

Synthesis, characterization and photoelectrochemical properties of polyindole-CdTe hybrid material



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ABSTRACT

Polyindole-CdTe (PIN-CdTe) films were prepared by electropolymerization of indole on Pt electrode followed by electrodeposition of CdTe. The synthesized composites were characterized by Raman spectra, UV-vis absorption spectra and SEM images. Photoresponses and photostability of Pt/PIN-CdTe electrodes were determined in polysulphide solution and compared with results obtained for CdTe electrodes without polymer. It was found, that the photocurrent for Pt/PIN-CdTe electrodes is nearly two fold higher and more stable than for Pt/CdTe electrodes. Raman spectra recorded after photo measurements in polysulphides revealed CdS formation. Energy dispersive X-ray spectra (EDS) indicated that amount of CdS formed was higher for CdTe deposits without polymer.

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1. Introduction

Electrodeposited thin films of cadmium chalcogenides (CdX, where X = S, Se or Te) have received considerable attention due to their proven application as photoanodes in photoelectrochemical cells. In particular, thin films of polycrystalline n-CdTe have been reported as a very promising photovoltaic material for thin film solar cells due to their high optical absorption coefficient and maximum absorption wavelength in the range of the solar spectrum.

The main problem in applying low band gap semiconductors (SC) such as CdTe in wet photocells lies in their extreme susceptibility to photocorrosion in aqueous electrolytes. This photocorrosion is even more extensive in polycrystalline films than in single-crystal electrodes. Photocorrosion of the CdTe photoanode occurs due to the photogenerated holes, which oxidize the semiconductor itself. The process results in the decomposition of the CdTe film and precipitation of Te according to the following reaction:



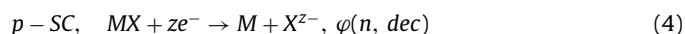
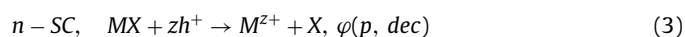
One of the methods of protecting low band gap semiconductors against photocorrosion is the use of redox systems in aqueous or organic solutions.

The presence of a redox couple at the n-CdX surface can help to either slow down or eliminate photodecomposition through scavenging the holes in the reaction (2):



The stability of the system against photocorrosion will depend on competition between reactions (1) and (2), with the dominant reaction determined by thermodynamic and kinetic factors.

The theory of the protection of semiconductors against photocorrosion is based on the results of early work of Gerischer [1], Bard and Wrighton [2], Memming [3] and Park et al. [4]. In this theory, the thermodynamic model describes the relationship between the potential of semiconductor decomposition (φ , dec) by minority carriers (holes in the case of n-SC and electrons for p-SC) created in excess during illumination shown in equations 3 and 4 and the redox potential of the applied redox couple shown in equation (2):



According to this theory, the redox system can protect the semiconductors against photocorrosion when the value of its redox potential is more negative than the value of the decomposition

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potential of the SC. To create the proper potential or energy diagram some other parameters should be considered. These might include flat band potential, position of the valence and conduction bands in a potential or energy scale and the position of Fermi energy of minority carriers under illumination. The details are described and summarized by Gerischer [5], Memming [6] and Pleskov [7].

The stability of n-CdTe photoanodes has been investigated in aqueous electrolytes that contain one of the redox couples such as sulphite, polyiodide or polychalcogenides (polysulphide, polyselenide, polytelluride). Detailed information is available in the literature [8–12]. These studies show, that polytellurides have the best protective properties against photocorrosion of n-CdTe [8,9]. However, since polytellurides are experimentally very difficult to handle, the behavior of CdTe was also investigated in polyselenide and polysulphide solutions [9,13]. Unfortunately, CdTe is not stable in these systems.

Among all stabilization methods of semiconductors, the application of conducting polymers as protective coatings has been widely studied. Conducting polymers such as polypyrrole (PPy), polythiophene (PTh) or derivatives of polythiophene (3-methylthiophene), (3-MeTh) were used for protection of n-CdS, n-CdSe, n-GaAs or n-Si in pioneering work by Skotheim et al. [14], Noufi et al. [15] and Rajeshwar et al. [16].

A thin layer of conducting polymer was used as a redox couple and as a protective coating separating the semiconductor from the solution. Additionally, the p-n heterojunction formed between SC and conducting polymer improved the efficiency of charge separation and accelerated the charge transport process. This resulted in an improvement of photovoltaic properties. In some works, two systems were applied: a redox couple in the solution and a polymer protective coating [17,18].

However, conducting polymer seem to have been little explored for CdTe protection against photodecomposition [18]. Most works have concentrated on the formation of nano CdTe - polymer composites and their application in optoelectronics [19], sensors [20] and hybrid polymer/semiconductor solar cells [21]. Recent development in polymer/semiconductor photovoltaic cell science were recently reviewed by Skompska [22].

In our previous publication [23], we showed that as-deposited CdTe films are unstable during illumination in polysulphide solutions. This provided a motivation for further studies.

The present paper describes the formation of polyindole-CdTe composites and shows that the application of a thin layer of polymer results in improved performance of CdTe thin film photoanode in polysulphide solution. An applied polyindole (PIN) layer stabilizes the photoresponses and increases the photocurrent values by two fold. Polyindole was chosen as it is stable in aqueous solution and has been used for the protection of steel against corrosion [24].

2. Experimental

The polyindole (PIN) and CdTe films were synthesized electrochemically on Pt electrode (geometric surface area 0.5 cm²). Before deposition, the Pt disc was polished to a mirror finish with aluminum slurry and washed subsequently with acetone, ethanol and Milli-Q grade water. For spectrophotometric measurements the samples were deposited on ITO (indium-thin oxide/glass) electrodes with an area of about 2.5 cm² (the active area of electrode immersed in solution was 1–1.2 cm²), treated with organic solvent and then cleaned ultrasonically. All electrochemical measurements were performed using Autolab (Ecochemie) in a conventional three-electrode cell with a Pt counter electrode and SCE reference electrode. Before electrodeposition, argon was purged through the bath for 15 minutes in order to remove oxygen from the solution.

The polyindole was synthesized from a solution containing 10⁻² M of monomer and 0.1 M LiClO₄ in acetonitrile (ACN). Cyclic voltammetry was used for polymer formation and the potential range was set from 0 V to 1.2 V, and back to 0 V, at a sweep rate 20 mV/s. The polymerization process was carried out in five cycles. The average charge which passed during polymerization was used for the estimation of the polymerization charge density (Q_{pol}). The average charge density (Q_{pol}) was estimated to be 0.3 C/cm². The amount of electroactive polymer (in mol/cm²) was determined using the equation: $\Gamma = Q/zF$, where Q is the average charge density spent on oxidation and reduction of the polymer film during cycling between -0.3 V and 0.7 V in the ACN solution of 0.1 M LiClO₄ (average charge density is equal to 0.005 C/cm²), z is the number of electrons involved in redox reaction of one monomer unit, and F is a Faraday constant. Using value of z equal to 0.25, as in the case of polypyrrole [25] the amount of PIN on the electrode was estimated to be 205 nmol/cm².

Electrodeposition of CdTe on Pt and Pt/PIN electrodes was carried out from an acidic aqueous solution (pH 2) containing 5 mM Cd(ClO₄)₂, 1 mM Na₂TeO₃ and 0.1 M LiClO₄ (concentration ratio of Cd(II)/Te(IV) ions sources 5:1) at a temperature of 70 °C. The pH of the solution was adjusted with HClO₄. The deposition was performed using the following potentiostatic conditions: the Pt or Pt/PIN electrodes were kept for 100 s at potential of -0.65 V vs. SCE and then three pulses were applied from -0.65 V to 0.3 V for 10 s with intervals 100 s between them, then the process was completed at -0.65 V for 1800 s. The values of the potential -0.65 and 0.3 V were chosen based on our previous work [23]. For electrodeposition of CdTe on Pt or Pt/PIN electrodes the average charge density was estimated to be 0.43 C/cm². The solutions were prepared from Millipore Milli-Q grade water and analytical-grade reagents (Sigma-Aldrich).

Raman spectra were obtained with a Labram HR800 (Horiba Jobin-Yvon) confocal microscope system using Nd:YAG laser (785 nm) as the excitation source. A scanning electron microscope (LEO 435VP) equipped with a Roentec EDX analyzer was used for imaging the surface of samples and for recording energy dispersive X-ray spectra (EDS). UV-vis spectra were obtained using a Shimadzu (2401) spectrometer.

Photoactivity of as-deposited CdTe films was tested in polysulphide solution (0.5 M Na₂S, 0.5 M NaOH, 0.5 M S). The measurements were carried in three-electrode photocell equipped with a quartz window, containing Pt sheet (counter electrode) and Ag/AgCl, Cl⁻ (1 M) (reference electrode). The Pt/CdTe or Pt/PIN-CdTe electrodes were illuminated by a 1000 W tungsten lamp (LEO 435VP). The water filter (18 cm long) was used to avoid direct heating of the cell. To prepare the polysulphide solution, 12 g of Na₂S*9H₂O, 2 g of NaOH and 2 g of sublimed sulphur were added to 100 ml of Ar-purged Milli-Q water. The solution was heated to 50 °C for one hour and sonicated for two hours. This resulted in a solution that was clear and had an orange color.

3. Results and discussion

3.1. Synthesis of PIN-CdTe composites on Pt electrode

Polyindole (PIN) was electrodeposited on a Pt electrode from 0.1 M LiClO₄ acetonitrile solution containing 10⁻² M of monomer by cycling electrode within a potential range from 0 to 1.2 V, and back to 0 V, at a sweep rate 20 mV/s. An exemplary CV curves are shown in Fig. 1. The anodic peak associated with oxidation of monomer is observed at 1.2 V (curve 1). As expected, the PIN is electroactive in acetonitrile solution. The CV curves recorded during oxidation and reduction of polyindole in 0.1 M LiClO₄ acetonitrile solution are presented in Fig. 1 as an inset. Two redox couple are observed

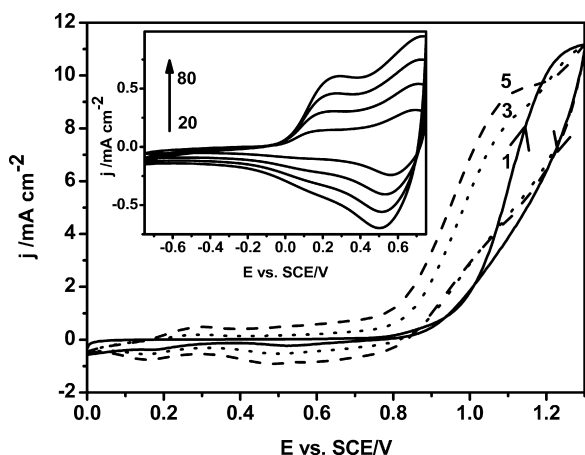


Fig. 1. CV curves recorded during electropolymerization of indole on Pt electrode from acetonitrile solution containing 0.01 M indole and 0.1 M LiClO₄; 1st, 3rd and 5th cycle, scan rate 20 mVs⁻¹. Inset: CV recorded for Pt/PIN electrode in acetonitrile solution containing 0.1 M LiClO₄; polymerization charge density $Q_{\text{pol}} = 0.3 \text{ C/cm}^2$; scan rates: 20, 40, 60, 80 mVs⁻¹, respectively.

on CV curves in this case. The values of redox potentials of PIN are in the range from 0.1 V to 0.3 V for the first redox couple and in the range from 0.6 V to 0.8 V for the second redox couple. These values are in an agreement with the literature [26,27]. In order to check the permeability of the polymer film to the solution, polyindole films of different thickness (produced by varying the polymerization charge density from 0.1 to 1.5 C/cm²) were tested in 0.1 M LiClO₄/ACN solution containing 5 mM of TCNQ. Based on the CV results, it was found that polyindole films that were electropolymerized with density charges up to about 1 C/cm² are permeable and can be used for electrodeposition of different materials at negative potentials.

For deposition of CdTe polyindole films were obtained in five cycles (polymerization charge density $Q_{\text{pol}} 0.3 \text{ C/cm}^2$). Typical CV curves recorded during CdTe deposition on Pt and Pt/PIN electrodes in the solution containing 5 mM Cd(ClO₄)₂, 1 mM Na₂TeO₃, 0.1 M LiClO₄ (pH 2, 70 °C) are shown in Fig. 2. As may be seen for the Pt electrode, the cathodic wave (at about -0.25 V) is followed by plateau from -0.4 V to -0.65 V. It was accepted [28–32] that Te and CdTe deposition takes place in this potential range according to equations (5) and (6):

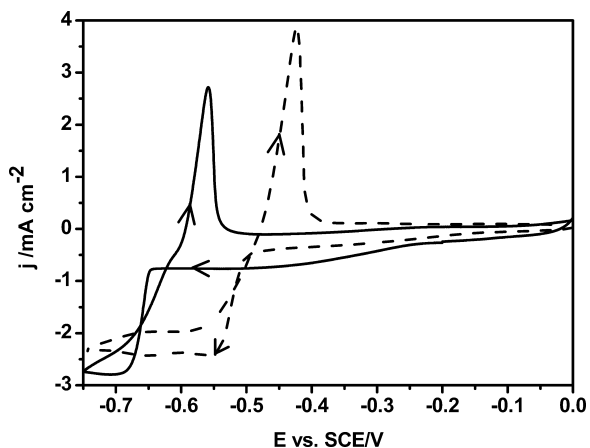
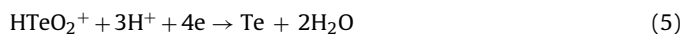


Fig. 2. CV curves recorded on Pt (—) and Pt/PIN (---) electrodes in solution containing 5 mM Cd(ClO₄)₂, 1 mM Na₂TeO₃, 0.1 M LiClO₄, pH 2, scan rate 20 mVs⁻¹, Temp. = 70 °C, $Q_{\text{pol}} = 0.3 \text{ C/cm}^2$.

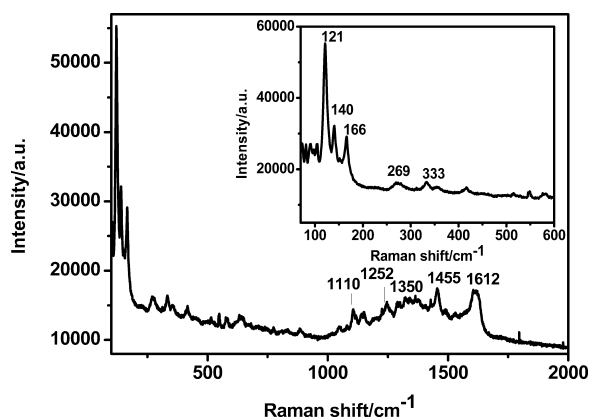


Fig. 3. Raman spectrum of the PIN-CdTe composite film on Pt electrode. Inset: Raman spectrum indicating formation of CdTe on the polymer.

At potentials more negative than -0.65 V a sharp current increase is observed due to Cd deposition and probably H₂ evolution. The reverse cathodic scan revealed a peak at -0.56 V, which can be attributed to stripping of electrodeposited cadmium. In the case of the Pt/PIN electrode, a slight linear increase of current is observed in the potential range from -0.2 V to -0.45 V. We suppose that in this range, the Te is deposited. The formation of CdTe takes place after Te deposition at potentials more negative than -0.45 V. In comparison to Pt bare electrode, the polyindole film facilitates the processes of CdTe formation. The influence of deposition condition on the properties as-deposited CdTe films and possible mechanisms of CdTe electrodeposition have been previously presented [23]. Based on these results, a potential of -0.65 V was chosen for CdTe deposition.

3.2. Characterization of Pt/PIN-CdTe electrodes

Raman spectroscopy was used to show that a PIN-CdTe hybrid system is formed on Pt. In Fig. 3 the ex-situ Raman spectrum is shown for a Pt/PIN-CdTe electrode. The Raman spectra of Pt/CdTe and PIN were discussed elsewhere [23,26]. The Raman spectrum can be divided into two parts. In the first part, where the wavenumber ranged from 50 to 500 cm⁻¹, the spectrum reveals three sharp bands at 120 cm⁻¹, 140 cm⁻¹, 166 cm⁻¹, and two broad peaks at 269 cm⁻¹ and 333 cm⁻¹ (inset in Fig. 3). The presence of the bands at 140, 166 and 333 cm⁻¹ indicates the formation of CdTe [33]. The band at 120 cm⁻¹ can be ascribed to elementary tellurium [34]. The appearance of this band in Raman spectra of CdTe can be caused by Te electrodeposition during CdTe formation or by decomposition of CdTe in the laser beam [35]. The broad band at 260 cm⁻¹ most likely is due to cadmium oxide [36]. The bands in the second part of the spectrum in the range from 1000 to 1700 cm⁻¹ are characteristic of polyindole. The bands of polyindole at about 1350 cm⁻¹ can be ascribed to stretching vibration of a pyrrole ring and the bands in the vicinity of 1600 cm⁻¹ are due to stretching vibration of a phenyl ring. The bands at 1455 cm⁻¹, 1252 cm⁻¹ and 1110 cm⁻¹ are ascribed to vibrational mode of $\delta\text{C}_5\text{H} + \nu\text{C}_5\text{N} + \nu\text{C}_4\text{C}_5$, $\delta\text{C}_5\text{H} + \delta\text{C}_4\text{H}$, $\nu\text{C}_6\text{C}_7 + \delta\text{C}_5\text{H} + \delta\text{C}_4\text{H}$, respectively [26,37].

The optical properties of PIN-CdTe composite films deposited on ITO were investigated by recording UV-vis spectra in the wavelength range of 300–750 nm. The comparison of a) in-situ spectrum of PIN recorded in 0.1 M LiClO₄/ACN solution at -0.2 V, b) ex-situ spectrum of CdTe and c) ex-situ spectrum of PIN-CdTe is presented in Fig. 4. As may be seen, a well-defined band with a maximum at 360 nm is observed in the spectrum of PIN, and a broad band with a maximum at 500 nm is observed for CdTe. This latter band is more pronounced in the spectrum of PIN-CdTe. In this case, the polymer

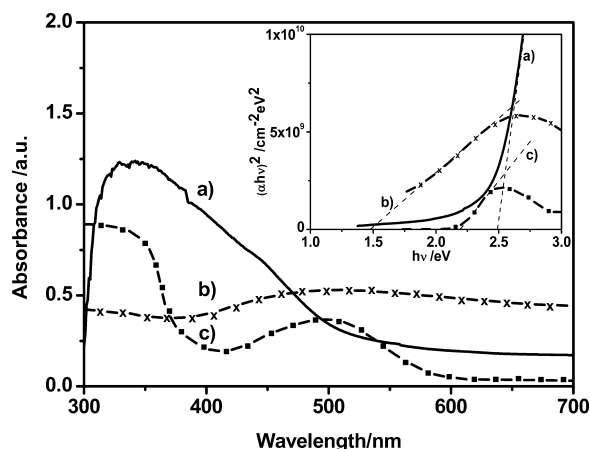


Fig. 4. UV-vis spectra of: a) PIN, b) CdTe and c) PIN-CdTe deposited on ITO. Inset: The $(\alpha hv)^2$ vs. hv dependence obtained for: a) PIN, b) CdTe and c) PIN-CdTe deposits.

band at 360 nm usually connected with $\pi \rightarrow \pi^*$ transition is not seen, however a significant increase of absorption is observed.

The variation of absorbance with a wavelength was analyzed in order to find the band gap energy of CdTe deposits using the Tauc's relation which is applied frequently [38–40] for determination of optical band energy of amorphous and polycrystalline films of semiconductors:

$$hv\alpha = B(hv - E_g)^n$$

where hv is photon energy, B is a constant, $\alpha(\nu)$ is absorption coefficient, E_g is an optical band gap energy. As CdTe is a direct band gap material (for direct transition $n=0.5$), the E_g energy of band gap could be obtained from the intercept of $(hv\alpha)^2$ vs. hv plot presented in Fig. 4 (inset). The values of $\alpha(\nu)$ coefficient can be calculated from absorbance data as $\alpha(\nu)$ is defined by the Beer-Lambert's law: $\alpha(\nu) = 2.303A/d$, where d and A are the film thickness and film absorbance, respectively. The main problem in calculation of $\alpha(\nu)$ coefficient is the film thickness which can be estimated from the charge passing during deposition (assuming 100% efficiency of the process) or independently from microscopic measurements. For our purpose, the thickness of CdTe and PIN films was determined very roughly from the density charge which passed during CdTe deposition on ITO ($Q_{dep} = -0.48 \text{ C/cm}^2$, density of CdTe = 5.85 g/cm^3 , number of electrons = 6), and from the density of oxidation charge of polymer deposited on ITO ($Q_{ox} = 0.006 \text{ C/cm}^2$, density = 1.5 g/cm^3 , number of electrons = 0.25 [25]). We obtained the thickness of the CdTe film and PIN films as 340 nm and 200 nm, respectively. For calculation of $\alpha(\nu)$ of PIN-CdTe samples, we used the thickness obtained from the charge which passed during CdTe deposition on PIN ($Q_{dep} = -0.43 \text{ C/cm}^2$), in this case the thickness was 300 nm. The E_g energy band gap estimated from the intercept of $(hv\alpha)^2$ vs. hv plot are equal to 1.50 eV, 2.15 eV, 2.45 eV for CdTe, PIN-CdTe, PIN, respectively. The obtained values are in good agreement with literature data for CdTe [38,41] and for PIN [42]. The results show that for a CdTe-PIN composite, the band gap energy is higher than for CdTe itself.

The morphology of Pt substrate covered with one of the components (either PIN or CdTe) and with the PIN-CdTe composite was examined using SEM. The SEM images are presented in Fig. 5a, b, c, respectively. It is clearly seen that in the case of PIN, the thin film of polymer is formed on Pt and on the top of it the polyindole globules grow and aggregate forming cauliflower like structures (Fig. 5a). In the case of CdTe deposition on Pt (Fig. 5b), almost a homogeneous CdTe film is formed by very small crystallites with size of about 10–25 nm. The deposited film is cracked in some places though (see spherical holes), which might be a result of gas

evolution. Different morphology was observed for a Pt electrode covered first with the polymer and then with CdTe (Fig. 5c). In this case, the polymeric film is covered with almost spherical particles of CdTe with a size of about 50 nm. These particles can aggregate forming larger structures.

3.3. Photoactivity and photostability

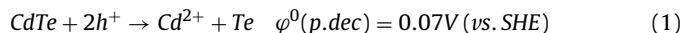
It was shown that CdTe films deposited at -0.65 V are n-type semiconductors [23]. They are unstable in polysulphide solution and their photoactivity is much smaller than those of CdTe single crystals [8,9]. The usual cause of smaller photoactivity of polycrystalline semiconductor films is the recombination of hole-electron pairs at the grain boundaries and at the surface. In order to improve the separation of the charge carriers, and in consequence to increase the photoactivity and also to improve the photostability of CdTe, a thin layer of polyindole was applied. During deposition, the crystallites of CdTe were formed in/on polymer layer.

Fig. 6a presents the changes of open circuit potential (OCP) in the dark and under illumination before and after current measurements on Pt/CdTe in polysulphide solution. In Fig. 6b the changes of the current measured at different potentials on Pt/CdTe electrodes in polysulphide solution in dark and under illumination are shown. The measurement procedure was as follows: 1) first the Pt/CdTe electrode was conditioned in polysulphide solution and the OCP of the electrode was measured in the dark, 2) then the electrode was illuminated with 50 s pulses over 10 minutes and the OCP changes during pulses were measured, 3) after that the current was measured at selected potential in the dark and under illumination with 50s pulses over 10 minutes and 4) again the OCP was determined in dark and under illumination over 10 minutes. The procedure was repeated at different potentials and also was carried out for Pt/PIN-CdTe electrodes however in this case, the measurements were carried out over a duration of 2 hours (Fig. 6 c, d).

In the case of the Pt/CdTe electrode, the values of the photopotential at OCP ($\varphi_{ph} = \varphi_{light} - \varphi_{dark}$) decreased after the photocurrent measurements. The best obtained value of φ_{ph} was about -0.16 V . The value of the photocurrent ($i_{ph} = i_{light} - i_{dark}$) at -0.5 V was about 0.2 mA/cm^2 and decreased over time. For the Pt/PIN-CdTe electrode the φ_{ph} at OCP was slightly higher, about -0.2 V and after 2 hours of current measurements at -0.5 V , also slightly decreased. However, the photocurrent measured over 2 hours was stable and was about two fold higher than the photocurrent recorded in the case of the bare Pt/CdTe electrode at the same potential.

The increase of the photocurrent might be caused by 1) a better separation of the charge carriers at the boundary of CdTe crystals/PIN, or 2) inhibition of the electron-hole recombination and the transport of holes to PIN (the polymer at these potentials is in neutral form and can work as hole acceptor) and subsequently to the polysulphide solution. The increase of the current can also be caused by an increase of photoactive surface area resulting from the distribution of CdTe crystals in/on polymer films. However, the amount of CdTe in both cases is similar as the charges of CdTe deposition on Pt and on Pt/PIN electrodes differs not more than 10%.

As was mentioned earlier [8,9], CdTe is stable and does not undergo photodecomposition in polytelluride solution. Photodecomposition



is completely quenched by the redox reactions in the polytelluride system [9,12]



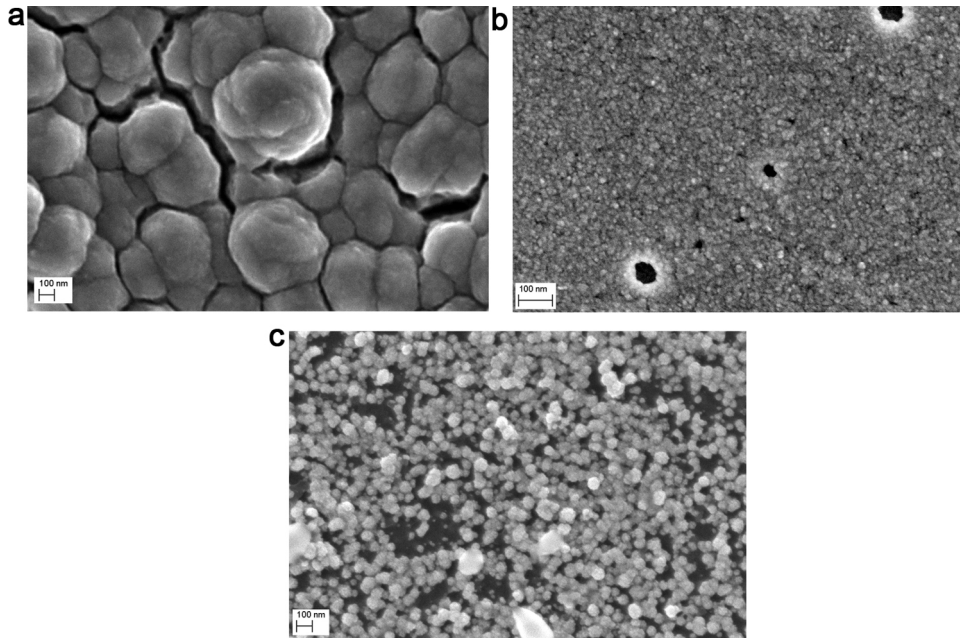


Fig. 5. SEM images of: a) PIN (polyindole), b) CdTe, c) PIN-CdTe deposited on Pt electrode.

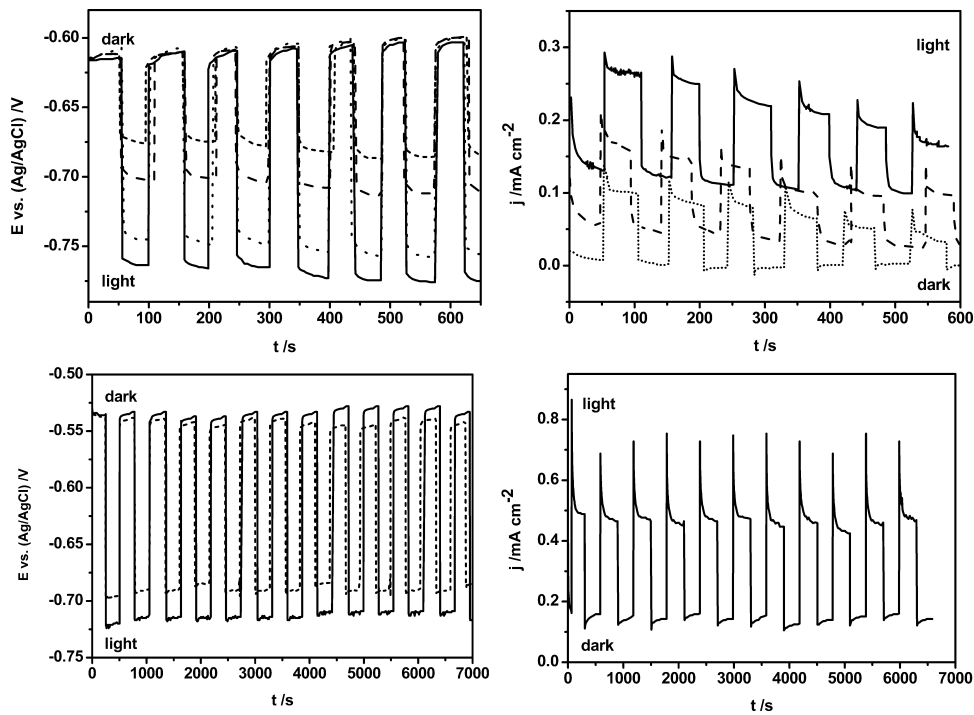
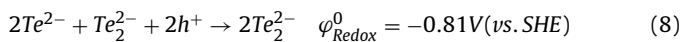


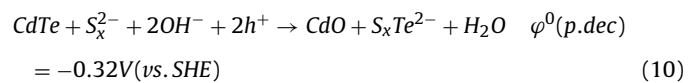
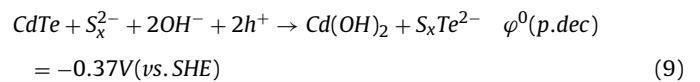
Fig. 6. Photoelectrochemical results for CdTe deposited on Pt and Pt/PIN electrodes recorded in polysulphide solution: a) Pt/CdTe. OCP changes vs. time recorded in dark and under illumination before (—), and after current measurements at potentials: -0.5 V (\cdots), -0.6 V ($---$), -0.7 V ($\cdot\cdot\cdot$). b) Pt/CdTe. Current changes vs. time recorded in dark and under illumination at potentials: -0.5 V (—), -0.6 V ($---$), -0.7 V ($\cdot\cdot\cdot$) c) Pt/PIN-CdTe. OCP changes vs. time recorded in dark and under illumination before (—) and after current measurement at potential -0.5 V (\cdots). d) Pt/PIN-CdTe. Current changes vs. time in dark and under illumination at potential -0.5 V .

or



In polysulphide solution, the reactions of photodecomposition (photocorrosion) with participation of holes are more complicated. Thermodynamic data [11,12] indicate that CdTe can be photooxidized to hydroxides/oxides following the reactions shown

in equations (9) and (10):



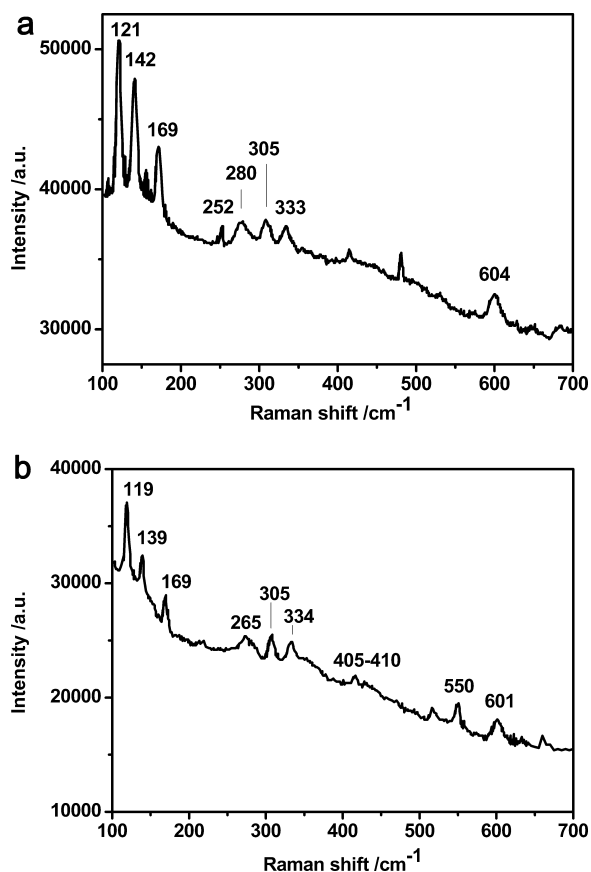
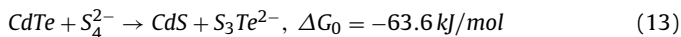
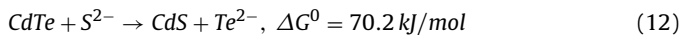
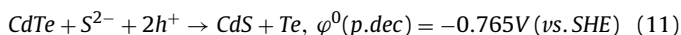


Fig. 7. Raman spectra recorded for: a) Pt/CdTe and b) Pt/PIN-CdTe electrodes after photo measurements in polysulphide solution.

Furthermore, reactions resulting in CdS formation are also possible:



Comparing the value of the standard potential of $\text{S}^{2-}/\text{S}_x^{2-}$ redox couple, $\varphi^0_{\text{Redox}} = -0.48 \text{ V}$ [12] with the values of the CdTe decomposition potentials (equations 9, 10) it is seen, that since those values are close, the polysulphide solutions cannot protect the CdTe against photodecomposition. Better results for stabilizing the CdTe electrode were obtained using polyindole. Polyindole may work not only as an effective acceptor of generated holes but also as a mediator in effective transport of the holes to the polysulphide system. It also may help to reduce the access of the solute species to the CdTe. In order to have a closer look at the process occurring on Pt/CdTe and Pt/PIN-CdTe electrodes in polysulphide solution, Raman spectra were recorded after photo measurements. The spectra are shown in Fig. 7a and 7b for both Pt/CdTe and Pt/PIN-CdTe electrodes, respectively. The bands in the vicinity of 120 cm^{-1} (Te), 140 , 169 , 330 cm^{-1} (CdTe), and 265 cm^{-1} (CdO) were described above (see Fig. 3). As may be seen, two new bands appear in the Raman spectra in both cases, one at 305 cm^{-1} and another in the vicinity of $601\text{--}604 \text{ cm}^{-1}$. Both bands are characteristic of CdS [43]. There are some bands, such as 252 cm^{-1} , 280 cm^{-1} , 480 cm^{-1} , and 550 cm^{-1} , and in the vicinity of 400 cm^{-1} , which cannot be unequivocally ascribed. Some of these bands may be assigned to the ions adsorbed on the electrode surface. For example, band at

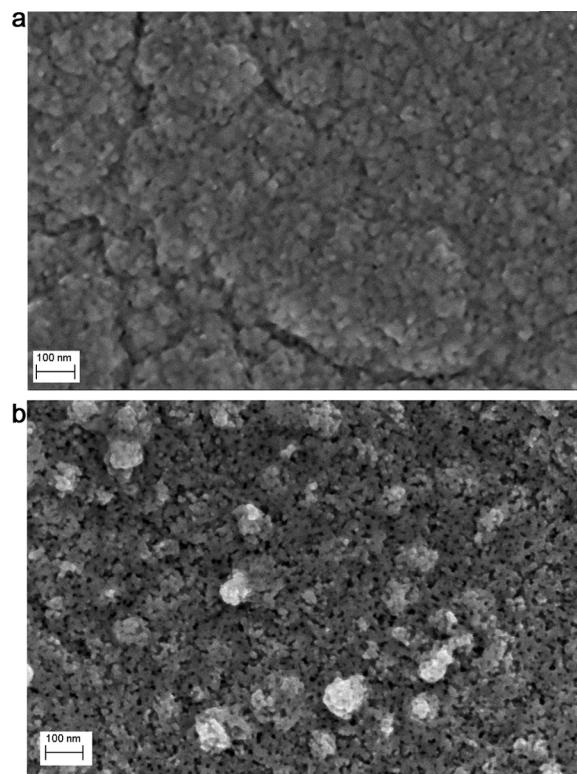


Fig. 8. SEM images of: a) Pt/CdTe and b) Pt/PIN-CdTe electrodes after photo measurements in polysulphide solution.

482 cm^{-1} has been previously assigned to polycrystalline polysulphide Na_2S_4 [44]. The EDS spectra recorded for Pt/CdTe and Pt/PIN-CdTe electrodes before and after the photo measurements in polysulphide solution also revealed changes in the composition of the deposits. For both deposits, CdTe and PIN-CdTe, a small excess of Te about 2–3% in comparison with Cd is observed before photo measurements. After photo measurements the amount of Te decreases and becomes lower than the Cd amount. Some amount of sulfur is then seen in spectra. The amount of sulfur determined in the CdTe deposit is about 10%–12% higher than in the PIN-CdTe deposit, and it pointed to the formation of CdS in both cases. Significant changes were also observed in the morphology of the deposits after the photo measurements. In both cases, SEM images (Fig. 8a and 8b) showed a porous sponge like structure.

In summary, the gathered experimental results show that polyindole improved the photoelectrochemical responses and photostability of CdTe, but did not protect CdTe against chemical exchange reaction with polysulphide ions and formation of CdS on the surface of CdTe crystallites.

4. Conclusions

Pt/CdTe and Pt/PIN-CdTe electrodes were prepared by electrochemical methods. The formation of PIN-CdTe deposits were carried out in two steps: first, a polyindole film was formed on a Pt electrode and then CdTe was deposited. SEM images showed that in such deposits, the CdTe crystallites are formed either on the polymer films or are embedded into the polymer layer. Photoelectrochemical measurements carried out in polysulphide solution showed that the applied polyindole layer improved the photocurrent and photostability of CdTe, but did not protect CdTe against chemical exchange reaction and formation of CdS. This lack of protection probably results from the way that polyindole is electrodeposited. It is not possible to obtain thin,

not-permeable polyindole films on the top of the CdTe surface because the electrooxidation of monomer and polymer formation occurs at potentials higher than the oxidation and dissolution potentials of CdTe in the dark. Since the CdTe crystals were formed upon or embedded into PIN, the polymer did not fully cover them. Another point which should be considered is alkalinity of the polysulphide solution, which can affect the polyindole structure and cause peeling of the polymer from the Pt surface.

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