Journal of Electroanalytical Chemistry 650 (2011) 176–181

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

journal homepage: www.elsevier.com/locate/jelechem

Preparation and electrochemical behaviour of PPy–CdS composite films

Ahmed Madani [a,*], Belkacem Nessark [a], Rabah Boukherroub [b], Mohamed M. Chehimi [c,*]

[a] *Laboratoire d'Electrochimie et Matériaux, Département de Génie des Procédés, Faculté des Sciences de l'Ingénieur, Université Ferhat Abbas de Sétif, 19000 Sétif, Algeria*
[b] *Biointerfaces Group, Interdisciplinary Research Institute (IRI), FRE 2963 IRI, IEMN Avenue Poincaré, BP 60069 59652 Villeneuve d'Ascq, France*
[c] *Laboratoire Interfaces, Traitements, Organisation et Dynamique des Systèmes, Université Paris Diderot, CNRS (UMR 7086) Bâtiment Lavoisier, 15 rue Jean de Baïf, 75205 Paris Cedex 13, France*

ARTICLE INFO

Article history:
Received 25 February 2010
Received in revised form 6 October 2010
Accepted 7 October 2010
Available online 23 October 2010

Keywords:
Polypyrrole
CdS
Composites
Electroactivity
Photoelectrochemistry

ABSTRACT

PPy/CdS composite films made from polypyrrole (PPy) with embedded semiconductor (CdS) quantum dots were obtained by electropolymerization of pyrrole in the presence the CdS nanoparticles dispersed in the electrolytic aqueous solution. For the characterization of the modified surface electrode by PPy–CdS, the scan electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and UV–visible were used. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) have been used to investigate the electrochemical behaviour of the resulting materials. The illumination effects are also observed in the reduced form of the polymer. This study showed that the presence of CdS nanoparticles in the polypyrrole film improves the optical properties of PPy via a simple preparation method and show that these films have potential in the photoelectrochemical applications such as photovoltaic cells.

1. Introduction

The optoelectronic properties of organic–inorganic composites depend not only the semiconductor material but also on the host polymer. Conducting polymers such as polypyrrole, polyaniline, and so forth are good candidates for serving as the host matrix for inorganic semiconductors in optoelectronic applications due to their relatively high conductivity and excellent chemical and electrochemical stability. Furthermore, their hole-conducting ability, when combined with the electron-conducting inorganic semiconductors, can increase the radiative electron–hole recombination rate so as to improve the optoelectronic performance of the inorganic semiconductor [1,2].

Beneficial mechanical, optical, electrical, electrooptical, electrochemical, and chemical properties render conducting polymer-semiconductor heterojunctions to be useful in a number of applications, including solar energy conversion [3,4]. On the one hand, surface coating by polypyrrole (PPy) has been shown to stabilize cadmium sulfide particles against photodegradation [5,6]. On the other hand, inorganic and organic molecules such as dyes, drugs, or semiconductors particles have been incorporated into PPy matrix and related conducting polymers [7–15] and have been used as sensors and electronic and controllable release devices.

The incorporation of semiconducting nanoparticles in polymeric matrices has also been reported in the literature with various applications in mind [16–20]. The conducting polymer coating, on narrow-band semiconductor photoelectrodes was proposed as a means to avoid photocorrosion in the early work on photoelectrochemical cells [21,22]. Early studies related to organic–inorganic junction generally involved polypyrrole (PPy) and bulk cadmium sulfide (CdS) [23–25], poly(*p*-phenylene vinylene) (PPV) and CdS films [26] and polyaniline (PAn) and silicon (Si) [27].

The polymer–semiconductor composites are usually prepared in the form of bilayers of conducting polymer/semiconductor [28]. The substrates may be covered with the conducting polymer by electropolymerization or spin-casting a solution of the polymer soluble in chloroform. Semiconductor can be synthesized as a film by chemical bath deposition [29], self-assembling [30] or deposited in the form of dispersion of nanoparticles in soluble conducting polymer. However, in the case of the insoluble polymers, the dispersion of the nanoparticles is carried out by stirring during electropolymerization. We note that the previous similar studies [31–33] have shown that TiO_2 incorporation into PPy films during electrochemical synthesis under magnetic stirring in order to improve the composite performance to anticorrosion [34].

In the present work, stable films of polypyrrole/cadmium sulfide (CdS) were prepared on glassy carbon disc or on indium tin oxide (ITO) by a simple electropolymerization of pyrrole in presence of CdS nanoparticles. The objective of the new modified electrode was to optimize the conditions to obtain the composite material of enhanced photoactivity in comparison with that of

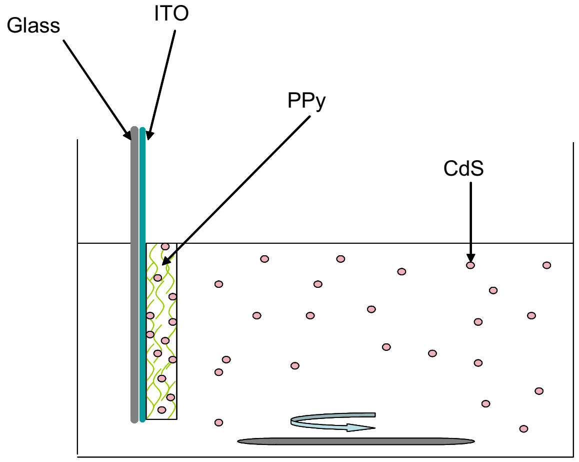
---

* Corresponding authors.

E-mail addresses: madanidz2002@yahoo.fr (A. Madani), chehimi@univ-paris-diderot.fr (M.M. Chehimi).

1572-6657/$ - see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jelechem.2010.10.017

pure conductive polymer. SEM and XPS were used to characterize the morphology and the surface chemical compositions of the films, respectively.



Scheme 1. Schematic illustration of preparation of the modified electrode (ITO/PPy–CdS).

2. Experimental

2.1. Materials

Pyrrole (Aldrich, 99.9%) was purified using an activated Al_20_3 (Aldrich, 150 mesh) column. Other chemicals including lithium perchlorate ($LiClO_4$), ethylene glycol (Acros), thiourea (Aldrich), cadmium acetate (Fluka) were used without further purification. Prior to use, the working and auxiliary electrodes were ultrasonically cleaned in acetone. All aqueous solutions were prepared with deionised water.

2.2. Electrodes and apparatus

A three electrodes one-compartment electrochemical cell system was used in all experiments. A glassy carbon disc (GC) (4 mm diameter) was used as working electrode, a platinum grid as a counter electrode and saturated calomel electrode (SCE) in cannula as reference electrode. Indium tin oxide (ITO) coated glass and platinum plates were used as working electrodes in the case of the UV–vis and photoelectrochemical analysis respectively. Photoelectrochemical measurements, cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) techniques were

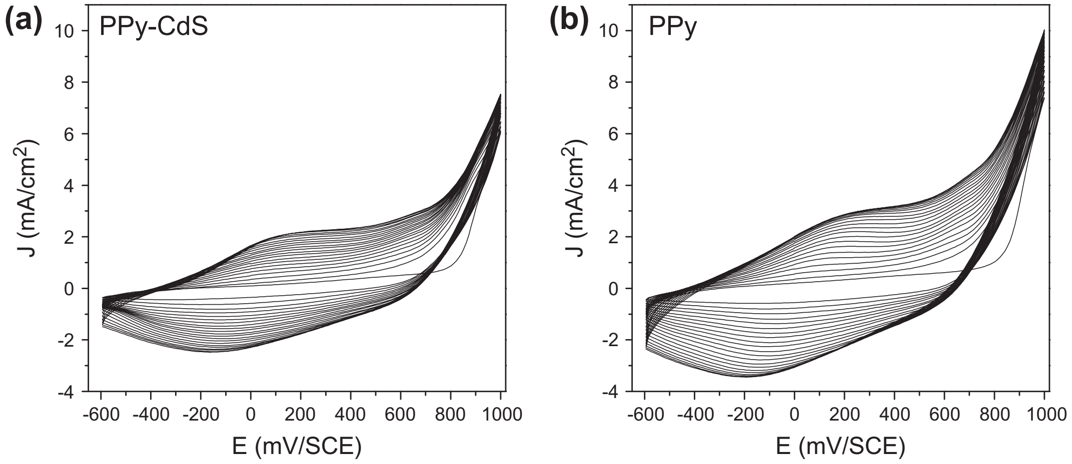


Fig. 1. Cyclic voltammograms for the electropolymerization of pyrrole in $LiClO_4$ (10^{-1} M) aqueous solution, in the presence (a) or without (b) CdS (10^{-3} M). The voltammograms represent 20 sweep segments from −0.6 to 1.0 V, v = 50 mV/s.

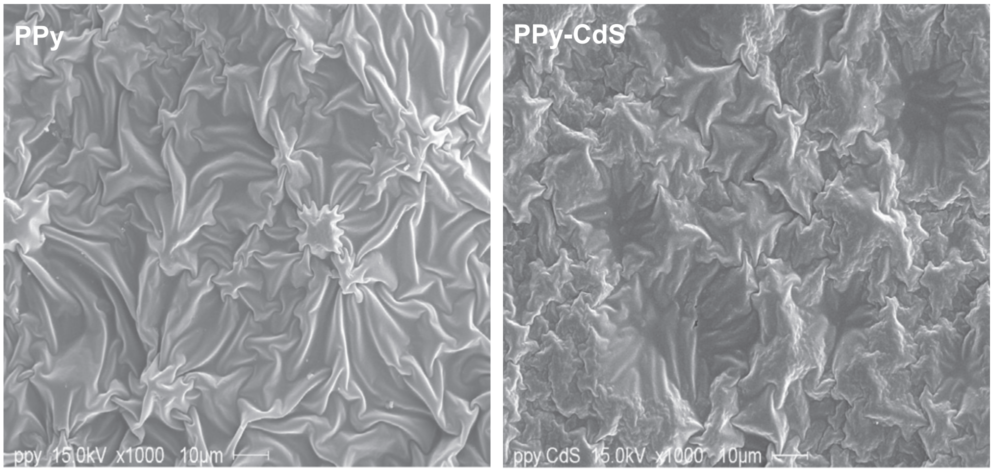


Fig. 2. SEM images of PPy and PPy–CdS electrodeposited on ITO-electrode.