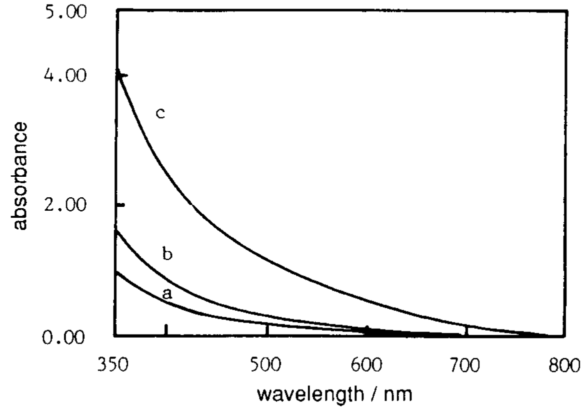

Fig. 5 UV–VIS spectra of the colloids with different $H_2S : Pb^{2+}$ molar ratios in the mixed solvent. Spectra (a), (b) and (c) correspond to 0.75 : 1, 1 : 1 and 2.5 : 1 colloids, respectively; the reference solution is the mixed solvent.

implied that an increasing number Pb—OOC bonds were broken as the molar ratio increased from 0.75 : 1 to 2.5 : 1. It is assumed that after the formation of PbS particles, most of the Pb—OOC bonds were concentrated on the particle surface, so the difference between the spectra was mainly caused by the changes of Pb—OOC bonds on the particle surface. For the spectra of the 0.75 : 1 and 1 : 1 colloids, the peak located at *ca.* 1546 cm^{-1} can still be distinguished, but it becomes indistinct for the 2.5 : 1 colloid. However, the spectrum of the 2.5 : 1 colloid was more defined at 1693 cm^{-1}, compared with that of the 0.75 : 1 and 1 : 1 colloids. This result proved that when the molar ratio was $\leqslant 1$, there are still some lead ions on the particle surface combining with the carboxylic groups. As the molar ratio increased to 2.5 : 1, most of carboxylic groups were removed.

The variations of P-Pb molecular weight before and after reacting with H_2S proved our assumption that almost all the Pb—COO bonds are concentrated on the particle surface after the formation of the PbS nanoparticles. The molecular weights of P-Pb were measured before and after reacting with H_2S (using different $H_2S : Pb^{2+}$ molar ratios). The data are listed in Table 1.

The changes in the molecular weight as the molar ratio increased implies that the Pb—COO bonds were concentrated on the particle surface, which makes the PbS nanoparticles act as cross-linking agents and causes a significant increase of the molecular weight. The changes in the hydrodynamic radii of the P-Pb before and after reacting with H_2S also proved this result.[18]

The UV–VIS absorption spectra of the 0.75 : 1, 1 : 1 and 2.5 : 1 organosol solutions are shown in Fig. 5. The absorption coefficients of the colloids increase markedly with increasing molar ratio. This was attributed to changes of the surface modification. From previous reports, we know that if the ability of the particle surface in trapping electron–hole pairs decreases, the spatial overlap of the electron and hole wavefunctions increases, as does the absorption coefficient.[15] This implies that the ability of the colloids in trapping electron–hole pairs decreases with increased molar ratios. From the IR spectra analysis, we know that the number of Pb—OOC bonds on the particle surface decreases with increasing molar ratio, so that the ability of the particle surface in trapping electron–hole pairs is related to the Pb—OOC bonds on the particle surface. It was deduced that the chemical bonds of the Pb—OOC groups on the PbS particle surface form a strong surface electrofield gradient, which can trap the electron–hole pairs and result in the loss of light-absorption oscillator strength and absorption coefficient. For the 2.5 : 1 colloid, most of the Pb—OOC bonds are broken, and so the ability of the surface in trapping the electron–hole pairs becomes the weakest among the three colloids. Hence, the spatial overlap of the electron and hole wavefunction becomes largest, as does the absorption coefficient. In contrast, the 0.75 : 1 colloid has the smallest coefficient. On the other hand, as the molar ratio increases, the particle surface will be covered with —SH groups instead of Pb—OOC bonds. This causes the stability effect from the copolymer to decrease and the particle size and its distribution to increase. As a result, a slight red shift of the absorption edge for the colloids was found (Fig. 5). It was established that when the molar ratio increases to 5 : 1, the organosol becomes unstable and precipitation of PbS is observed.

Table 1 Molecular weight of P-Pb before[a] and after reacting with H_2S in different $H_2S : Pb^{2+}$ molar ratios

sample	$H_2S : Pb^{2+}$	$10^{-4}M_w$
1	0 : 10	3
2	3 : 10	5.1
3	5 : 10	5.6
4	7 : 10	5.9
5	9 : 10	6.1

[a] A different sample to that mentioned in the text (weight percentage Pb = 2.2).

The laser-induced luminescence spectra of PbS organosol solutions with different $Pb^{2+} : H_2S$ molar ratios are presented in Fig. 6 (the wavelength of the excitation line was 4880 Å). All the sharp peaks in the luminescence spectra are caused by Raman vibrations. Fig. 7 shows the luminescence spectrum of P-Pb in the mixed solvent. Comparing Fig. 6 and 7, it can be deduced that the luminescence of PbS above 17 000 cm^{-1} may be masked by that from P-Pb molecules. In Fig. 6, two broad luminescence bands can be observed for the 0.75 : 1 and 1 : 1 colloids at wavenumbers $< 17\,000$ cm^{-1}; the first one located at *ca.* 14 200 cm^{-1} (*ca.* 700 nm) and the second at $< 12\,000$ cm^{-1} (> 800 nm) which cannot be detected fully because of the limitation of our apparatus. In order to identify these two luminescence bands appearing for the 0.75 : 1 and 1 : 1 colloids, the 0.75 : 1 colloid was activated by adding diaminoethane. Fig. 8 shows that the intensity of the second luminescence band of the activated colloid decreases as the concentration of the diaminoethane increases. This result proved that this luminescence, which can be quenched by adding diaminoethane, was caused by the surface defects of sulfur vacancies. Fig. 9 shows the fluorescence spectra of the 1 : 1 organosol excited with a 150 W

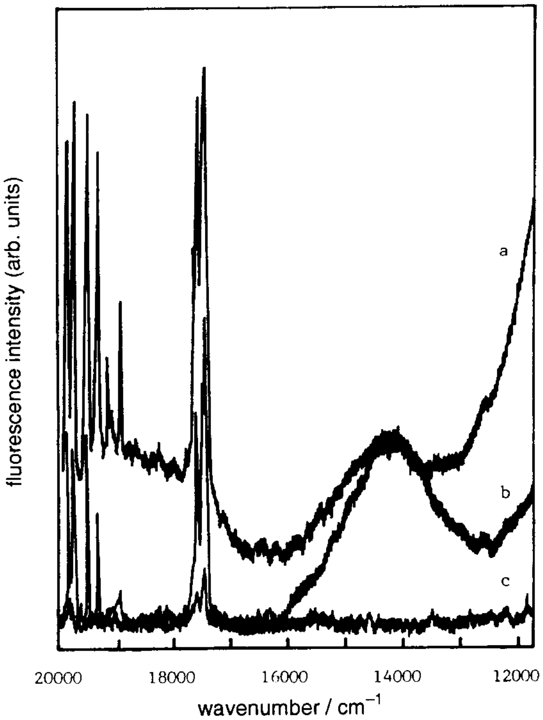

Fig. 6 Laser-induced luminescence spectra of the colloids with different $H_2S : Pb^{2+}$ molar ratios in the mixed solvent. Spectra (a), (b) and (c) correspond to 0.75 : 1, 1 : 1 and 2.5 : 1 colloids, respectively; the wavelength of the excitation line is 4880 Å.

Xe lamp at different wavelengths. From the results that the emission band located at 725 nm, which is lower than the absorption onset, does not shift along with the exciting wavelength, it can be predicted that the first luminescence band located at 14200 cm^{-1} was another surface defect luminescence. From the luminescence spectra of the activated colloid, no evident changes in intensity could be found for the first luminescence band as the concentration of diaminoethane increased, so it can be deduced that the defect sites where the radiation recombination of the charge carriers occurred and gave the first luminescence band, are related to the strong chemical bonds of the Pb—OOC groups on the particle surface. From Fig. 6 we can also see that as the molar ratio increases from 0.75 : 1 to 1 : 1, no evident changes in intensity occur for the first band, while a drastic decrease is shown by the second luminescence band. As the molar ratio increases further to 2.5 : 1, the two luminescence bands disappear completely. This implies that removal of the sulfur vacancies by H_2S was greater than that for surface bonding carboxylic groups, when the molar ratio increases from 0.75 : 1 to 1 : 1. As the molar ratio increases further, the bonding carboxylic groups are substituted by —SH groups and the sulfur vacancies are saturated by the excess of H_2S. It has been demonstrated that the accumulation of —SH groups on the particle surface destroyed the sites where radiation recombi-

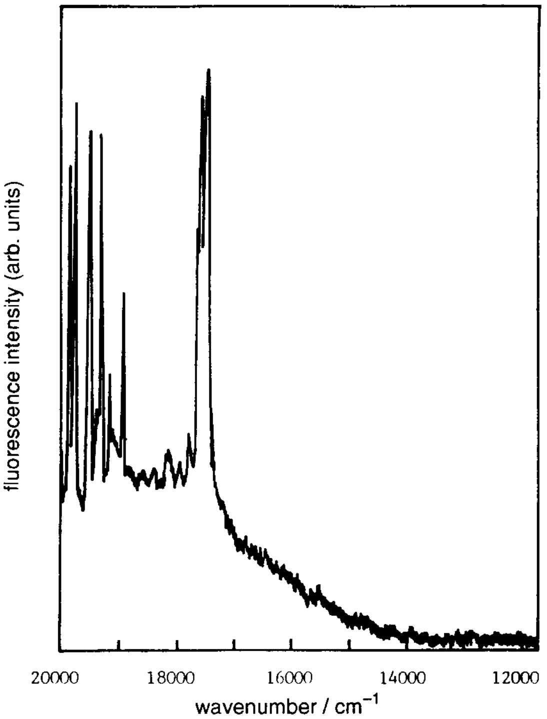

Fig. 7 Laser-induced luminescence spectrum of the P-Pb copolymer in the mixed solvent. The wavelength of the excitation line is 4880 Å.

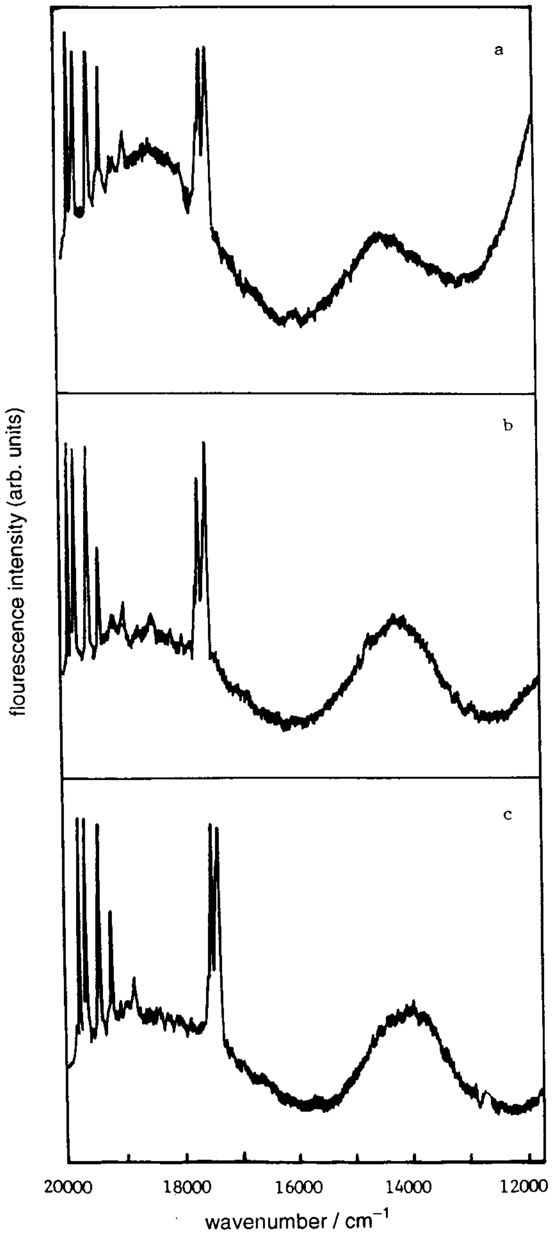

Fig. 8 Laser-induced luminescence spectra of the 0.75 : 1 colloid activated by adding diaminoethane. Concentrations of diaminoethane are 0, 1.5 × 10^{-2} and 3.0 × 10^{-2} mol l^{-1} for the spectra (a), (b) and (c), respectively.

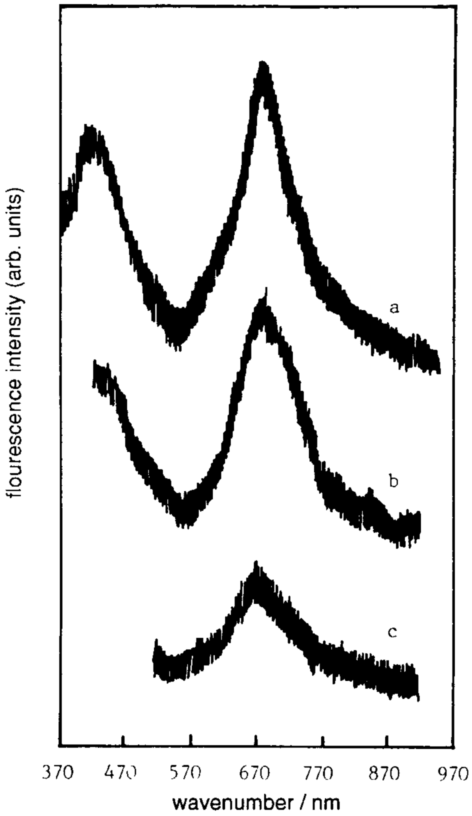

Fig. 9 Fluorescence spectra (a), (b) and (c), obtained from the 1 : 1 organosol solution excited at 360, 400 and 515 nm, and recorded from 370, 420 and 520 nm, respectively

nation of charge carriers occurred.[5] As a result, the luminescence bands caused by the radiation combination of the charge carriers trapped at the sites of surface Pb—OOC bonds, together with the sulfur vacancies, disappear completely.

In conclusion, the surface binding situations not only affect the stability properties but also play a very important role in controlling the optical properties of the PbS nanoparticles.

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Referee's Report MS: 5/01662B
The Effect of Surface Chemical Modification on the Optical Properties of PbS....
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This paper is one of a continuing series from the Jilin Group on the preparation, characterization and performance of PbS nanoparticles. As usual the scientific work is of a high standard but there are the usual problems associated with producing a MS in one's second language. This paper needs close attention to English in places.

I have one overriding concern about the approach the authors have to the presentation and this is illustrated by the title. There is a tacit assumption on their part that they are altering the **surface** properties of the PbS particles and this is responsible for the change in optical properties. This may well be the case but it is not established in the paper by surface analytical results. Indeed, as the authors point out on p1, most of the ions/molecules are at the surface anyway for these extremely fine particles. This leads us to the more philosophical question of whether the term "Surface Modification" has any relevance, in the usual sense, to these materials. This is a question that has been addressed by the catalysis community in the past, and the authors should at least mention this dilemma in the text.

There are numerous minor points that I have highlighted on the MS.

Once these matters are attended to the paper will be suitable for publication in J Chem Soc Farad Trans.