

OPTICAL STUDY ON SPUN FILMS LEAD PHTHALOCYANINE (PbPc)

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Abstract. Nano-composite spun films lead phthalocyanine (PbPc) were prepared by for the first time by exposure of thin spun films of a lipophilic lead phthalocyanine derivative to H₂S gas. The formation of lead sulphide was confirmed by Raman and UV-vis spectroscopy measurements. The characteristic spectral transformations at 625–650 cm⁻¹ and 1000–1400 cm⁻¹ correspond to bending and stretching vibrations of phthalocyanine macrocycles, respectively. The spectra undergo dramatic changes after the treatment with H₂S gas. A Q-band double peak is shifted to the lower wavelengths (680/745 nm). From the blue spectral shift of the fundamental adsorption band, the size of the PbS clusters was estimated to be 2.24 nm.

Keywords: Nano-composite, lead phthalocyanine, exposure of thin spun films

Abstrak. Film nano-komposit *lead phthalocyanine* (PbPc) pertama dibuat dengan mengekspos gas H₂S pada film turunan *lipophilic lead phthalocyanine* yang dibuat dengan teknik spincoating. Terbentuknya *lead sulphide* dikonfirmasi dengan pengukuran spektroskopi Raman dan UV-Vis. Perubahan spektrum pada 625–650 cm⁻¹ dan 1000–1400 cm⁻¹ masing-masing berkaitan dengan vibrasi *bending* dan *stretching* dari phthalocyanine. Tampak bahwa terjadi perubahan spektrum yang cukup signifikan akibat eksposur gas H₂S. Tampak terjadi pergeseran puncak ganda Q-band ke arah panjang gelombang pendek (680/745 nm). Dari pergeseran pita absorpsi tersebut diperkirakan ukuran dari kluster PbS sekitar 2.24 nm.

Keywords: Nano-komposit, *lead phthalocyanine*, eksposur film tipis

I. Introduction

Nanometer-size lead sulphide (PbS) particles have been fabricated using chemical routes for a variety of applications including single-electron devices [1], light-emitting devices [2], programmable memory in organic field-effect transistor [3] and multiscale nonlinear switching [4]. Chemical methods of formation of such nanostructures attract a great deal of attention because of their cost effectiveness when compared to expensive solid-state technologies such as molecular beam epitaxy. It has been reported that mono dispersed PbS nanoparticles can be produced by exposing self-assembled monolayers (SAMs) of 11-mercaptoundecanoic acid-adsorbed Pb ions on gold substrates to an H₂S atmosphere [5]. The average particle size was estimated to be of 3.2–0.4 nm. The current-voltage characteristics of a single nanoparticle exhibited the effect of Coulomb blockade and the staircase width depended upon the gap between an STM tip and the PbS nanoparticle [6]. In further studies, PbS doped-silica gels showing a visible absorption onset were prepared by the sol-gel method [7]. II–VI semiconductor nanoparticles have also been produced within Langmuir–Blodgett (LB) films of appropriate fatty acid metal salts upon exposure to H₂S gas [8]–[10].

In this paper, we report for the first time the formation of a nanostructured composite material of lead sulphide in a phthalocyanine matrix. This has been achieved by exposing spin coated films of 1-, 4-, 8-, 11-, 15-, 18-, 22-, and 25-octahexyl-phthalocyanine to lead to H₂S gas for at least 12h.

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Figure 1(a) presents the chemical structure of the molecule, which will be referred to as C6PbPc throughout this paper. UV-visible and Raman spectra were obtained for thin films of C6PbPc molecules before and after the H₂S treatment. We have shown that, in these molecules, the Pb atoms are lost on exposure to H₂S to afford the metal-free analog C6H₂Pc [for chemical structure, see Figure 1(b)]. This implies that the Pb ions are rather weakly bound to the Pc moiety because of the large ion radius and geometrically are out of the molecular plane [11]. As a consequence of this, two plausible transformations of spun C6PbPc films may take place under prolonged exposure of H₂S gas according to the following scheme [12]:

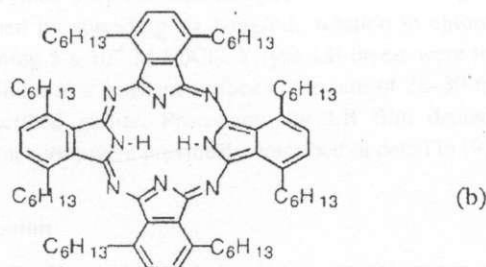
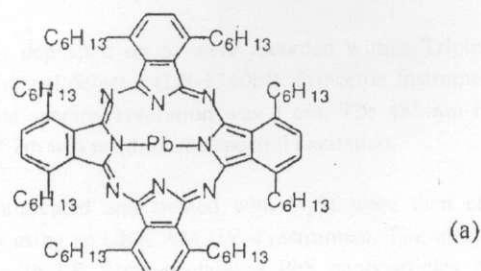
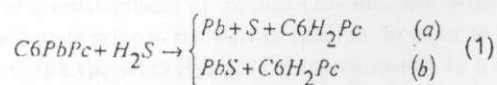


Figure 1. Chemical structure of: (a) 1-, 4-, 8-, 11-, 15-, 18-, 22-, 25- octahexylphthalocyaninato lead (C6PbPc) and (b) 1-, 4-, 8-, 11-, 15-, 18-, 22-, 25-octahexylphthalocyanine metal free (C6H₂Pc) molecules.

A comparison of properties of C6PbPc and C6H₂Pc spun films with LB films of lead stearate allows us to PbS nanoparticles indicating that path (b) in (1) is followed, at least partially. It is also possible that some residual Pb atoms will remain attached to the Pc ring, producing a composite material consisting of PbS nanoclusters: metal free and lead phthalocyanines. The PbS nanoparticles may form aggregates in a way similar to those in LB films [9] or alternatively intercalate with Pc molecules and form a nanocomposite material consisting of C6H₂Pc and PbS or some combination of lead and sulphur.

Further experiments have now been performed to identify the precise route of the formation of the PbS nanophase in C6PbPc spun films involving Raman spectroscopy method. This paper provides these experimental evidences. The size of PbS nanoclusters is also estimated from the analysis of

UV-visible absorption spectra. It is found that these particles are much smaller than those previously reported [5].

2. Experimental Details

Solutions of both C6PbPc and C6H₂Pc compounds in chloro-form at a concentration of 2 mg/mL were used for spin coating. Film deposition was carried out with a Photo-resist Spinner (model 4000, Electronic Micro System, Downton, Wiltshire, U.K.) at a constant spin speed of 2000 *r/min* for 40 s. Solid substrates of different types (e.g., glass slides, pieces of silicon wafer) were fixed on a rotating stage, and a small amount of solution (20–30 μ L) was dispensed with a micropipette onto the center of the substrate prior to the start of rotation. In order to produce the PbS phase in the films, the samples were exposed to H₂S gas for approximately 12 h (usually overnight) in a sealed container, as was described earlier in [8] for nanocomposite LB films.

Raman spectra of films deposited on Si were recorded with a Triplemate SPEX spectrometer equipped with a multichannel detector (LN-1340PB, Princeton Instruments, Trenton, NJ) in back-scattering geometry. The spectral resolution was 5 cm. The 488-nm line of a 50-mW Ar laser focused to a diameter of 2 mm was used for the spectral excitation.

Both types of films (untreated and treated with H₂S) were then characterized with UV-vis absorption spectroscopy using an UNICAM UV-4 instrument. The spectral properties of the above films were compared with LB films containing PbS nanoparticles produced by conventional techniques [8]. The LB films were obtained using an NIMA 611 Langmuir trough. Monolayers of stearic acid were formed by spreading its 1-mg/mL solution in chloroform onto the surface of Millipore water containing 5 \times 10⁻⁴ M CdCl₂. Y-type LB layers were transferred onto the surface of hydrophobic glass slides at a constant surface pressure of 28–30 mN/m and then exposed to H₂S gas, as was described earlier. Procedures for LB film deposition, as well as sample preparation (hydrophobization) were previously described in detail in [9].

3. Results and Discussion

Raman spectra of C6PbPc films before and after H₂S treatment are presented in Figure 2(I) (curves a and d). The modes in the range from 200 to 1400 cm⁻¹ correspond to intramolecular vibrations of the phthalocyanine macrocycle. The detailed assignment of the vibrations are given in [13] and [14]. The characteristic spectral transformations at 625–650 cm⁻¹ and 1000–1400 cm⁻¹ correspond to bending and stretching vibrations of phthalocyanine macrocycles, respectively. These indicate the formation of C6HPc after treatment of C6PbPc film by H₂S. The spectral features appearing at approximately 300 and 220 cm⁻¹ in C6PbPc film after H₂S treatment can be associated with the formation of PbS. The results of a detailed Raman investigation (with the beam focused on the cluster assembly spot on the sample) are presented in Figure 2(II), clearly showing the spectral line at 220 cm⁻¹, which corresponds to local oscillator (LO) phonons in bulk PbS [15]–[17] in the galena crystallographic modification [18,19]. The line at 300 cm⁻¹ may, therefore, be related either to other weaker PbS phonon lines or to some sort of impurities in the film. Test samples of C6HPc spun films do not show any spectral changes following H₂S treatment (see Figure 2(I), curves c and d).

Figure 3 shows a set of typical reproducible UV-visible spectra of the C6PbPc samples. The curve (a) represents the spectrum of the C6PbPc spun film as deposited, e.g., before the treatment with H₂S. The observation of a band double peak (700 and 755 nm) and a Soret band below 500 nm are characteristic features for this compound.

The spectra undergo dramatic changes after the treatment with H_2S gas [Figure 3, curve (b)]: a Q-band double peak is shifted to the lower wavelengths (680/745 nm). The spectra bear resemblances to ones obtained for C_6H_2Pc film [see Figure 3, curve (c)]. This correspondence clearly indicates that C_6PbPc molecules have lost Pb atoms and have been transformed to metal-free C_6HPc . Curve (d), which represents the difference between curves (b) and (c), shows the absorption monotonically rising toward wavelengths below 650 nm.

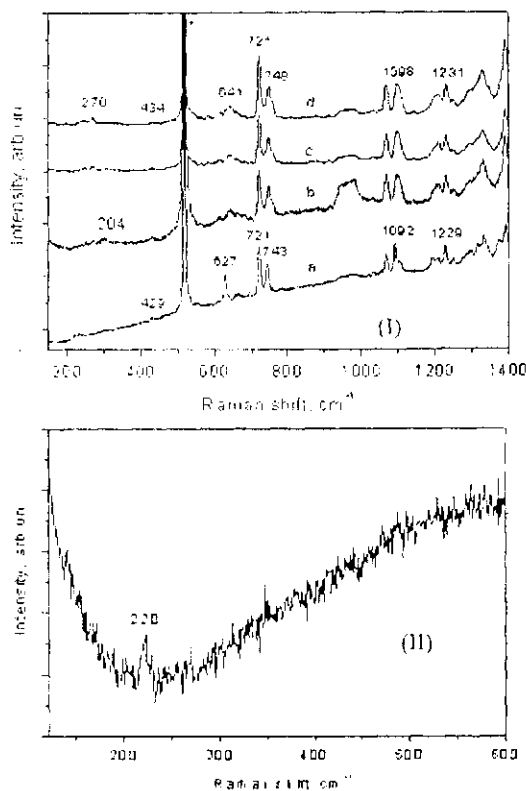


Figure 2. (I) Raman spectra of C_6PbPc film before H_2S treatment (curve a), C_6PbPc film after H_2S treatment (curve b), C_6HPc film before H_2S treatment (curve c), and C_6HPc film after H_2S treatment (curve d). (II) Detailed Raman spectrum of C_6PbPc film after H_2S treatment.

Curve (e) in Figure 3 was obtained for PbS nanoparticles in the stearic acid LB film matrix, showing the dominant absorption in the same spectral range as for (d). An exact match is not expected because of the different matrices used and variation in particle sizes. However, the observation of the tendency for the absorption to rise may be attributed to the formation of a PbS phase in the C_6PbPc film as a result of the reaction with H_2S gas (1b). The interpretation of the observed spectral transformations in C_6PbPc films and the extraction of the spectra of the PbS phase are quite difficult tasks because the phthalocyanine film matrix is also absorbing in the visible spectral range.

Since the absorption spectra of phthalocyanine films depend not only on the electron levels of individual Pc molecules, but largely on their arrangement in the films, the observed spectral transformations in C6PbPc films can be caused by a combination of three following processes:

- 1) formation of C6HPc molecules as a result of the reaction shown above (1);
- 2) inclusions of PbS phase (either as a fine intercalation of C6H₂Pc and PbS molecules or the formation of PbS clusters);
- 3) changes in the structure of C6H₂Pc films (intermolecular distances and angles) due to the presence of the PbS phase.

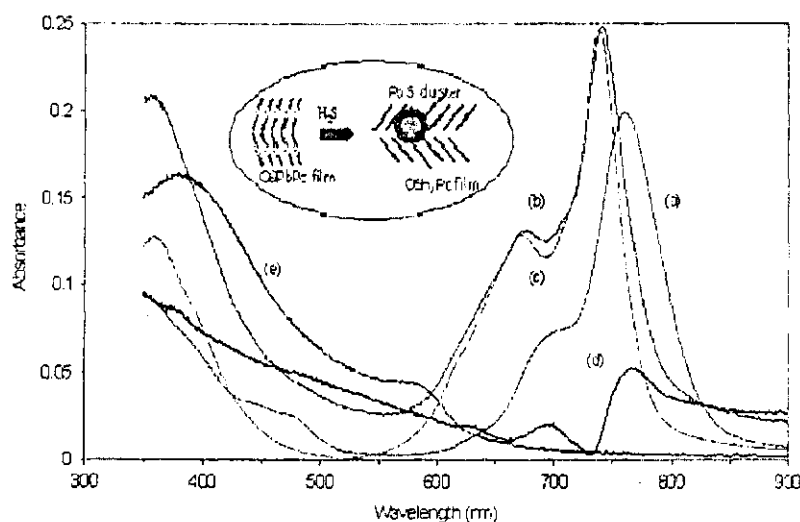


Figure 3. UV-vis absorption spectra of: (a) C6PbPc film before H₂S treatment, (b) C6PbPc film after H₂S treatment, (c) C6H₂Pc film, (d) subtracted spectra (b) and (c), (e) PbS in 20-layer-thick stearic acid LB film. The inset shows proposed changes in the C6PbPc film structure caused by exposure to H₂S gas.

The analysis of the results presented in Figure 3 implies the formation of PbS clusters in the film. There has not been any dramatic change in the arrangement of stacks of C6H₂Pc molecules. However, slight randomization of stacks has taken place near PbS nanoclusters, as illustrated by the scheme in the inset of Figure 3. The size of PbS clusters (a) can be calculated from the energy shift (ΔE) of their absorption band edge (E_g) in respect to that for a bulk material E_{g0} [20] as follows:

$$\Delta E = E_g - E_{g0} = \frac{h^2 \tau^2}{2 \mu a^2}$$

where $(1/\mu) = (1/m_e) + 1/m_h$ is the reduced exciton mass. Using the values of $E_g = 1.91$ eV for PbS clusters, obtained from the absorption edge of 650 nm on the experimental spectra [see Figure 3, curve (d)], and $E_{g0} = 0.41$ eV for bulk PbS (galena) [21], [22], as well as the values of $m_e = m_h = 0.1m_0$ for bulk PbS [23], the above calculations yield the PbS cluster size $a = 2.24$ nm.

4. Conclusion

The results of this paper show the formation of PbS clusters in the spun films of the substituted lead phthalocyanine as a result of reaction with H₂S gas. The spin-coating method is much simpler and less laborious than the commonly used LB technique for the formation of II-VI semiconductor

nanoparticles. The existence of the PbS Galena phase in the H₂S treated C6PbPc films was confirmed using Raman spectroscopy and XPS. The latter shows a complex composition of the material having several different phases of both lead and sulphur, but obviously including PbS. Both UV-visible absorption and photoluminescence spectral measurements indicate the presence of PbS in the film after reaction with H₂S. The formation of PbS clusters seems to be more probable than an intercalated PbS/C6H₂Pc structured film. The size of the PbS clusters of 2.24 nm was estimated from the blue spectral shift of the optical absorption edge in respect to its bulk value.

References

1. P. Jiang, Z. F. Liu, Y. C. Wang, and S. M. Cai, "Room temperature single electron tunnelling in nanoparticle-STM tip assemblies", *Mol. Cryst.* 337 (1999), 317-320.
2. M. A. Hines and G. D. Scholes, "Colloidal PbS nanocrystals with size-tunable near-infrared emission: Observation of post-synthesis self-narrowing of the particle size distribution", *Adv. Mater.* 15 (2003), 1844-1849.
3. B. Mukherjee & M. MukherjeeHines "Programmable memory in organic field-effect transistor based on lead phthalocyanine", *Organic Electronics*, 10 (2009), 1282-1287.
4. C. Sheng, R. A. Wang, J. Thomas, J. Steeves, D. Kimball & N. Peyghambarian "Nonlinear optical transmission of lead phthalocyanine-doped nematic liquid crystal composites for multiscale nonlinear switching from nanosecond to continuous wave", *Applied Optics*, 48 (2009), 2731-2734.
5. P. Jiang, Z. F. Liu, and S. M. Cai, "Growing monodispersed PbS nanoparticles on self-assembled monolayers of 11-mercaptoundecanoic acid on Au substrate," *Langmuir*, vol. 18, no. 11, (2002) pp. 4495-4499.
6. P. Jiang, Z. F. Liu, and S. M. Cai, "Single-electron tunnelling in a single PbS nanocrystal nucleated on 11-mercaptoundecanoic acid self-assembled monolayer at room temperature", *J. Appl. Phys.* 90 (2001), 2039-2041.
7. N. Pellegri, R. Trbojevič, O. de Sanctis, and K. Kadono, "Fabrication of PbS nanoparticles embedded in silica gel by reverse micelles and sol-gel routes", *J. Sol.-Gel. Sci. Technol.* 8 (1997), 1023-1028.
8. V. Erokhin, P. Facci, L. Gobbi, S. Dante, F. Rustichelli, and C. Nicolini, "Preparation of semiconductor superlattices from LB precursor", *Thin Solid Films* 329 (1998), 503-505.
9. J. Simon and J.J. Andre, *Molecular Semiconductors, Photoelectric properties and Solar Cells*, Springer-Verlag, Balm- Heidelberg, 1985.
10. A. V. Nabok, T. Richardson, F. Davis, and C. J. M. Stirling, "Cadmiumsulphide nanoparticles in Langmuir-Blodgett films of calixarenes," *Langmuir*, vol. 13, (1997) pp. 3198-3201.
11. V. Nabok, A. K. Ray, A. K. Iwantono, A. K. Hassan, and M. Simmonds, "II-VI semiconductor nanoparticles formed by Langmuir-Blodgett film technique: Optical study", *IEEE Trans. Nanotechnol.* 2 (2003), 44-49.
12. J. Simon and J. J. Andre, *Molecular Semiconductors, Photoelectric Properties and Solar Cells*, Berlin, Germany: Springer-Verlag, 1985.
13. T. V. Basova and B. A. Kolesov, "Raman spectra of copper phthalocyanine: Experiment and calculation," *J. Struct. Chem.* 41 (2000), 770-777.
14. D. Tackle, G. Dent, and W. Smith, "Phthalocyanines: Structure and vibrations," *Phys. Chem. Chem. Phys.* 3 (2001), 1419-1426.
15. L. L. Sveshnikova, S. M. Repinsky, A. K. Gutakovsky, A. G. Milekhin, and L. D. Pokrovky, "Semiconductor nanoclusters in the matrix of Langmuir-Blodgett films", *Chem. Sustainable Development*, 8 (2000), 73-77.
16. A. G. Milekhin, L. L. Sveshnikova, S. M. Repinsky, A. K. Gutakovsky, M. Friedrich, and D. R. T. Zahn, "Optical vibrational modes in (Cd, Pb, Zn)S quantum dots embedded in Langmuir-Blodgett matrices," *Thin Solid Films*, 422 (2002), 200-204.
17. J. T. Devreese, V. M. Fomin, and S. N. Klimin, "Phononinduced features in optical spectra of quantum dots: Breakdown of the adiabatic approximation", *Int. J. Modern Phys. B.* 15 (2001), 3579-3583.
18. G. D. Smith, S. Firth, R. J. H. Clark, and M. Cardona, "First- and secondorder Raman spectra of galena (PbS)", *J. Appl. Phys.* 92 (2002), 4375-4380.



19. *NIST Standard Reference Database*, 20. [Online]. Available: <http://srdata.nist.gov/xps/>, (2003) ver. 3, 4.
20. A. D. Yoffe, "Semiconductor quantum dots and related systems: Electronic, optical, luminescence and related properties of low dimensional systems", *Adv. Phys.* 50 (2000), 1–208.
21. R. Thielsch, T. Böhme, R. Reiche, D. Schläfer, H.-D. Bauer, and H. Böttcher, "Quantum-size effects of PbS nanocrystallites in evaporated composite films", *Nanostructured Mater.* 10 (1998), 131–149.
22. Y. Wang, A. Suna, W. Mahler, and R. Kasowski, "PbS in polymers—From molecules to bulk solids", *J. Chem. Phys.* 87 (1987), 7315–7322.
23. S. O. Kasap, Ed., *Electrical Engineering Materials and Devices*. New York: McGraw-Hill, 1997.
24. A.V. Nabok, A. V. Iwantono, A. K. Ray, I. Larkin, and T. Richardson, "Evolution of CdS nanoparticles within two-dimensional Langmuir–Blodgett layers", *J. Phys. D, Appl. Phys.* 35 (2002), 1512–1515.

