

CONDUCTIVE POLYMERIC MATRIX SYNTHESIZED BY CHEMICAL AND ELECTROCHEMICAL METHODS AND THE EFFECT OF PbS/Cu₂S NANOPARTICLES ADDED FOR SOLAR ABSORBING APPLICATIONS

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This paper reports the synthesis of poly (3-hexylthiophene) and the PbS/Cu₂S- poly (3-hexylthiophene) by chemical and electrochemical methods. The characterization by UV-Vis and PL show the interaction between the nanoparticles and the polymeric matrix as an increase in the optical properties in the visible range. The E_g values were calculated to be 1.9 and 1.77 eV for the polymer and the composite, respectively. The CV analysis shows the influence of the presence of the nanoparticles in the electrochemical behavior allowing to calculate the HOMO and LUMO positions. Nevertheless the IR spectra and the conductivity values suggest that the addition of the nanoparticles to the polymeric film reduces the polymeric chain length and decreases the conductivity value.

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1. Introduction

The synthesis and characterization of nanoparticles of semiconducting metal sulfide has been an intense field of research due to the interesting properties and the potential applications of those compounds [1-5]. Cu₂S-PbS heterojunction has been investigated recently due to its optical and photo thermal activation because in this type of heterostructure the photon can be absorbed by both of the two components (PbS-Cu₂S), making them a really interesting system for photovoltaic applications. [6] An important strategy to improve the nanoparticles efficiency and stability against photo-oxidation of various types of semiconductor is their surface passivation with the growth of a second semiconductor shell, resulting in core-shell system. Recently, we reported the synthesis and characterization of a material that contains PbS and Cu₂S with interesting optical properties when it is arranged in the core-shell structure, enhancing its luminescent properties. [7]

Over the last decades, conjugated polymers such as polyacetylene, polyaniline, polypyrrole and polythiophene have been the focus of research. Many studies have been developed to synthesis and characterization of these materials. Conjugated polymers are typically insulators and when they doped with an oxidizing or reducing agent, they become conductive. The doping process is removing/introducing the electrons from/to the polymer backbone to increase their charge carrier mobility and their conductivity [8,9]. Among the conductive polymers, although polythiophene and its derivatives have less solubility in water because of their higher crystallinity [8], they have attracted considerable attention due to their conductivity, high charge carrier mobility, longer wavelength absorption and chemical stability in air and moisture in both neutral and doped states compared to the other conductive polymers [9-12].

A great effort has been focused for last years on development of low-cost solar cells. One alternative is a new generation of photovoltaic cells, based on hybrid polymer-semiconductor

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materials. The maximum energy conversion efficiency achieved from this type of devices is still below 3%. An improvement of the photovoltaic efficiency requires a clear understanding of structure-properties relationships and numerous challenges related to synthesis of the composite materials and fabrication procedure of the device still remain to be overcome. [13]

This paper focuses on semiconductor-conducting polymer hybrid system of PbS/Cu₂S core-shell nanoparticles and poly(3-hexyl)thiophene and its characterization as solar absorbing layer for photovoltaic applications.

2. Materials, devices and methods

Anhydrous Acetonitrile ($\geq 99.99\%$) and Chloroform ($\geq 99.99\%$) were purchased from CTR Scientific, Mexico. Tetrabutylammoniumhexafluorophosphate ($\geq 98\%$), 3-hexylthiophene monomer ($\geq 99\%$), PbCl₂ ($\geq 99.99\%$), CuCl₂ ($\geq 99\%$), 3-mercaptopropionic acid ($\geq 99\%$) and Indium thin oxide (ITO, 15-25 Ω/sq) were purchased from Sigma Aldrich.

The Potentiostat Solartron SI 1278 was used to synthesize the polymer electrochemically. The polymer functional groups were determined with the FT-IR Perkin Elmer. The X-Ray diffractometer model Rigaku Miniflex Desktop Diffractometer was used to analyze the crystallinity of the samples. The optical characteristic of the samples was investigated by the UV-visible spectrometer Perkin Elmer Lambda 12. The Picoammeter/ voltage source Keithley 6487 was used to measure the conductivity of the polymeric films.

PbS/Cu₂S nanoparticles: The PbS/Cu₂S nanoparticles were synthesized as mentioned in reference 6. PbS nanoparticles were prepared with a 1 mL solution of thioacetamide (CH₃CSNH₂, TAA) and of lead(II) chloride (PbCl₂) both 30 mM. Previously, 50 mL of sodium citrate (C₆H₅O₇Na₃·2H₂O) 3.0 mM were prepared and the CH₃CSNH₂ and PbCl₂ were added to the sodium citrate solution. Then the pH was varied from 6 to 9 for the different experiments. The mixtures were placed under reflux conditions for 30 min to obtain the dispersed nanoparticles. The PbS nanoparticles previously prepared were used without any purification and 0.50 g of 3-mercaptopropionic acid (MPA, C₃H₆O₂S) were added to the reaction vessel and the pH was adjusted to 8. The mixture was reacted during 30 min under reflux conditions and it was degassed with N₂ flux. Then, a solution of copper chloride (CuCl₂·2H₂O) was added drop wise to the reaction vessel, with a flow rate of 0.30 mL/min. After the addition of the CuCl₂ solution, the mixture was reacted during 6 hours under reflux conditions. [6]

Poly(3-hexylthiophene) and PbS/Cu₂S-Poly(3-hexylthiophene) by chemical synthesis (referred as PC and PbS/Cu₂S-PC, respectively): A solution of FeCl₃ (4mmol) in 50 mL chloroform was placed in 3-necked flask. After stirring for 1 hour the monomer (1mmol) in 10mL of chloroform was added drop wise. For the synthesis of the composite a solution containing PbS/Cu₂S nanoparticles dispersed in chloroform was added in order to have 10 % w/w nanoparticles in the polymeric film. In both cases, the mixture was left under continuous magnetic stirring for 24 hours at room temperature and nitrogen atmosphere. The inert atmosphere was applied to prevent any side reactions. The black powder product was transferred to the methanol and filtered under vacuum filtration and dried at room temperature for further characterizations [14,15].

Poly(3-hexylthiophene) and PbS/Cu₂S-Poly(3-hexylthiophene) by electrochemical synthesis: Polymer E (referred as PE and PbS/Cu₂S-PE, respectively): Poly (3-hexylthiophene) was synthesized electrochemically in a 3-electrode cell using a Potentiostat. The reference electrode and counter electrode were Ag/AgCl and Pt wire respectively. The indium tin oxide glass (ITO) was used as working electrode. The substrate was cleaned by boiling in isopropyl alcohol and acetone for 30 minutes in each solvent following by sonication in 50:50 isopropyl alcohol: acetone for 15 minutes and finally rinsed several times in de-ionized water [16-17]. The 0.1 M solution of tetrabutylammoniumhexafluorophosphate (TBAPF₆) in acetonitrile was placed in the cell as electrolyte. Then the monomer 3HT (0.05M) was added to the solution. In the synthesis of composite a solution containing PbS/Cu₂S nanoparticles dispersed in chloroform was added in order to have 10 % w/w nanoparticles in the polymeric film. In both cases, the cyclic voltammetry

was applied for 5 cycles by sweeping the voltage between -0.5 V to +1.8 V with the scan rate of 50 mV/s. The electropolymerization carried out at room temperature. The black polymeric film on ITO was washed several times with acetonitrile and then dried at ambient temperature before characterization.

3. Results and discussions

The polymeric films synthesized from two methods, are clearly different as seen by eye. The PC film was brittle and had a rough surface while the PE film had a smooth surface and could be easily peeled off the ITO in one piece. The functional groups in polymer structure were observed with FT-IR spectroscopy. Figure 1 shows the Infrared spectra for the PE and PbS/Cu₂S-PE films. The signals in the PE spectrum at 2931 and 2852, 1736, 1458, 966 and 821 cm⁻¹, correspond to the CH₂ stretched vibration bond, C=C stretching, C-C stretching, C-H out of plane and the C-S bending, respectively. The signals corresponding to same vibrational modes were found for PbS/Cu₂S-PE with slight shifts of wavenumber. The same behavior was observed for PC and PbS/Cu₂S-PC. For both experiments, the results are in a good agreement with previous reports [18,19] indicating that the synthesized polymer from both methods is P3HT. In the case of the composite PE, the spectrum shows the same vibrational modes than the pure PE suggesting that PbS/Cu₂S nanoparticles may not influence the polymerization process by modifying the π conjugation in the chain. Nevertheless, the C-C stretching, the signal shift to smaller wavenumber (1320 cm⁻¹) and it becomes more intense. It was attributed to the presence of a larger number of oligomers that implies that the chain length and the chain substituent positions are affected for the presence of PbS/Cu₂S nanoparticles, suggesting that nanoparticles arrange themselves in the polymer without modifying the chemical nature nor the polymerization mechanism, but the electrical properties of the conductive matrix.

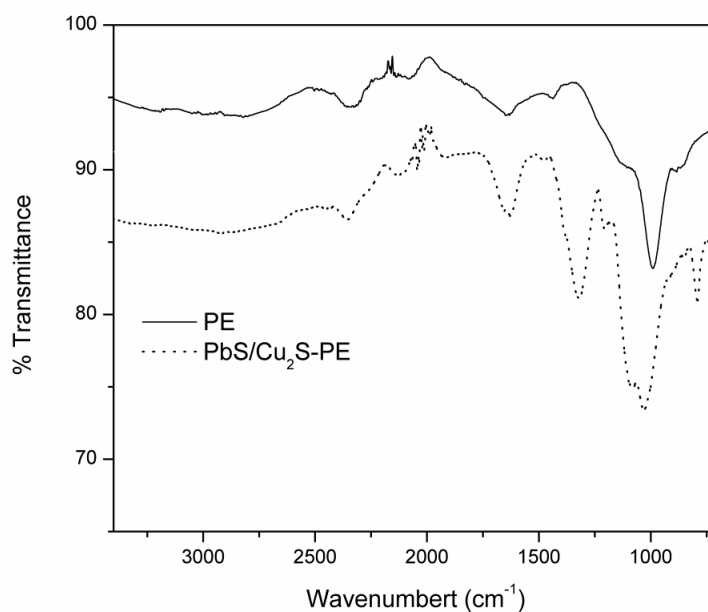


Fig. 1. FT-IR Spectra for the PE and PbS/Cu₂S-PE composite.

Figure 2 shows the UV-Vis spectra for the polymers and composites performed from 300 to 1000 nm at room temperature. The polymers chemically synthesized were dispersed in chloroform and the electrochemically synthesized were measured as film. The dashed line corresponds to the polymer E and the solid line shows the UV-Vis spectra of the polymer C. For polymer E two peaks were observed; one at 589 nm and the other one at 350 nm. The absorption band at 589 nm corresponds to the vibronic structure originated from π -electron orbital overlap between the adjacent thiophene rings. This peak blue shifted to the value of 498 nm for the

polymer C which also corresponds to the $\pi-\pi^*$ transition of the conjugated segments between the adjacent rings causing by moving an electron from a bonding pi orbital to an antibonding π^* orbital [20]. In conjugated polymers, the peak at maximum absorption represents the extent of the conjugated length. Therefore the polymer E with longer wavelength adsorption at 589 nm, has higher conjugated length which means less structural defects and disordering for this polymer. The peaks at 350 and 365 nm correspond to the $n-\pi^*$ transition for the polymer E and polymer C respectively which comes from moving an electron from a nonbonding electron pair to an antibonding π^* orbital [20].

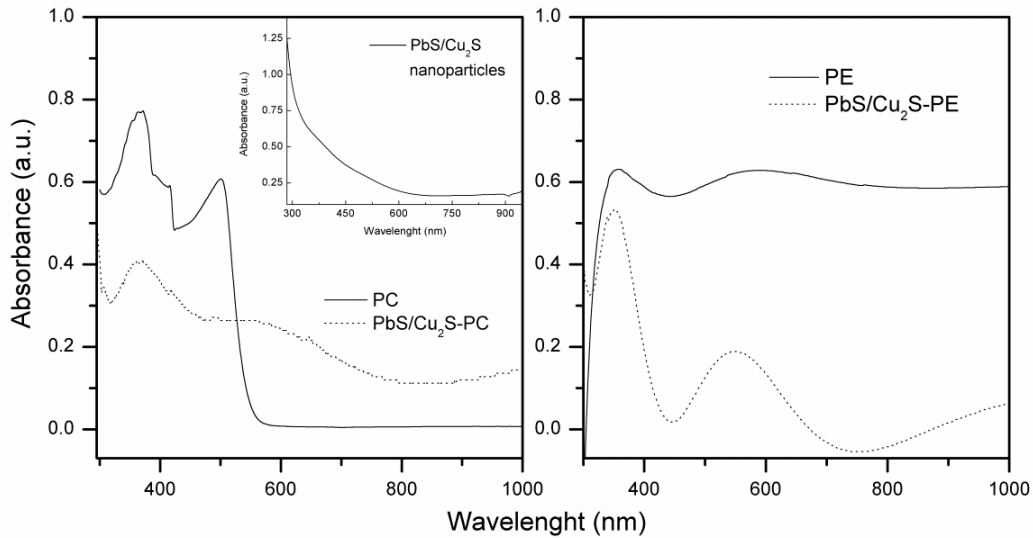


Fig. 2. UV vis analysis of a) PC and PbS/Cu₂S-PC and b) PE and PbS/Cu₂S-PE

For composites, it can be observed the influence of nanoparticles in the optical properties of the material. For the chemically synthesized composite, the spectrum shows absorption after 800 nm, with a mayor signal contribution around 600 nm, the same behavior was observed for the composite electrochemically synthesized but in this case, the absorption signal was better defined. The signal, as discussed before for the pure polymers, corresponds to the vibronic structure originated from π -electron orbital overlap between the adjacent thiophene rings. It is important to observe the inset in figure 2, it shows the nanoparticles absorption spectrum, where the main absorbance of the nanoparticles is located form 600 nm. It is clearly observed the interaction between the nanoparticles and the polymeric matrix, due to the separation of the electron-hole pair due to the interaction of nanoparticles with the visible radiation. This absorption signal in the middle of the visible range, support the efficiency of the composite to be activated and to separate the charge carriers (electron-holes) in a semiconductor behavior.

The conductivity of the polymeric films was calculated from the slope of I-V curve which indicates the resistance according to the Ohm's law and by using the formula below:

$$R = \rho \frac{L}{t.w} = \frac{1}{G} \quad (1)$$

Where R is resistance, ρ is resistivity, L is the length of contact, t is the thickness of the deposited materials, w is the contact width and G is the conductance. Hence:

$$G = \frac{t.w}{\rho.L} \quad (2)$$

$$\rho = \frac{1}{\sigma} \quad \text{So } \sigma = \frac{1}{R} \cdot \frac{L}{t.w} \quad (3)$$

Where σ is the conductivity [21-23]. The resistance was obtained from the slop of I-V curve and was 1778.87Ω for PE and 17930.2Ω for PC. To calculate the conductivity of PE, a $1.8 \text{ mm} \times 2.70 \text{ mm}$ carbon contact was painted on polymeric film with the thickness of 1099 nm . One electrode was placed on the carbon contact and the other one on ITO surface. The voltage from 0 to 5 was applied. At voltage 5V the current reached at $2.8 \times 10^{-3} \text{ A}$. To calculate the conductivity of PC, first the powder of polymer was compacted by hydraulic press machine resulting in polymeric film with the thickness of $560 \mu\text{m}$. Two contacts were painted by carbon paint and the electrodes were placed on contacts then the voltage from 0 to 5 was applied. At voltage 5V the current reached at 2.9×10^{-4} which is almost 10 times lower than the current reached by PE at 5V. The conductivity of the polymeric films was calculated by measuring their thickness and the distance between the contacts and it was 3.44 S/cm and 0.001 S/cm for PE and PC, respectively.

In the case of composites, the conductivity measurement was calculated only for the PbS/Cu₂S-PE film, the experimental conditions were the same than PE with a film with thickness of 1126 nm . The calculated conductivity value was 2.74 S/cm . The conductivity was lower for PbS/Cu₂S-PE than for PE what confirms the observation made from FTIR where the length of the polymer chain was compromised for the addition of the PbS/Cu₂S nanoparticles, which is reflected in a conductivity due to the breaking of the π -conjugation.

Due to the results with previously discussed techniques, the characterization of the luminescent properties was performed only into the PE and PbS/Cu₂S-PE films as well as the determination of the HOMO-LUMO positions. Figure 3 shows the PL spectra for PbS/Cu₂S, PbS/Cu₂S-PE and the PE all performed with excitation wavelength of 350 nm . The PE film presents a broad PL emission around 550 nm and the PL spectra for PbS/Cu₂S and PbS/Cu₂S-PE present signals centered around 700 nm . It is clear the influence of the nanoparticles in the luminescent properties of the composite spectrum, where the signal appears at the same wavelength than the particles by themselves and the PL intensity is enhanced. These suggest that the interaction between the particles and the polymer allows the charge transport along the film, that is important for absorbing applications.

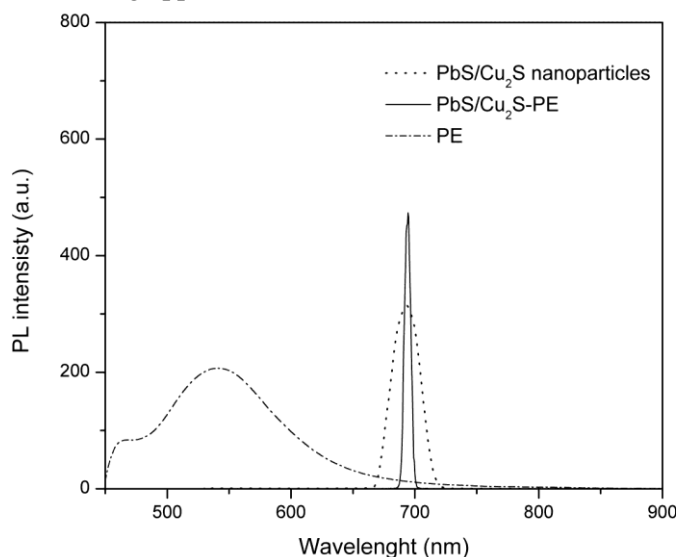


Fig. 3. PL spectra for PE, PbS/Cu₂S and PbS/Cu₂S-PE materials.

Finally, the HOMO and LUMO positions for the materials were calculated. The CV curves for the PE and PbS/Cu₂S-PE for 5th cycles are shown in Figure 4. The voltage increased from -0.1 to reach the anodic peak at $+1.12 \text{ V}$ in which the polymer is in its doped state with PF_6^- . Then the voltage arrived to the final value of $+1.8 \text{ V}$ and the process followed by sweeping back the voltage from this point to the initial point passing from the cathodic peak at $+0.47 \text{ V}$ in which polymer is in its un-doped state. Increasing the current peak after each cycle shows the formation and deposition of the polymeric layer on ITO. The doped/un-doped process was observed by changing the polymer color from black to red brown. P3HT and conjugated polymers in general

exhibit electro-, thermo- and solvato-chromisms during the strong interaction between the electronic structure and the polymer chain conformation [24,25].

In the case of the PbS/Cu₂S-PE film, the voltage increased from -0.1 to reach the anodic peak at +1.07 V and the process followed by sweeping back the voltage to the cathodic peak at +0.52 V in which polymer is in its un-doped state. It also clear than the gap between anodic and cathodic signals is smaller than the one for pure PE, and an increase in the anodic current is observed in the composite voltammogram. The inset figure shows the CV spectrum for PbS/Cu₂S nanoparticles which was used to determine the conduction and valence band positions, where the signals for cathodic and anodic process are in good agreement to the observed for the composite, suggesting the interaction between the polymer and the nanoparticles.

The HOMO and LUMO energy levels for organic materials can be calculated from the value of the oxidation and reduction peaks of voltammogram. According to Bredaset *al* HOMO and the E_g (band-gap) are calculated from the formulas below [55]:

$$E_{\text{HOMO}} = -e [E_{\text{ox}}(\text{onset}) + 4.44] \quad (4)$$

$$E_{\text{g}} = E_{\text{HOMO}} - E_{\text{LUMO}} \quad (5)$$

From the Figure 4 the onset of oxidation peak is equal to 0.6 V and by above formula the HOMO energy level was obtained is -5.04 eV in the case of PE. The onset of oxidation peak is equal to 0.7 V and by above formula the HOMO energy level was obtained is -5.14 eV in the case of PbS/Cu₂S-PE.

The direct optical band-gap of the polymer obtained from extrapolation of the straight line in $(\alpha h\nu)^2$ vs. $h\nu$ plot with the x-axis from calculations made with UV-Vis transmittance vs. wavelength data. The band-gap and the LUMO energy level were reported to be 1.9 eV and 3.14 eV, respectively for the PE polymeric film. In the case of PbS/Cu₂S-PE The band-gap and the LUMO energy level was reported to be 1.77 eV and 3.37 eV, respectively.

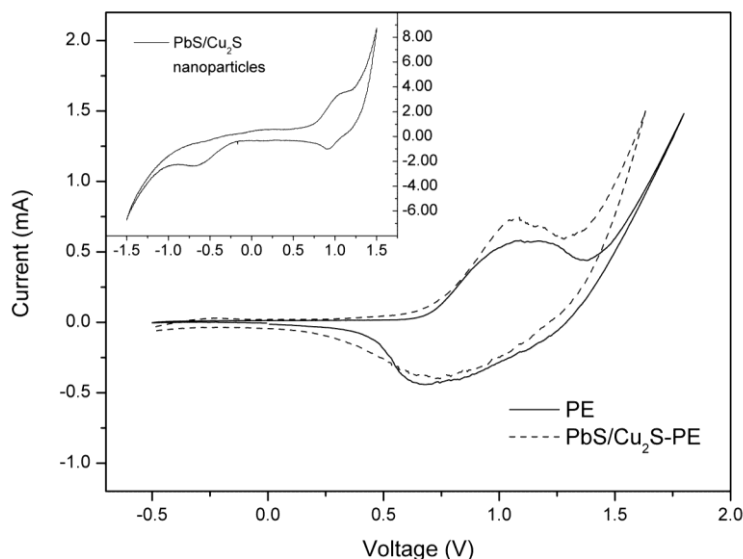


Fig. 4. Cycling Voltammetry for PE and PbS/Cu₂S-PE. Inset figure CV for PbS/Cu₂S nanoparticles

4. Conclusions

The synthesis of poly (3-hexylthiophene) and the PbS/Cu₂S- poly (3-hexylthiophene) composites were carried out by chemical and electrochemical methods. The UV-vis characterizations show the absorption range of bot materials and the E_g values were calculated to be 1.9 and 1.77 eV for PE and PbS/Cu₂S-PE, respectively. The characterization by UV-Vis and PL show the interaction between the nanoparticles and the polymeric matrix as an increase in the

optical properties of the material in the visible range, suggesting that composite polymeric matrix is a good candidate to be use for light absorbing applications. The CV analysis show the influence of the presence of the nanoparticles in the electrochemical behavior of the composite material and the HOMO- LUMO positions where calculated to be -5.04 and -3.14 eV for PE and -5.14 and -3.37 eV for PbS/Cu₂S-PE. Nevertheless, the IR spectra and the conductivity values suggest that the addition of the nanoparticles to the polymeric film reduces the polymeric chain length, that may decrease the conductivity value of the polymeric film.

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