Polymer/PbS Nanoparticles Composite Material

Mingyuan Gao[a], Yi Yang[a], Bai Yang[a], and Jiacong Shen[a,b]

[b] *Key Lab of Molecular Spectra and Structure,*
[a] *Department of Chemistry,*
Jilin University, Changchun, 130023, PR China

Introduction

The realization of electronic properties of semiconductor nanoparticles significantly differing from either the individual molecules or bulk species has sparked intensive interest in the past a few years[1,2]. It has been established that the electronic properties of the semiconductor nanoparticles change rapidly as their dimensions decrease toward the nanometer range, which is usually referred to as quantum-size effects[3-5], and this change yields many special phenomena, such as a large nonlinear optical response[6,7]. By doping polymers with nanoparticles, utilizing their large resonant third-order nonlinearity, new optically nonlinear composite materials can be prepared[6-8]. Polymer has been proved to be a useful matrix in assembling the nanoparticles[8-11]. First, the stability of the semiconductor nanoparticles can be improved greatly by being assembled in polymer matrices. Second, the size of the nanoparticles can be controlled from a few angstroms to hundreds of nanometers, providing a vehicle for studying the transition of the optical properties of a semiconductor from molecular to bulk. On the other hand, the optical properties of the semiconductor nanoparticles can also be modified by surface chemical modification other than the quantum size effects[12,13]. By assembling the nanoparticles in polymer matrices, the chemical surface modifications can be fixed, so nonlinear optical properties of the nanoparticles can be controlled through varying the surface microenviroment of the nanoparticles.

This paper is focused on the preparation of the Polymer/PbS nanoparticles composite material and the optical properties of the Q-size PbS nanoparticles which were doped in polymer matrix.

PbS nanoparticles of ~4 nm were prepared in styrene by H_2S treatment of a copolymer containing Pb^{2+}. After further polymerization upon addition of azo-iso-butyl nitrile (AIBN) as initiator, polymer/PbS nanoparticles composite bulk was prepared. TEM and Small Angle X-ray Scattering(SAXS) results indicated that the particles doped in the polymer matrix represented a narrow size distribution. The electron diffraction results proved that the PbS nanoparticles was in cubic rock salt structure. The Degenerate Four Wave Mixing (DFWM) experiment results

indicated that the molar ratio between Pb^{2+} with H_2S used for the preparation of the PbS nanoparticles not only affected the optical properties of the PbS nanoparticles, but also affected the nonlinear optical response of the composite material.

Experimental

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

Lead methylacrylate ($Pb(MA)_2$) was prepared from PbO and methylacrylic acid and purified twice through recrystallization in water. The structure was identified through 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 reaction was performed in a tetrahydrofuran solvent. First, 240 ml of St and 3.964 g of $Pb(MA)_2$ were dissolved into 450 ml of tetrahydrofuran in a tempered glass vessel. Then 1.52 g of AIBN was dissolved in the mixture as an initiator. After being bubbled with nitrogen for 5 minutes, the mixture solution was warmed to 60°C and maintained at this temperature for three hours by warm water. Lastly, a light cross-linking Pb^{2+}-containing microgel (P-Pb) precipitation was obtained by pouring the above solution into a beaker containing 1500 ml of methanol. The molecular weight of the microgel was measured as 6.5×10^4 by GPC method. The weight percentage of lead in this composite microgel was found to be 2.5 % by atomic absorption method.

A 0.2 g of the P-Pb was dissolved into 4 ml of styrene then reacted with H_2S gas at different molar ratios (i.e., 0.75:1, 1:1, 2:1, 2.5:1, the ratio is defined as the molar ratio of H_2S:Pb^{2+}) in a sealed container. After this procedure, it was found that using a low molar ratio and a high molar ratio the product turned the solution a brown color and dark red respectively, and no precipitation emerged during this process. The organosol represented a long-term stability, no precipitation was found after two year.

The styrene organosol obtained above were further polymerized upon addition of AIBN as initiator. After this procedure, the organosol turned to a red transparent bulk.

The particle size of PbS nanoparticles were measured by TEM and SAXS methods. The third-order optical susceptibility of the composite material was measured by DFWM method. The second harmonic of Nd:YAG pump dye laser was used as an excitation source, the wavelength was 532 nm.

Results

Fig. 1 is the TEM photograph of the composite bulk (obtained in a molar ratio of 1:1). It can be seen that the PbS nanoparticles are well assembled in the matrix, almost all the particles are round and even in size. Because the particles had a distribution in the vertical direction in the thin composite film which was attached on the surface of the copper grid, not all the particles can be observed clearly at one focus. The average size of the distinguish particles was found to be 40 Å from the photograph. This result fits well with that obtained SAXS method. The histogram of the nanoparticles (Fig. 2) shows a narrow distribution of the particle size. The diameters of PbS nanoparticles in the composite bulk obtained in the molar ratios of 0.75:1, 1:1, 2:1, and 2.5:1 were measured as 3.7 nm, 3.8 nm, 4.2 nm, and 4.5 nm respectively by SAXS method. It was proved from the relationships between the lnI (I is the X-ray scattering intensity) and the square of the scattering angle that the particle size were almost mono-dispersed for 0.75:1, 1:1 and 2:1 products and very narrow for the 2.5:1 product (the size of 4.2 nm particle took up 94.8%).

Fig. 1 TEM photograph (200K) of PbS nanoparticles doped in the composite bulk

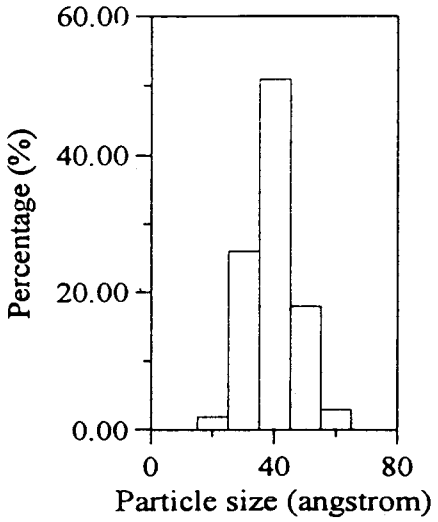

Fig.2 Histogram of particle size of the PbS nanoparticles shown in Fig.1

The electron diffraction method was adopted for identifying the structure of the PbS particles. Data obtained from the diffraction pattern (Fig. 3) are given in Table 1 which establishes a cubic rock salt structure for the PbS nanoparticles.

Table 1 Diffraction data for PbS nanoparticles with corresponding data for standard PbS given in parentheses

n_d	d/Å
5	0.9127(0.9050)
4	1.0297(1.0489)
3	1.188(1.212)
2	1.477(1.484)
1	2.081(2.099)

Fig. 4 is the transmission spectrum of the composite prepared in the molar ratio of 1:1. The transmittance in the non-absorbing range of PbS nanoparticles is up to that of polystyrene. This result indicated that there is no light scattering caused by the large particles and aggregations in the composite, that is to say the PbS nanoparticles were well dispersed in the polystyrene matrix.

The third order optical susceptibilities of the composite films prepared in the molar ratios of 1:1, 2:1 and 2.5:1 were measured by DFWM method, the second harmonic YAG laser was used as excitation source, λ=532nm. The composite modeling films were prepared by further polymerization of the styrene organosol. The data listed in table 2 proves that the third-order optical susceptibilities changes from 1.26×10^{-8} to 2.16×10^{-9} esu as the molar ratio increases from 1:1 to 2.5:1.

Fig. 3 Electron diffraction image of the PbS nanoparticles doped in the composite bulk

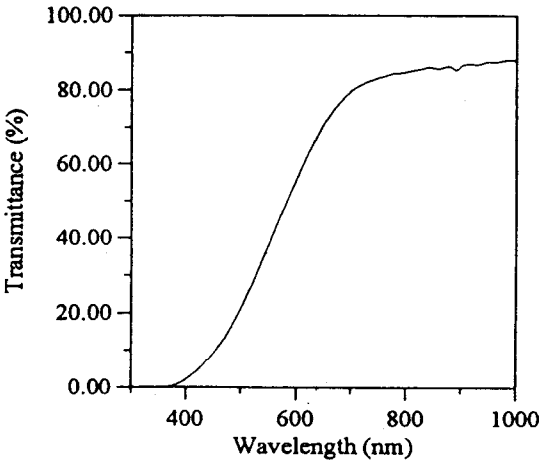

Fig. 4 Transmission spectrum of polystyrene composite modeling film doped with PbS nanoparticles

Table 2 The $\chi^{(3)}$ of the PbS/polymer composite films obtained by the DFWM method

Sample	$H_2S:Pb^{2+}$(molar ratio)	PbS Concentration (Mol/L)	Particle size (nm)	$\chi^{(3)}$ (esu)
1	1:1	1.28×10^{-2}	3.8	1.26×10^{-8}
2	2:1	1.28×10^{-2}	4.2	5.00×10^{-9}
3	2.5:1	1.28×10^{-2}	4.5	2.16×10^{-9}

* CS_2 was used as a reference sample in the DFWM measurement

Discussion

Fig. 5 is the IR spectra of the PbS powder samples prepared in the molar ratio of 0.75:1, 1:1 and 2.5:1 respectively. It can be seen from Fig. 5 that as the molar ratio increases, the vibration band located around 1693 cm^{-1} (C=O stretching vibration band of MA) increases and becomes distinct, while the vibration band located at 1546 cm^{-1} (C=O stretching vibration band of Pb-COO) decreases and

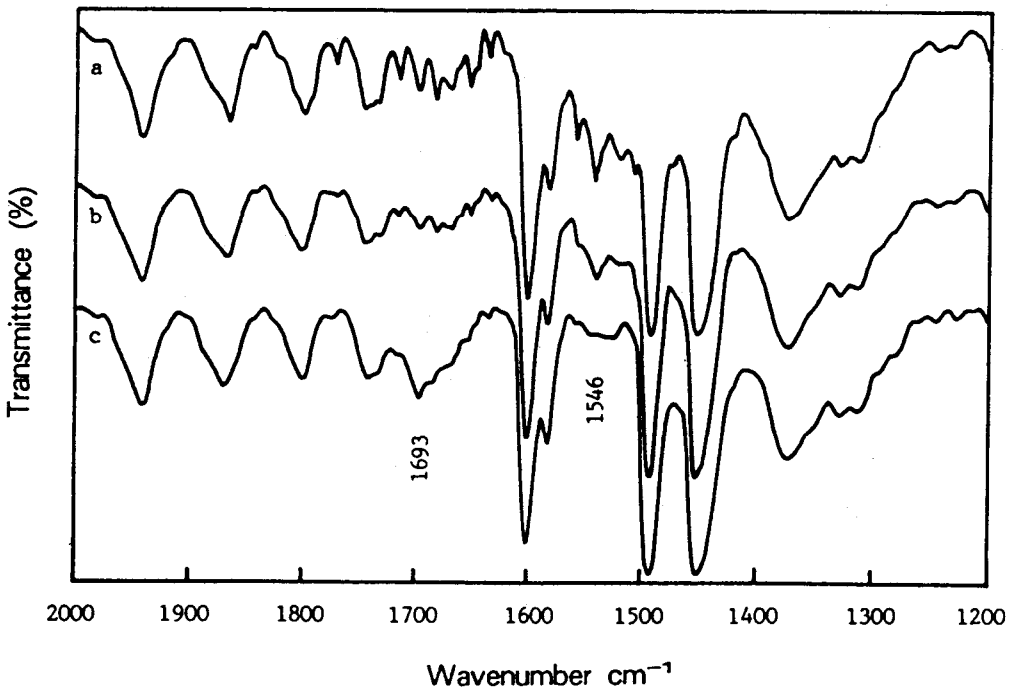

Fig. 5 IR spectra of PbS colloids prepared in different H_2S/Pb^{2+} molar ratios, spectrum a, b, c are correspondent to colloids with 0.75:1, 1:1, 2.5:1 respectively

becomes unclear. This implied that more and more 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 of 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 around 1546 cm^{-1} can still be distinguished, but it becomes unclear for the 2.5:1 one. But the spectrum of 2.5:1 colloid was more defined at 1693 cm^{-1} compared to that of the 0.75:1 and 1:1 colloids. This result proved that when the molar ratio was less than or equal to one, 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 assumption that most of the Pb-COO bonds are concentrated on the particle surface after the formation of PbS nanoparticles was proved by the changes of P-Pb molecular weight before and after reacting with H_2S. The molecular weight of P-Pb before and after reacting with H_2S in different H_2S/Pb^{2+} molar ratios were measured and listed in table 3.

Table 3 The molecular weight of P-Pb before and after reacting with H_2S in different H_2S/Pb^{2+} molar ratios

Sample	1	2	3	4	5
$H_2S:Pb^{2+}$ (mol)	0:10	3:10	5:10	7:10	9:10
$M_w(\times 10^4)$	3.0	5.1	5.6	5.9	6.1

The changes of the molecular weight with increase of the molar ratio implied that the Pb-COO bonds were concentrated on the particle surface, which makes the PbS nanoparticles act as a cross-linking agent and causes the increase of the molecular weight. The changes of hydrodynamic radii of the P-Pb before and after reacting with H_2S also proved this result[14].

The UV-Vis absorption spectra of the 0.7:1, 1:1, and 2.5:1 organosol solutions are recorded as Fig. 6. The absorption coefficient of the PbS nanoparticles increases greatly with increased molar ratios. This was attributed to the changes of the surface modification. From the previous report we know that if the ability of the particle surface in trapping electron-hole pairs decreases, the spatial overlap of the electron and hole wave function increases, as does the absorption coefficient[15]. The decrease of the absorption coefficient implies that the ability of the particle surface in trapping electron-hole pairs decreases with increased molar ratios. From above analysis we know that the amount of Pb-OOC bonds on the particle surface

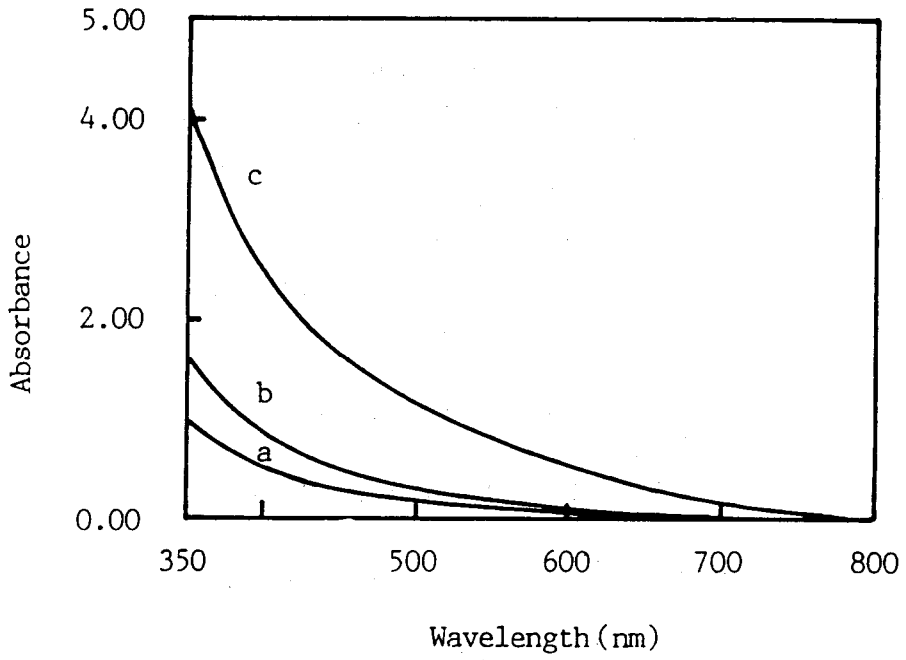

Fig. 6 UV-Vis absorption spectra of the PbS organosol prepared in different H_2S/Pb^{2+} molar ratios. Spectrum a, b, c are correspondent to 0.75:1, 1:1, 2.5;1 products respectively

decreases with increased molar ratios, so the absorption coefficient was related to Pb-OOC bonds on the particle surface. It can be deduced that the chemical bonds of Pb-OOC on PbS particle surface formed a strong surface electrofield gradient which can trap the electron-hole pairs effectively and resulted in the loss of light absorption oscillator strength and absorption coefficient, correspondingly. For the 2.5:1 colloid most of the Pb-OOC bonds were broken, the ability of the surface in trapping the electron-hole pair became the weakest among the three products, the spatial overlap of the electron and hole wave function became largest, as does the absorption coefficient. Whereas, the 0.75:1 colloid represented the smallest coefficient. On the other hand, as the molar ratio increased, the particle surface would be covered with Pb-SH groups instead of Pb-OOC bonds, the stability effect from the copolymer decreased, the particle and its distribution increased. As a result a slight red shift of the absorption edge for the colloids was presented in Fig. 6.

It has been proved that the strong interaction between the trapped carriers and the exciton can give rise to the optical nonlinearity[15], so the growth of the surface Pb-OOC bonds results in a increase of the nonlinear optical response of the composite materials.

References

1 M. L. Steigerwald and L. E. Brus, *Acc. Chem. Res.*, **1990**, *23*, 183.
2 A.. Henglein. *Chem. Rev.*, **1989**, *89*, 1861 and references therein.
3 AI. L. Efros and A. L. Efros, *Sov. Phys. Semicond.*, **1982**, *16*, 772.
4 L. E. Brus, *J. Phys. Chem.*, **1984**, *80*, 4403.
5 Y. Wang, and N. Herron, *J. Phys. Chem.*, **1991**, *95*, 525.
6 Y. Wang and W. Mahler, *Opt. Commun.*, **1987**, *61(3)*, 233.
7 Y. Wang, A. Suna, J. McHugh, E. Hilinski, P. Lucas, R. D. Johnson, *J. Chem. Phys.*, **1990**, *92*, 6927.
8 M. Y. Gao, Y. Yang, B. Yang, F. L. Bian and J. C. Shen, *J. Chèm. Soc., Chem. Commun.*, **1994**, 2779.
9 Y. Wang, A. Suna, W. Mahler and R. Kasowski, *J. Chem. Phys.*, **1987**, *87(12)*, 7315.
10 J. Yue, V. Sankaran, R. E. Cohen and R. R. Schrock, *J. Am. Chem. Soc.*, **1993**, *115*. 4409.
11 X. C. Li, J. R. Fryer and D. J. Cole-Hamilton, , *J. Chem. Soc., Chem. Commun.*, **1994**, 1715.
12 Spanhel, L; Haase, M.; Weller, H.; Henglein, A. *J. Am. Chem. Soc.*, **1987**, *109*, 5649.
13 Wang, Y.; Herron, N. *J. Phys. Chem.*, **1987**, *91*, 5005.
14 Y. Yang, M. Y. Gao, R. J. Ma, F. L. Bian and J. C. Shen, *Chemical Journal of Chinese Universities*, **1994**, *15*, 1719.
15 Y. Wang, *Acc. Chem. Res.*, **1991**, *24*, 133.