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Preparation and characterization of polystyrene films containing PbS nanoparticles

P. SREEKUMARI NAIR[‡], T. RADHAKRISHNAN[§,*], N. REVAPRASADU, G. A. KOLAWOLE
Department of Chemistry, University of Zululand, Private Bag X1001, Kwa Dlangezwa, 3886, South Africa
E-mail: tradha20@hotmail.com

A. S. LUYT
Department of Chemistry, University of the Free State (Qwaqwa Campus), Private Bag X13, Phuthaditjhaba, 9866, South Africa

V. DJOKOVIĆ[*]
Department of Chemistry, University of the Free State (Qwaqwa Campus), Private Bag X13, Phuthaditjhaba, 9866, South Africa; Institut of Nuclear Sciences "Vinča", P.O. Box 522, 11001 Belgrade, Serbia and Montenegro
E-mail: djokovic@vin.bg.ac.yu

During the last decades considerable research efforts have been directed to studying semiconductor-polymer nanocomposites [1–13]. The interest in nanocrystalline semiconductor materials is motivated by the fact that they exhibit unique optical and electronic properties that are different from those of their bulk counterparts. It was shown that it is possible to tune these properties solely by changing the size of the nanoparticles (when their diameter is smaller or comparable with the diameter of the bulk exciton). Polymers are, on the other hand, excellent matrices for nanostructured semiconductors because they show good long-term stability and can be easily processed in almost any size and shape demanded by the application.

Lead sulfide, a narrow band gap semiconductor ($E_g = 0.41$ eV at room temperature), is very sensitive to finite size effects due to a large exciton Bohr radius (180 Å). Since a large blue shift occurs when the size of the PbS nanoparticles falls below the radius of the bulk exciton, this offers the possibility to adjust their optical properties in the spectral region between 1 and 2 μm, which is important for many technological applications. So far several methods for the synthesis of nanostructured PbS in different host matrices, such as polymers [2–8], micelles [14], monolayer surfaces [15], zeolites [16] and glasses [17], have been developed.

In the present letter we suggest a procedure for the incorporation PbS nanoparticles in a polystyrene (PS) matrix. The method is based on the thermal decomposition of a lead xanthate complex within the solid polymer. The lead xanthate was prepared by the reaction of lead acetate (0.001 mol) and potassium ethylxanthate (0.001 mol) in ethanol at room temperature. The solid formed is immediately filtered, washed with ethanol and acetone, and finally dried. After that, 25 mg of the complex was dissolved in a chloroform solution of polystyrene (1 g of PS in 50 ml of chloroform). The solution was sonicated and cast into 30 μm thick films on a glass plates. The wine-red nanocomposite material was obtained by keeping the films in an air oven for 30 min at a temperature of 333 K. Pure PS films were prepared in a similar way.

The UV-VIS spectra (Perkin Elmer Lambda 3B UV-VIS spectrophotometer) of pure PS and the PS-PbS nanocomposite are shown in Fig. 1. It can be seen that pure PS shows negligible absorption in the visible part of the spectrum. Knowing that the band gap of bulk PbS is 0.41 eV, it can be concluded that the optical absorption of the nanocomposite (Fig. 1) originates from the blue shifted absorption of the PbS nanoparticles in the PS matrix. It should also be noted that the observed optical properties of the PS-PbS nanocomposite are similar to the results obtained by Zeng *et al.* [8] on a poly(methyl methacrylate-*co*-methacrylic acid)-PbS nanocomposite. The comparison of our data with the data of Zeng *et al.* suggests that the size distribution of the PbS nanoparticles is relatively broad with an average size of about 7–8 nm.

For the transmission electron microscopy (TEM) measurements (Jeol JEM-1200EXII transmission electron microscope), the samples were deposited onto carbon-filmed grids using a fine pipette, air-dried and immediately examined (operating voltage 80–100 kV). The TEM micrograph of the nanocomposite (Fig. 2) clearly shows the presence of the nanoparticles.

In order to establish possible chemical interaction between the matrix and the nano-filler, FTIR measurements were performed. To record the IR spectra of pure PS and the PS-PbS nanocomposite, a Nicolet Impact 410 FTIR spectrometer, connected to a photoacoustic cell, was used. The scanning range was from 400 to 4000 cm^{-1} with a resolution of about 8 cm^{-1}. No significant differences between the FTIR spectra of both materials were noticed (Fig. 3). However, the presence

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[*] Author to whom all correspondence should be addressed.

[†] *Present address*: Department of Chemistry, Lash-Miller Chemical Laboratories, University of Toronto, Ontario, M5S 3H6, Canada.

[‡] *Present address*: Department of Chemistry, University of Toronto at Mississauga, Mississauga, Ontario, Canada, L5L 1C6.

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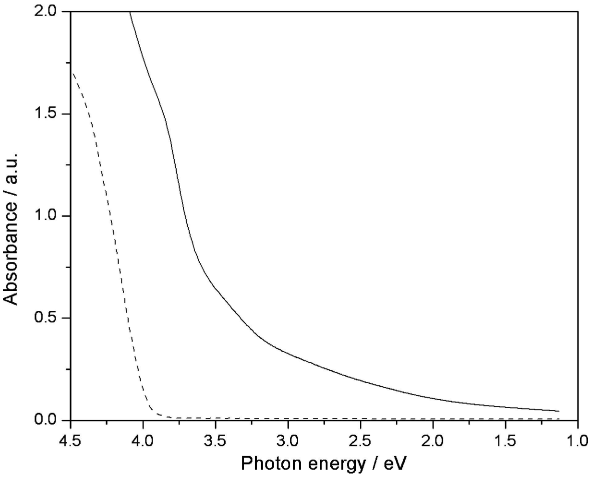

Figure 1 Absorption spectra of pure PS (dashed line) and the PS-PbS nanocomposite (solid line) in chloroform.

Figure 2 Transmission electron microscopy (TEM) image of the PS-PbS nanocomposite.

of a weak band, at 650 cm^{-1}, in the spectrum of the nanocomposite, which corresponds to the stretching vibration of C-S groups, suggests possible interaction between the sulphur at the surface of nanoparticles and the polymer chains. This additional band was also noticed by Nedeljković *et al.* [11] in the spectrum of a PS-CdS nanocomposite.

Thermogravimetric analyses (Perkin-Elmer TGA7) of pure PS and the PS-PbS nanocomposite were carried out under a nitrogen atmosphere in the temperature range from 320 to 773 K (heating rate 10 K min^{-1}). No apparent changes in the TGA curves of both samples were noticed and the curves will not be reported. However, from the residual wt% at the end of the TGA measurement it was found that the content of the inorganic phase in the nanocomposite was 2.1 wt%.

Differential scanning calorimetry (DSC) analyses were carried out on a Perkin-Elmer DSC7. Pure PS and

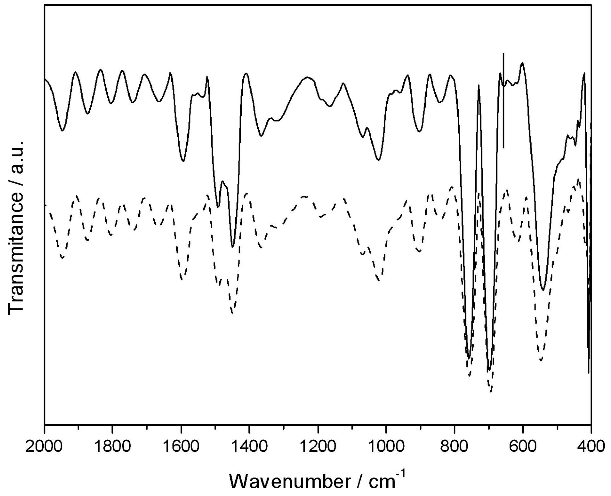

Figure 3 FTIR spectra of pure PS (dashed line) and the PS-PbS nanocomposite (solid line). Straight line at 650 cm^{-1} indicates the new band in the spectrum of the nanocomposite.

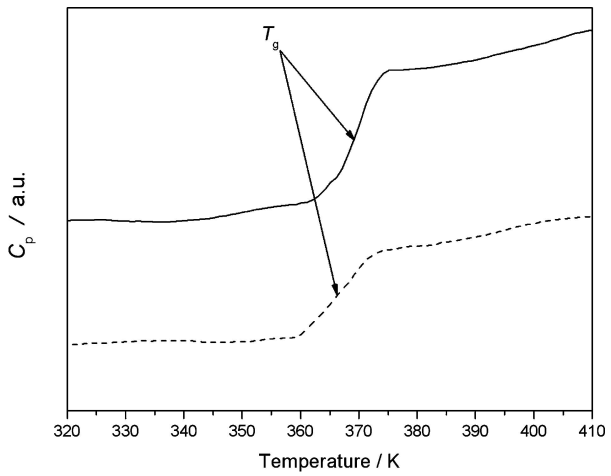

Figure 4 DSC heat capacity curves of pure PS (dashed line) and the PS-PbS nanocomposite (solid line). Arrows indicate the glass transition temperatures of both materials ($T_g = 367$ K for PS and $T_g = 369$ K for the PS-PbS nanocomposite) chosen as the centre of the slope on the corresponding curve.

nanocomposite samples were initially heated from 303 to 413 K at a rate of 20 K min^{-1}, held at that temperature for one min to eliminate thermal history effects, cooled to 303 at 20 K min^{-1}, and reheated at the same rate. The reported heat capacity curves in Fig. 4 were obtained in the second run. It can be seen that the glass transition temperature of the nanocomposite is slightly shifted (by about 2 K) towards a higher temperature, which indicates that the nanoparticles do not considerably affect the chain mobility. Nevertheless, another effect should also be taken into account, and that is the broadening of the glass transition region of the nanocomposite (Fig. 4). Bearing in mind the fact that the glass transition in real polymers is not the phase transition in a strict physical sense (since it correspond to a series of glass transition temperatures related to the activation of the chain segments of different lengths), the observed effect suggests that in the presence of the nanoparticles the segmental distribution of the chains was changed. Probably, there is a change in the packing density of the polymer chains in the regions close to the extremely high specific surfaces of the nanoparticles. Our previous results support these conclusions. It was found that HgS and Ag nanoparticles induce broadening of the glass transition regions of PS and polyvinyl alcohol matrices respectively, with a significant increase in the glass transition temperature [13, 18]. On the other hand, about 20 wt% of CdS microparticles was necessary to induce a 2 K change in the glass transition temperature of PS [19]. At the same time, with respect to pure PS, no change in the segmental distribution, i.e. the glass transition region, was observed.

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To conclude, a procedure for preparation of PS-PbS nanocomposites is introduced. Further investigations are underway in our laboratories in order to optimize this synthetic approach and obtain better control of the size of nanoparticles in the matrix, which is essential for a possible application of nanocomposite materials.

References

1. D. Y. GODOVSKY, *Advan. Polym. Sci.* **165** (2000) 153.
2. W. CASERI, *Macromol. Rapid Commun.* **21** (2000) 705.
3. Z. QIAO, Y. XIE, Y. ZHU and Y. QIAN, *J. Mater. Chem.* **9** (1999) 1001.
4. Z. QIAO, Y. XIE, M. CHEN, Y. XU, Y. ZHU and Y. QIAN, *Chem. Phys. Lett.* **321** (2000) 504.
5. Y. WANG, A. SUNA, W. MAHLER and R. KASOWSKI, *J. Chem. Phys.* **87** (1987) 7315.
6. R. S. KANE, R. E. COHEN and R. SILBEY, *Chem. Mater.* **8** (1996) 1919.
7. S. WANG and S. YANG, *Langmuir* **16** (2000) 389.
8. Z. ZHENG, S. WANG and S. YANG, *Chem. Mater.* **11** (1999) 3365.
9. H. DU, G. Q. XU, W. S. CHIN, L. HUANG and W. JI, *ibid.* **14** (2002) 4473.
10. S.-H. YU, M. YOSHIMURA, J. M. C. MORENO, T. FUJIWARA, T. FUJINO and R. TERANISHI, *Langmuir* **17** (2001) 1700.
11. D. ŠAJINOVIČ, Z. V. ŠAPONJIČ, N. CVJETIĆANIN, M. MARINOVIĆ-CINCOVIĆ and J. M. NEDELJKOVIĆ, *Chem. Phys. Lett.* **329** (2000) 168.
12. V. DJOKOVIĆ and J. M. NEDELJKOVIĆ, *Macromol. Rapid Commun.* **21** (2000) 994.
13. P. SREKUMARI NAIR, T. RADHAKRISHNAN, N. REVAPRASADU, C. G. C. E. VAN SITTERT, V. DJOKOVIĆ and A. S. LUYT, *Mater. Lett.* **58** (2004) 361.
14. A. J. I. WARD, E. C. O'SULLIVAN, J.-C. RANG, J. NEDELJKOVIĆ and R. C. PATEL, *J. Colloid Interface Sci.* **161** (1993) 316.
15. X. K. ZHAO, S. Q. XU and J. H. FENDLER, *Langmuir* **7** (1991) 520.
16. K. MOLLER, T. BEIN, N. HERRON, W. MAHLER and Y. WANG, *Inorg. Chem.* **28** (1989) 2914.
17. T. OKUNO, A. A. LIPOVSKII, T. OGAWA, I. AMAGAI and Y. MASUMOTO, *J. Lumin.* **87-89** (2000) 491.
18. Z. H. MBHELE, M. G. SALEMANE, C. G. C. E. VAN SITTERT, J. M. NEDELJKOVIĆ, V. DJOKOVIĆ and A. S. LUYT, *Chem. Mater.* **15** (2003) 5019.
19. J. KULJANIN, M. VUČKOVIĆ, M. I. ČOMOR, N. BIBIĆ, V. DJOKOVIĆ and J. M. NEDELJKOVIĆ, *Euro. Polym. J.* **38** (2002) 1659.

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