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Synthesis and Characterization of P3HT Metal Nanoparticles Hybrid Junction

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Abstract
Due to the important of potential properties of metal-semiconductor nanostructures, conductive Poly(3-hexylthiophene-2, 5-diyl) P3HT with (Al, Ag and Cu) as metallic nanoparticles (NPs) hybrid was synthesized. Pulsed Laser Ablation (PLA) technique was used to synthesis the metallic nanoparticles in P3HT as a liquid. The morphological and structural properties of pure P3HT and P3HT metallic nanoparticles samples were studied. The Fourier Transformer Infrared (FTIR) for all samples indicate the chemical interaction between the polymer and the nanoparticles. The formation of the nanoparticles was informed by Scanning Electron Microscopic (SEM) analysis and the particle size for nanoparticles was around 50 nm. Energy Dispersive X-ray (EDX) spectra show the existing of metallic nanoparticles. Hall effect showed the n-type conductivity for P3HT-ALNPs and P3HT-CuNPs samples while for P3HT-AgNPs was p-type conductivity which may be due to the differences of work function.

Key words
P3HT, metallic nanoparticles, Ag , Al, Cu.

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تصنيع وتشخيص المفرق الهجين بولي (3 - هيكسيل ثيوفين) والدقائق المعدنية النانوية

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الخلاصة
نتيجة للاهمية البالغة للخصائص المحتمله لمعدن-شبه موصل للتراكيب النانويه، تم في هذا العمل تصنيع مفرق هجين من بولي (3- هيكسيل ثيوفين) والدقائق المعدنية النانوية (Al,Ag,وCu). أستُخدمت تقنية التذرية بالليزر النبضي (PLA) لتخليق الدقائق النانوية في P3HT كسائل. دُرست الخصائص التشكيلية والتركيبة لعينات البوليمر النقي P3HT وعينات البوليمر والدقائق النانوية المعدنية. اشارت الأشعة تحت الحمراء لمحول فورييه (FTIR) لجميع العينات إلى التفاعل الكيميائي بين البوليمر والدقائق النانوية المعدنية. وثقت تشكيل الجسيمتن النانوية عن طريق تحليل المسح الإلكتروني المجهري (SEM) وكان حجم الجسيمات لعينات البوليمر مع الدقائق النانوية المعدنية بحدود 50 نانومتر. تُظهر أطياف الطاقة المشتتة من أشعة الطاقة (EDX) كمية الجسيمات النانوية المعدنية الموجودة. اظهر تاثير هول توصيلية نوع n لعينات البوليمر مع الدقائق النانوية للالمنيوم والنحاس بينما التوصيلية نوع p لعينة البوليمر-الدقائق النانوية للفضة ويرجح السبب الى اختلاف دالة الشغل.

Introduction

The use of organic semiconductor have great interest because of their good facilities, light weight, easy fabrication under ambient condition at low cost. The important of organic semiconductors appear in devices such as transistors, solar cell, sensor, light emitted diode which is serve as active materials. Although, these materials typically exhibit low charge carrier mobility, poor environmental stability and short operational life time comparing with inorganic counterparts. Many fabrication methods can be obtained including spin-coating, blade coating, ink-jet printing, roll to roll processing [1].

Among the organic semiconductors poly(3-hexylthiophene) P3HT is a promising material for industrial application. The structure of P3HT is a conjugated polymer commonly used for hole transport in organic solar cell because of the high mobility of charge carriers in the material ($0.1cm^2/V.S$) [2]. The Noble metal nanoparticles NPs, are extensively studied because of their unique physical and chemical properties, which are different from those of the bulk metal. Their properties are attributed to intra-band quantum excitations of the conduction electrons, mimicking the interactions of light on metal surface via the photoelectric absorption and Compton scattering. This makes nanoparticles a very good candidate for technological applications, for instance in surface enhanced resonance Raman scattering, optical biosensor, and photo-catalysis. The metal NPs can be prepared by different techniques such as liquid chemical method, laser ablation in liquids with pico and femtosecond laser pulses (LAP), and by deposition of the metal on a substrate followed by thermal annealing [3].

This work present the preparation of various metal nanoparticles (Ag, Cu, Al) as a nanocomposite with P3HT using LAP and study its structural and morphological properties.

Experimental work

1-Materials

Conductive polymer Poly(3-hexylthiophene-2, 5-diyl) P3HT, Regio-regular was used with molecular weight (28000) supplied by American dye source, Inc. Canada. Three metals were used (Al, Cu, Ag) of high impurity supplied by educational scientific laboratory equipment. Chloroform ($CHCl_3$) with high purity was used as solvent.

2- Preparation of P3HT/Metallic Nanoparticles Hybrid

The mixture were as prepared by adding 20mg of P3HT to each 1ml of $CHCl_3$ to dissolve the polymer. Then the mixture put on a stirrer with a magnetic bar for 30min with temperature 60°C and leave it to the next day in the darkness for perfect dissolving. Then three mixtures were prepared by the same way for the three used metals (Cu, Ag, Al), by putting these metals inside the mixtures. Later shelled the new three mixtures by laser in PLA method with power 1000 Watt for 500runs, then the mixtures substrate on glass slides by using spin coating method. Several specimens for each metal for morphology and structural properties was prepared.

3- Morphological and Structural Characteristics

FTIR investigations were performed on Perkin–Elmer 1760 in the region 2000–400 cm^{-1} with 32 scans by using KBr pellet mode. The morphology of the hybrid samples were investigated by a scanning electron microscopy (SEM) (FEI, Model: Quanta 200).

Results and discussion

1- Fourier Transform Infrared Radiation (FTIR)

FTIR spectroscopy get analyze for multi-component systems and obtained necessary information respect to the material's phase composition and interactions existing between various compounds and polymers. Fig.1 shows the molecular nature of pure P3HT and with metallic nanoparticles which is confirmed by FTIR analysis. In

Fig.1(a), all the characteristic peaks of P3HT were found in FTIR spectrum. Peaks at 2925.18 cm^{-1} and 3444.63 cm^{-1} are due to C–H vibration in the aliphatic chain of hexyl groups. The peak intensity of this peak is high due to high proportion of carbon–hydrogen bonds in the polymer. The symmetric stretching vibration C=C is shown in peak at 1672.81 cm^{-1} it's the characteristic of thiophene ring. Peak at 1107.06 cm^{-1} show the presence of C-H aromatic ring. The stretching vibration of the thiophene ring were detected at 860.16 cm^{-1} these results are agree with [4-6].

In Fig. 2(b) the effect of adding CuNPs on P3HT is illustrated, as it can be seen there is a red shift, peak is observed at 3429.72 cm^{-1} because of copper hydroxide presence. The bands the FTIR of P3HT-AlNPs is illustrate in Fig.1(c), the peaks around 3450.41 cm^{-1} to 2364.57 cm^{-1} is related to the C-H stretching, peaks at 1774.39 cm^{-1} [8]. Finally Fig. 1(d) for P3HT-AgNPs, the absorption peaks 3444, 2923 and 1641 cm^{-1} belong to the vibration N–H, C–H and C=C stretching of covalent bonds, respectively. The wave numbers of 1221 and 773.41 cm^{-1} correspond to the C–C in the ring, C–N stretching in ring vibrations of covalent bonds, respectively, this result deal with Gharibshahi [9].

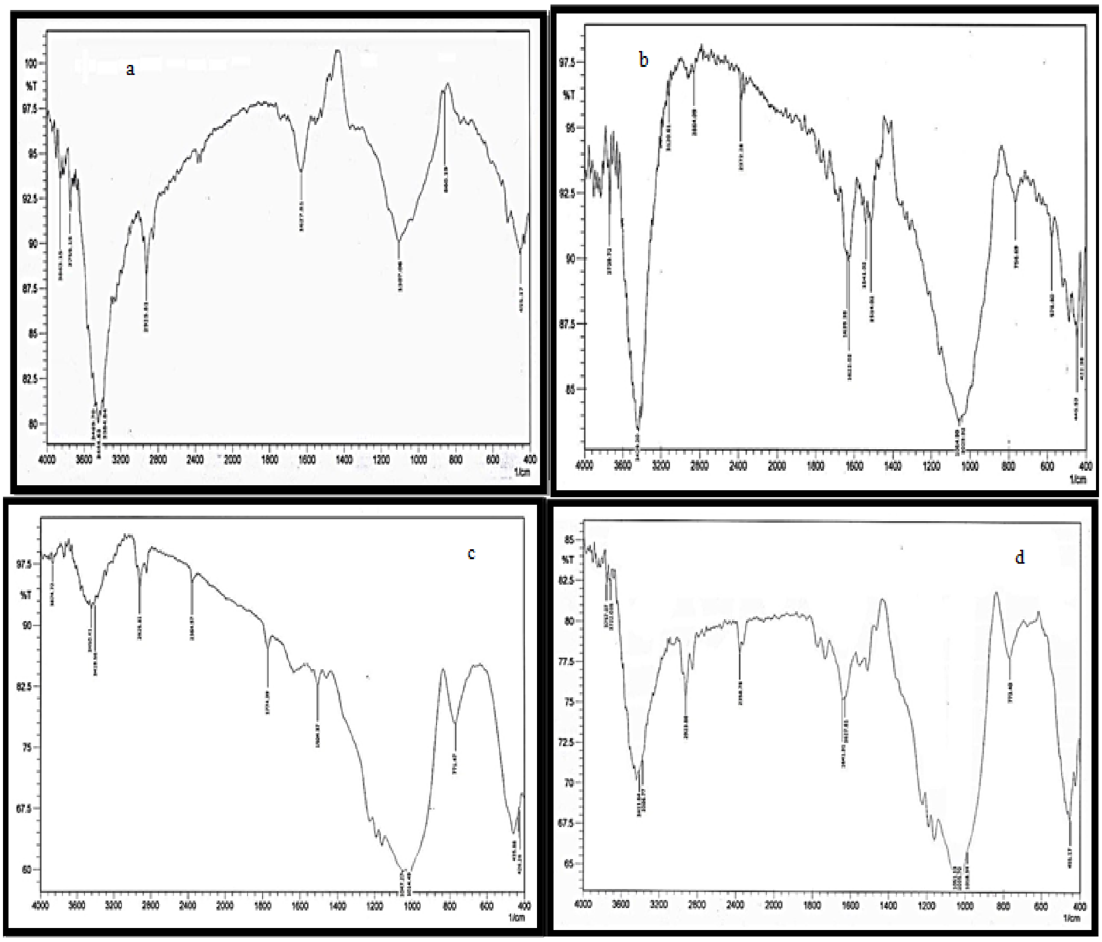

Fig.1 :FTIR for a)P3HT b)P3HT+Cu nanoparticles c) P3HT+Al nanoparticles and d) P3HT+Ag nanoparticles.

2- Scanning Electron Microscopy (SEM)

The morphology properties of the pure P3HT and P3HT-metallic nanoparticles samples were investigated by scanning electron microscopy (SEM). The surface morphology of a P3HT is shown in Fig. 2. As seen in Fig.2(a), show the structure of P3HT which is distributed almost homogeneously on semiconductor surface.

In Fig. 2(b, c, d) the nucleation of NPs already formed. During the PLD and because of the heat electron will release from medium materials and formed more NP atoms. The NP tend to agglomerate in order to form larger NP. Because the NPs surrounding be conduction electrons, the repulsion force will prevent the nanoparticles from further agglomerations. And that make the particles size limited between 20-30 nm. This explanation is true for all metallic nanoparticles.

For P3HT-AlNp, It was also observed that NPs were flakes as seen in Fig.2(c). The SEM images clearly showed that the particles were bound with an amorphous surface of organic residue obtained from the decomposition of the polymer, this explanation is agreed with [8].

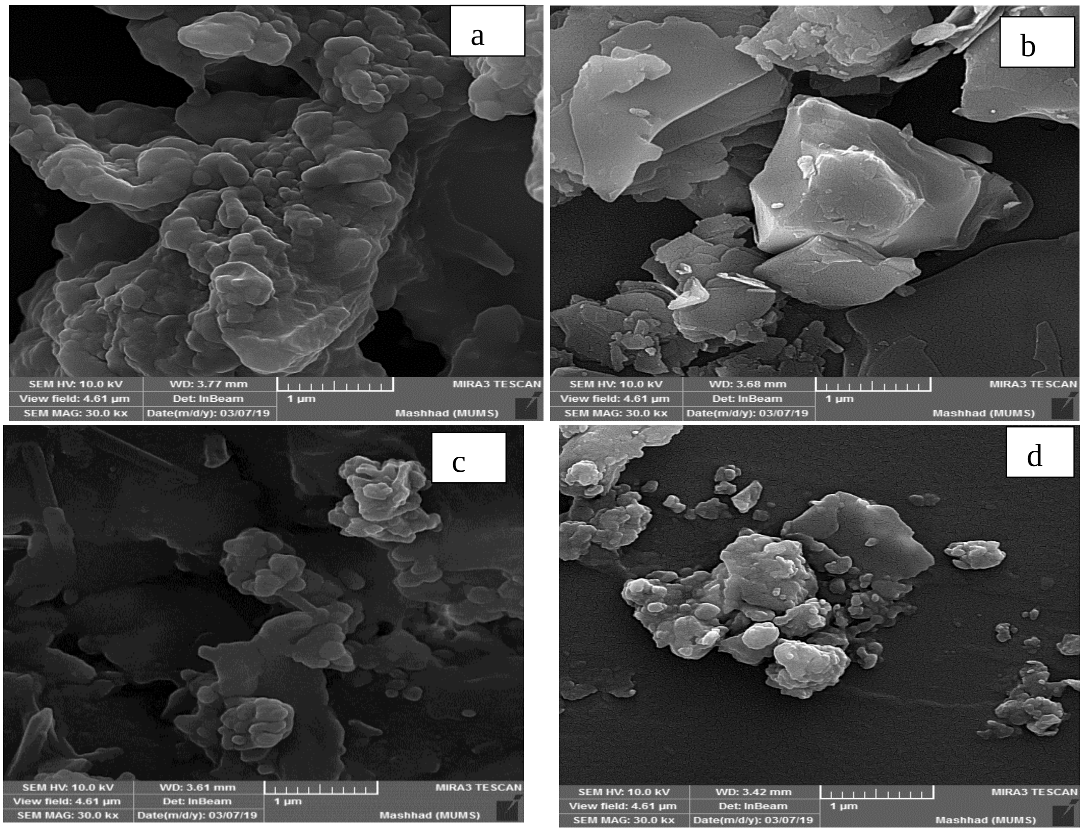

Fig. 2: Image of specimens with magnification (1 µm) for (a): P3HT, (b) Ag, (c) Al and (d) Cu.

3- Energy Dispersion Spectroscopy (EDX)

The energy dispersive X-ray (EDX) was used to investigate the elemental composition of P3HT and the nanoparticles which is formed by pulsed laser ablation. EDX for AgNPs is showed in Fig.3. From the spectrum, the respective peak of the all NPs element are presented. The EDX analysis indicate the formed of the NPs through P3HT. Fig.3 shows there is no impurities. Table 1 illustrate the EDX values for all samples.

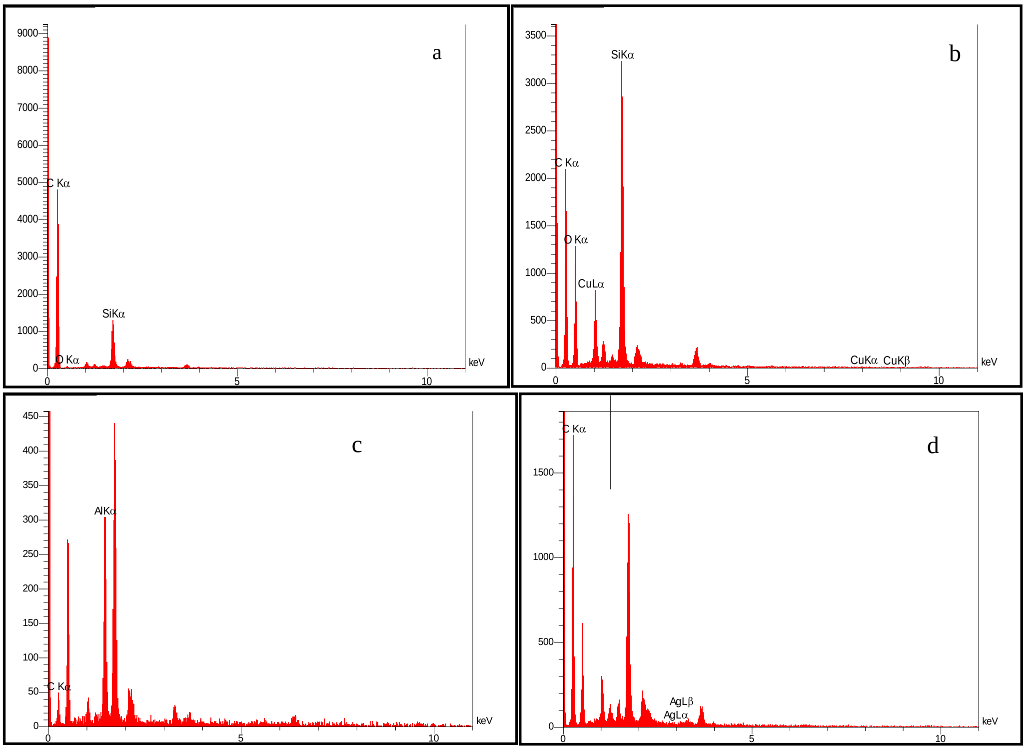

Fig.3: P3HT b)P3HT+Cu nanoparticles c) P3HT+Al nanoparticles and d) P3HT+Ag nanoparticles.

Table 1: EDX values for all samples.

Sample	Elements	Weight %	Atomic%
P3HT	C	99.99	99.99
	O	0.01	0.01
Ag	C	99.40	99.93
	Ag	0.06	0.07
Cu	C	99.56	99.92
	Cu	0.44	0.08
Al	C	96.65	98.48
	Al	3.35	1.52

4- Hall effect

Table 2 demonstrates the major parameters rated from the measurements of Hall effect for pure P3HT and NPs metallic nanoparticles hybrid. It is clear from this table that the Hall coefficients for AlNPS and CuNPs prepared films are negative, which means that the electrons are the majority charge carriers in the conduction process and the type of conduction is n-type except for Ag NP which can be attributed to the difference in the work function.

Table 2: Hall Effect measurements for pure P3HT and metallic nanoparticles

Sample	RH (m^2/c)	σ (Ω.cm)	ρ $(\Omega.cm)^{-1}$	n_o $(cm)^{-3}$	μ (cm^2/V.s)	Type	ϕ eV
P3HT	7.569×10^{7}	3.769×10^{-5}	2.634×10^{4}	8.247×10^{10}	2.873×10^{3}	P-type	3.6
P3HT+ Cu	-2.134×10^{8}	4.270×10^{8}	2.342×10^{4}	-2.925×10^{10}	9.112×10^{3}	n-type	5.10
P3HT+ Ag	5.548×10^{6}	5.482×10^{-4}	1.824×10^{3}	1.125×10^{12}	3.042×10^{3}	p-type	4.26
P3HT+ Al	-3.895×10^{7}	1.561×10^{-5}	6.408×10^{4}	-1.603×10^{11}	6.078×10^{2}	n-type	4.20

Conclusions

In this paper conductive Poly(3-hexylthiophene-2, 5-diyl) P3HT with (Al, Ag and Cu) as metallic nanoparticles (NPs) hybrid was synthesized by using PLA. FTIR shows the chemical interaction between the polymer and the metallic nanoparticles. While the formation of the metallic nanoparticles was inform by SEM analysis and the particle size for nanoparticles was around 50 nm. The EDX spectra show the existing of metallic nanoparticles. Hall effect showed the n-type conductivity for P3HT-ALNPs and P3HT-CuNPs samples except for P3HT-AgNPs which was p-type conductivity.

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