Synthesis of PbS Nanoparticles in Polymer Matrices

Mingyuan Gao, Yi Yang, Bai Yang, Fenglan Bian and Jiacong Shen*
Department of Chemistry, Jilin University, Changchun 130023, PR China

A new kind of PbS nanoparticles/polymer composite is synthesized whose microstructure observed under TEM proves that the nanoparticles are well dispersed and even in size; electron diffraction results identify the PbS nanoparticles to be of the cubic rock salt structure, and the particle size can be varied from 4 to 11 nm.

The realization of electronic properties of semiconductor nanoparticles significantly differing from either the individual molecules or bulk species has sparked intensive interest recently.[1,2] It has been established that their electronic properties 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] Theory and experiments have proved that small size and narrow distribution of nanoparticle sizes can improve their nonlinear optical response,[8] thus a synthesis which controls particle size distribution is of importance.

Recently PbS, CdS and CdS_xSe_{1-x} have been synthesized in polymer matrices in our laboratory using a variety of methods. In this paper, the synthesis of PbS nanoparticles in polymer matrices is described.

Styrene, lead oxide, methylacrylic acid (MA), methanol and tetrahydrafuran used in the present work were all analytical grade reagents; styrene and methylacrylic acid were distilled at 5 mmHg.

Lead methylacrylate was prepared from PbO and methylacrylic acid. Since it is known that there are two C=C bonds in each $Pb(MA)_2$ molecule, it is clear that in copolymerization with styrene, it works as a cross-linking agent. 240 ml of styrene and 3.964 g of $Pb(MA)_2$ were dissolved in 450 ml of THF and 1.52 g of AIBN (azoisobutyl nitrile) was added as an initiator. After bubbling with N_2 for 5 min, the vessel was warmed to 60 °C and maintained at this temperature for 3 hours with warm water. A light cross-linking Pb^{2+}-containing microgel (P–Pb) precipitate was obtained by pouring the above solution into a beaker containing 1500 ml of methanol. The molecular mass of the microgel was 6.5×10^4 as measured by GPC. The mass percentage of lead in this composite microgel was 2.5% as obtained by atomic emission.

0.2 g of the P–Pb microgel was dissolved in 4 ml of styrene, and then treated with 540 µl of H_2S gas (molar ratio $Pb^{2+}: H_2S$ 1 : 1) in a sealed container after which the solution turned dark red, but with no precipitation. This organosol showed long-term stability, with no precipitation even after a year.

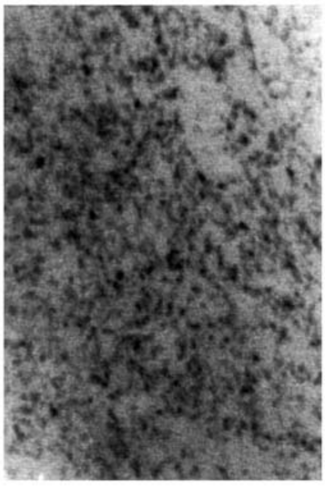

Fig. 1 TEM photograph (× 200000) of PbS nanoparticles doped in the composite bulk

The styrene organosol obtained above was further polymerized upon addition of 20 mg of AIBN at 60 °C for 3 hours and then 75 °C for 3 hours. After this procedure, the organosol turned into a red transparent solid.

TEM was utilized to observe PbS nanoparticles in this composite bulk. The composite bulk was cut into thin films using a LKB 8800-III microtome and attached onto a copper grid for TEM detection. It can be seen from the photograph (Fig. 1) that the PbS nanoparticles are well assembled in the matrix with almost all the particles being round and even in size. Because the particles were at various depths in the thin composite film, they could not all be clearly observed at a given focus. The average size of the particles was found to be 40 Å. This result fits well with that obtained from a small-angle scattering measurement. Data obtained from the diffraction pattern (Fig. 2) are given in Table 1 which establishes a cubic rock salt structure for the PbS nanoparticles. The histogram of the nanoparticles (Fig. 3) shows a narrow distribution of particle size. IR spectroscopy indicates that some P–Pb molecules are still bonded to the particle surface after reacting with H_2S, which can prevent the PbS particles from growing further after nucleation, so resulting in their small size and narrow size distribution. The particle size can be varied in a range of 40–110 Å if the amount of $Pb(MA)_2$ added to P–Pb is varied (Table 2).

The composite bulk obtained showed large optical nonlinearities, *i.e.* the third-order optical susceptibility was as

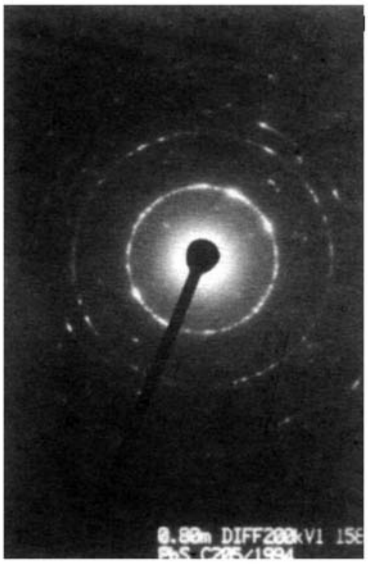

Fig. 2 Electron diffraction image of the PbS nanoparticles doped in the composite bulk

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

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

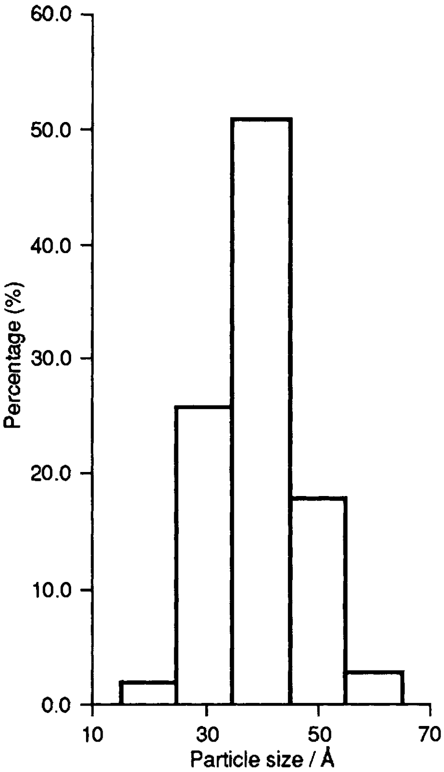

Fig. 3 Histogram of particle size of the PbS nanoparticles shown in Fig. 1

Table 2 Variation of PbS particle size with ratio of added $Pb(MA)_2$ to P–Pb

$Pb(MA)_2$: P–Pb	Particle size/Å
0 : 1	40
5 : 1	103[a]
70 : 1	113[a]

[a] Obtained by small angle X-ray scattering.

high as 10^{-8} esu (degenerate four-wave mixing method, the second harmonic of YAG laser was used as excitation source, λ = 532 nm) using an experimental setup as in ref. 7.

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