

# Electrochemical synthesis and photoelectrochemical characterization of organic-inorganic compounds

Leila Lamiri <sup>(1)</sup>, Belkacem Nessark<sup>(1)</sup>, Farid Habelhames<sup>(1)</sup>, Hanen Khantite<sup>(1)</sup>, Kouider Feria <sup>(2)</sup>

**Abstract** An electrochemical deposition procedure by cyclic voltammetry, in an electrolyte solution was adopted for the preparation of thin films of polypyrrole–gallium arsenide composites materials. The properties of the composite layers were studied by: cyclic voltammetry, electrochemical impedance spectroscopy and photoelectrochemical measurements. The p and n type semiconductor behaviour of the polypyrrole (PPy) and gallium arsenide (GaAs) were studied by photocurrent measurements. It was found that the composite material (PPy–GaAs) have a (p-n) heterojunction behaviour.

**Key-Word** organic-inorganic compounds, semiconductors, electrochemical properties, p–n heterojunction.

## INTRODUCTION

A hybrid solar cell consists of a combination of both organic and inorganic semiconductor materials. It combines the unique properties of inorganic semiconductors with the film-forming properties of the organic conjugated polymers [1] Organic materials usually are inexpensive, easily processable, and their functionality can be tailored by molecular design and chemical or electrochemical synthesis. On the other hand, inorganic semiconductors can also be manufactured as processable nanoparticulate colloids. By varying the size of the nanoparticles, their band gap can be tuned and their absorption/emission spectra can be modified [2].

An effective strategy for hybrid solar cell fabrication is to use blends of nanocrystals with organic conjugated polymers as bulk heterojunction [1-6].

Leila Lamiri, Laboratoire d'électrochimie et matériaux, Département de Génie des procédés Faculté des Sciences de l'ingénieur Université Ferhat Abbas, 19000 Sétif Algérie.

Belkacem Nessark, Laboratoire d'électrochimie et matériaux, Département de Génie des procédés Faculté des Sciences de l'ingénieur Université Ferhat Abbas, 19000 Sétif Algérie.

Farid Habelhames, Laboratoire d'électrochimie et matériaux, Département de Génie des procédés Faculté des Sciences de l'ingénieur Université Ferhat Abbas, 19000 Sétif Algérie.

Hanen Khantite, Laboratoire d'électrochimie et matériaux, Département de Génie des procédés Faculté des Sciences de l'ingénieur Université Ferhat Abbas, 19000 Sétif Algérie.

Kouider Feria, Département d'optique et mécanique de précision Faculté des Sciences de l'ingénieur Université Ferhat Abbas, 19000 Sétif Algérie.

Excitons created upon photoexcitation are separated very efficiently into free charge carriers at interfaces between organic semiconductors and inorganic semiconductor nanoparticles in a hybrid composite thin film. Hybrid solar cells concept has been demonstrated for conjugated polymer blends containing CdSe [3, 6, 7], CuInS<sub>2</sub> [1, 4], CdS [5] or PbS [8,9] nanocrystals.

The usage of these inorganic semiconductor nanoparticles embedded into organic conjugated polymer blends is interesting for two reasons at least: first the inorganic semiconductor nanoparticles can have high absorption coefficients and higher photoconductivity compared to many organic semiconductor materials, second the n- or p-type character of the nanocrystals can be varied by synthetic routes [4].

Polypyrrole (PPy) is an especially promising conducting polymer for different applications, due to its good conductivity, environmental stability and ease synthesis. Its use as new material has opened up entirely new field for polymeric materials. Therefore, several approaches to prepare composite materials consisting of nanoparticles and polypyrrole have been reported [10–12]. The principal advantage of the electrochemical polymerization method is related to the better conducting properties and long-term stability [13, 14].

In the present study, PPy–GaAs composite is electrochemically prepared using cyclic voltammetry on platinum electrode. The microstructures PPy–GaAs composite was analyzed by Scanning Electron Microscopy (SEM) coupled with EDX analyzer. The characterizations of samples were carried out by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and photoelectrochemical analyses were done by photocurrent measurements.

## EXPERIMENTAL

Pyrrole (Aldrich product) was used after distillation under reduced pressure. The electrolyte used was the lithium perchlorate (LiClO<sub>4</sub>, Fluka product) dissolved in the acetonitrile (CH<sub>3</sub>CN, Aldrich). The gallium arsenide (GaAs) particles having 20-40 nm of diameter (Sigma-Aldrich product) were used as inorganic semiconductor.

The cyclic voltammetry study and the electrochemical syntheses were carried out in a one-compartment cell containing the solution of electrolysis, using three electrodes. The working electrode was a platinum disc ( $\varnothing = 2$  mm), the reference electrode was a saturated calomel electrode (SCE) and the auxiliary electrode was a platinum plate. The system solvent/supporting electrolyte used CH<sub>3</sub>CN/LiClO<sub>4</sub> 10<sup>-1</sup> mol.l<sup>-1</sup>.

The electropolymerization of Py was carried out from the solution containing Pyrrole ( $10^{-2}$  mol.l $^{-1}$ ) and LiClO $_4$  ( $10^{-1}$  mol.l $^{-1}$ ) in CH $_3$ CN with gallium arsenide powder (GaAs) at concentration of  $5 \cdot 10^{-2}$  mol.l $^{-1}$  and dispersed by a weak agitation. Prior to polymerization, the solution was deoxygenated by passing nitrogen gas. The study was related to films of polypyrrole doped or not by GaAs particles. In this case, the working electrode was the platinum disc ( $\varnothing = 2$  mm) modified by this film, obtained electrochemically by cycling on a potential domain ranging between  $-0.3$  and  $1.3$  V/SCE, at  $v = 100$  mV/s. The analysis of film was carried out in a system solvent/supporting electrolyte, in absence of the monomer.

The SEM micrographs of PPy and composite material (PPy-GaAs) deposited on platinum (used as a working electrode), were taken out by using a Sirion-200, FEI, USA scanning electron microscope. The elemental compositions of the composite film surface were determined by using an energy dispersive X-ray detector coupled to this microscope (EDX; Serion-200 132-10).

The photoelectrochemical analysis was recorded with a 500 W halogen lamp as polychromatic light source, and the illumination intensity is  $100$  mW.cm $^{-2}$ . The composite layers for photocurrent measurements were prepared on platinum electrodes with an illuminated area of  $1$  cm $^2$  in the electrolyte solution. All the electrochemical and photoelectrochemical measurements were carried out using a standard potentiostat PGZ-301 Voltalab, coupled with a microcomputer equipped with a software voltmaster 4 program.

### III. RESULTS AND DISCUSSION

#### A. Electrochemical synthesis of film

Fig. 1 shows a successive cyclic voltammograms corresponding to CH $_3$ CN/(LiClO $_4$   $10^{-1}$  mol.l $^{-1}$ ) solution containing the pyrrole (Py)  $10^{-2}$  mol.l $^{-1}$  and gallium arsenide powder (GaAs)  $5 \cdot 10^{-2}$  mol.l $^{-1}$  (dispersed by a weak agitation) and recorded in the potential range:  $-0.3$  and  $1.3$  V/ECS, with a scan rate of  $100$  mV/s. During the positive potential scan, the voltammograms show an anodic wave which is observed at the potential  $0.5$  V/ECS and during negative potential scan a cathodic wave at  $-0.1$  V/ECS corresponding to the oxidation and the reduction of the polypyrrole respectively. During the successive recording of the cyclic voltammograms, the anodic peak potential move weakly to the more positive values and the cathodic peak potential to the more negative value. The displacement of the potential peaks is accompanied by an increase in the current intensity of the oxidation and reduction peaks. Also, the difference between anodic and cathodic peak  $\Delta E_p$  ( $\Delta E_p = E_{Pa} - E_{Pc}$ ) increase during cycling. This corresponds in the same time to the accumulation of the deposit of polypyrrole on the electrode surface.

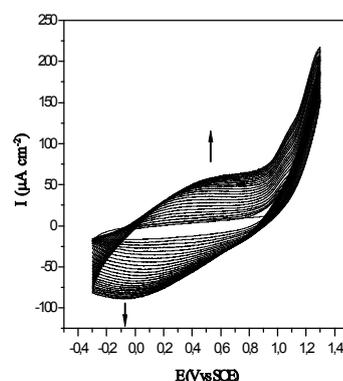


Fig. 1. Cyclic voltammogram corresponding to the Polymerisation of Py in presence of GaAs on Pt electrode, between  $-0.3$  and  $1.3$  V, with scan rate of  $100$  mV/s

#### B. MORPHOLOGY OF FILMS AND EDX ANALYSIS

Fig. 2 shows SEM micrographs of the PPy and PPy-GaAs composite films electrochemically prepared. In Fig. 2a, the typically granular raspberry morphology of pure PPy is presented [15,16]. Scanning electron microscopy analyses showed gallium arsenide distribution at the PPy surface (Fig. 2b). The white dots represent the gallium arsenide pigment. This pigment may be found in agglomerated form and is distributed in a homogeneous way compared to the distribution of other inorganic materials in PPy matrix [16-18]. However, the surface morphology change of PPy-GaAs is ascribable to the existence of GaAs nanoparticles in the electropolymerization process.

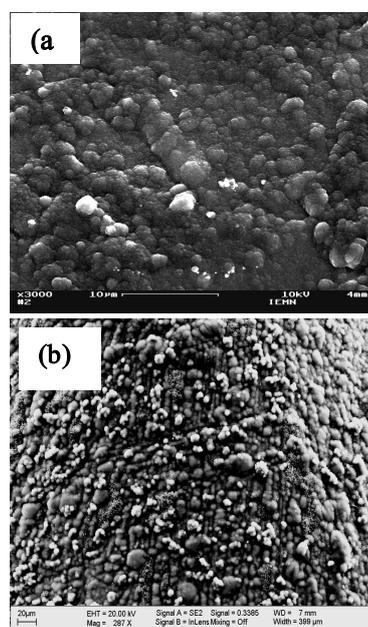


Fig. 2. SEM micrographs of PPy (a) and PPy-GaAs (b) film electrochemically prepared.

The incorporation of gallium arsenide in the polymer is confirmed by the EDX (energy dispersive X-ray spectroscopy) analysis, which shows the presence of the intense rays of gallium (Ga) located at 1.1 keV and of Arsenide (As) at 1.3 keV (Fig. 3). Also, the EDX spectrum of the electrochemically prepared composite material film shows a signal of carbon (C) at 0.25 keV and nitrogen (N) at 0.4 keV characteristic of the PPy polymer. The signals of Cl at 2.62 and 2.82 keV and oxygen (O) at 0.53 keV indicates that the PPy film is doped by the perchlorate ( $\text{ClO}_4^-$ ) ions [16]. This anion results from the  $\text{LiClO}_4$ , which was used as supporting electrolyte. Thus, the GaAs particles can be incorporate in the polymer during the electropolymerization of the pyrrole, which led to the pigmentation of the polymer film, and the obtaining of the composite material PPy-GaAs on the electrode.

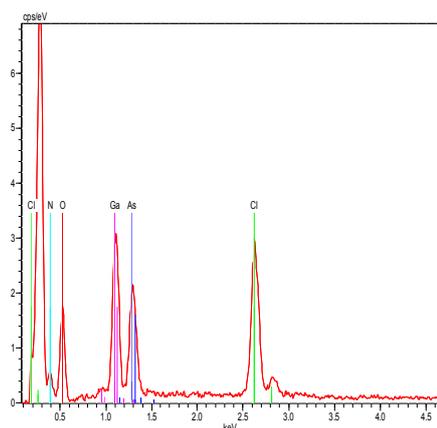


Fig. 3. EDX spectrum of PPy-GaAs, deposited on platinum electrode.

### C. CYCLIC VOLTAMMETRY

Fig. 4 shows cyclic voltammogram (CV) corresponding to the electrochemical analysis composite material in electrolyte solution, carried out in the potential range between -0.3 and 1.3 V, with scan rate of 50 mV/s. The cyclic voltammogram show the anodic and cathodic peaks at 0.6 and 0.1 V vs ECS respectively, corresponding to oxidation and reduction of the polypyrrole film [16]. It was found that the composite material has stable electrochemical properties because the GaAs semiconductor showed no electrochemical activity.

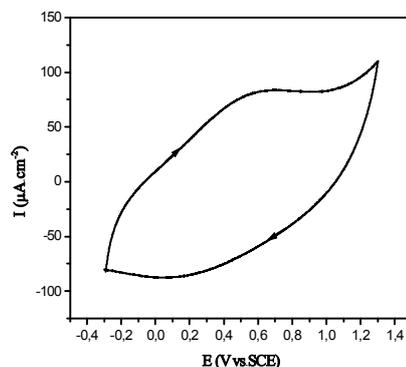
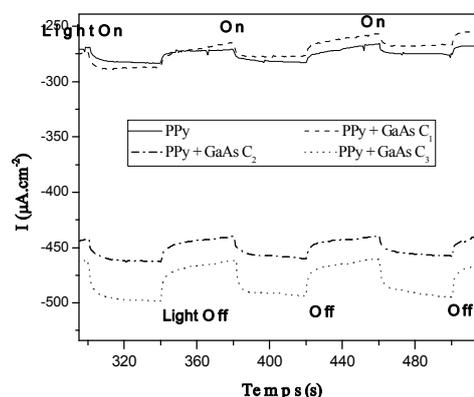


Fig. 4. CV corresponding to PPy-GaAs film in  $\text{CH}_3\text{CN}/\text{LiClO}_4$  ( $10^{-1}$  mol.l<sup>-1</sup>) solution, between -0.3 and 1.3 Vvs.SCE, scan rate  $v = 50$  mV/s

### D. PHOTO-ELECTROCHEMISTRY

The preparation of PPy and PPy + GaAs films, the electrode was further rinsed with acetonitrile and transferred into photoelectrochemical cell. Typical photocurrent-time curves for experiments run in  $\text{CH}_3\text{CN}$  and  $\text{LiClO}_4$  without the monomer are given in Fig. 5 upon switching the light On and Off it can be seen from the figure that the polymer and all composite materials featured a pronounced cathodic photocurrent, which is typical for polypyrrole polymers [19,20] The presence of the space-charge region suggests that these polymers may produce photocurrents when illuminated with light.



Furthermore, it has been shown that polymers modified with GaAs semiconductor particles could feature higher photocurrent as compared to the pure polymer, and the p-n heterojunction was observed (Fig. 6), or inorganic semiconductor (GaAs) presents an response in the positive field potential (n-type) and the organic polymer conductor (PPy) presents an response in the negative field potential (p-type). Who give information on the possibility of photovoltaic cells' application.

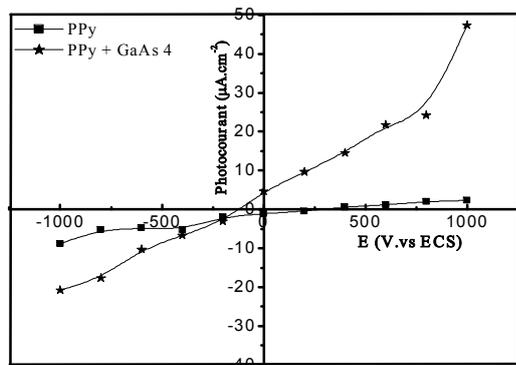


Fig. 6. Photocurrent-potential dependence of PPy and PPy-GaAs composite material measured at light intensity of  $100 \text{ mW.cm}^{-2}$ .

#### IV. CONCLUSION

Composite material PPy-GaAs have been successfully prepared by cyclic voltammetry method. The films were synthesized on platinum electrode. The effect of gallium arsenide content was analyzed by cyclic voltammetry and impedance spectroscopy. We observed that the incorporation of an amount of GaAs particles modified the morphology properties of the PPy film.

Polymer photocurrent increased with inorganic semiconductor GaAs concentration and the p-n heterojunction behaviour was observed. This indicated the importance of composite films and their possible application for photovoltaic cells.

#### REFERENCES

[1] Arici E, Sariciftci N S, Meissner D, Hybrid Solar Cells Based on Nanoparticles of  $\text{CuInS}_2$  in Organic Matrices, *Adv. Funct. Mater.* 2003;13:165-171.  
 [2] Weller H A, Colloidal semiconductor Q-particles: Chemistry in the transition region between solid state and molecules, *Chem., Int. Ed. Engl.* 1993; 32: 41-53.

[3] Huynh W, Dittmer J, Alivisatos A P, Hybrid Nanorod-Polymer Solar Cells, *Science* 2002; 295 :2425-2427.  
 [4] Arici E, Meissner D, Schäffler F, Sariciftci N S, Core/shell nanomaterials in photovoltaics, *Int. J. Photoenergy* 2003; 5:199-208.  
 [5] Greenham N C, Peng X, Alivisatos A P, Charge separation and transport in conjugated-polymer/semiconductor-nanocrystal composites studied by photoluminescence quenching and photoconductivity, *Phys. Rev. B* 1996; 54:17628-17637.  
 [6] Huynh W, Peng X, Alivisatos A P, CdSe nanocrystal rods/poly(3-hexylthiophene) composite photovoltaic devices, *Adv. Mater.* 1999; 11: 923-923.  
 [7] Alivisatos A P, Semiconductor Clusters, Nanocrystals and Quantum Dots, *Science* 1996; 271: 933-937.  
 [8] McDonald S A, Konstantatos G, Zhang S, Cyr P W, Klem E J D, Levina L, Sargent E H, Solution-processed PbS quantum dot infrared photodetectors and photovoltaics, *Nat. Mater.* 2005 ; 4 :138.  
 [9] Günes S, Fritz K, Neugebauer H, Sariciftci N S, Kumar S, Scholes G, Hybrid solar cells using PbS nanoparticles, *Sol. Energy Mater. Sol. Cells* 2007 ; 91: 420-423.  
 [10] Miyauchi S, Abiko H, Sorimashi Y, Tsubata I, Preparation of barium titanate-polypyrrole compositions and their electrical properties, *J. Appl. Polym. Sci.* 1989; 37: 289-293.  
 [11] Yoneyama H, Kishimoto A, Kuwabata S, Charge-discharge properties of polypyrrole films containing manganese dioxide particles, *J. Chem. Soc. Chem. Commun.* 1991; 15: 986-987.  
 [12] Bhattacharya A, Ganguly K M, De A, Sarkar S, A New conducting nanocomposite PPy-zirconium (IV) Oxide, *Mater. Res. Bull.* 1996; 31: 527-530.  
 [13] Avlyanov J K, Kuhn H H, Josefowicz J Y, MacDiarmid A G, In-situ Deposited Thin Films of Polypyrrole: Conformational Changes Induced by Variation of dopant and Substrate Surface, *Synth. Met.* 1997; 84: 153-154.  
 [14] Balci N, Bayramli E, Toppare L, Conducting polymer composites: Polypyrrole and poly (vinyl chloride-vinyl acetate) copolymer, *J. Appl. Polym. Sci.* 1997; 64: 667-671.  
 [15] Skotheim T A, *Handbook of Conducting Polymers*, Marcel Dekker, New York, 1986.  
 [16] Habelhames F, Nessark B, Bouhafis D, Cheriet A, Derbal H, Synthesis and characterisation of polypyrrole-indium phosphide composite film, *Ionics* 2010;16:177-184  
 [17] Lenz D M, Delamar M, Ferreira C A, Improvement of the anticorrosion properties of polypyrrole by zinc phosphate pigment incorporation, *Prog. Org. Coat* 2007;58:64-69  
 [18] Chen W, Li C M, Chen P, Sun C Q, Electrosynthesis and characterization of polypyrrole/Au nanocomposite, *Electrochem. Acta* 2007;52: 2845-2849  
 [19] Kim H, Chang W, Preparation and photoelectrochemical behaviour of polypyrrole with platinum nanoparticles, *Synth. Met.* 1999; 101: 150-151.  
 [20] Miquelino F L C, De Paoli M-A, Geniès E M, Photoelectrochemical response in conducting polymer films, *Synth. Met.* 1994; 68: 91-96.