



The improved photooxidation stability of the SILAR deposited copper sulfide on polypyrrole



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ABSTRACT

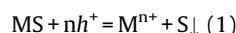
The copper sulfide is successfully deposited onto electrochemically formed polypyrrole, by successive ion-adsorption and reaction (SILAR) processes. The photoelectrochemical behavior of the polypyrrole, copper sulfide and copper sulfide modified polypyrrole are investigated in the sulfide based solution, under cathodic and anodic polarization. The improvement of the photooxidation stability, as well as activity of copper sulfide modified polypyrrole is achieved. Such behavior is explained by recombination of electrons from Cu_{2-x}S conducting band with the holes of the PPy LUMO.

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1. Introduction

The conversion of light into photoelectrochemical energy is widely studied using different semiconducting metal sulfides, because of their easy synthesis and morphology control [1,2]. Such materials can be used alone, or as a band gap tailor for wide band semiconductor materials in different applications, like photovoltaic, photocatalysis, water splitting, photocatalytic degradation of organic waste *etc.* [3–7].

As observed in the early stage of investigations [8] if illuminated under anodic bias in contact with an aqueous electrolyte the metal sulfides is oxidized to elemental sulfur and M^{n+} . In the metal sulfides with narrower energy gap (*e.g.* PbS , FeS_2 , Cu_2S , CuS , *etc.*) holes are already present in the dark and lead to the same anodic reaction [8]:



A surface layer of molecular sulfur rapidly develops, and gradually slows down the anodic process and disintegration of the metal sulfide.

The conducting polymers are well-known materials, which could decrease or prevent corrosion of many materials. Therefore, the application in corrosion prevention of metal sulfide was the

reasonable step. Among different conducting polymers polyaniline (PANI) and polypyrrole (PPy) were the most widely investigated. Between them only PPy exhibit activity in alkaline solutions [9]. Frank and Honda [10] observed that CdS covered with PPy and activated with the RuO_2 under anodic potentials of 0.4 V (vs. SCE) in 0.5 M Na_2SO_4 increases the rate of the oxygen production from 1% for pure CdS , to 21% for PPy covered, and up to 68% for RuO_2 activated. Recently, different authors investigated the influence of the PPy on the photoelectrochemical behavior of some semiconductors, CdS [11], InP [12], Bi_2S_3 [13,14] and GaAs [15]. In all the investigations, the PPy-semiconductor was prepared as a composite film, with semiconductor particles incorporated under mixing conditions, during pyrrole electropolymerization. It is interesting to note that although successive ion-layer adsorption and reaction (SILAR) process was extensively investigated [1,2,16], no attention was paid on preparation and photoelectrochemical investigations of the PPy-MS films [17]. It should be also noted, that during chemical or electrochemical polymerization over-oxidized species like $=\text{O}$, $-\text{OH}$, [18] are always produced and could serve as the reduction groups during metal ion-layer adsorption step.

As pointed out by Page et al. [19], among different metal sulfides, copper sulfides can be considered, in some way, as an ideal light absorbing materials – being non-toxic, inexpensive, and with good absorption characteristics. The electronic characteristics of copper sulfides are in general very poor, because fast electron–hole recombination times. Different Cu_{2-x}S phases ($x=0-1$) tend to

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coexist, resulting in the many possible phases. Some of the most common phases of the copper sulfide at room temperature are covellite (CuS), anilite (Cu_{1.75}S), digenite (Cu_{1.8}S), djurleite (Cu_{1.94–1.96}S), chalcocite (Cu₂S) and others [19–22].

The main goal of this paper was investigations of the photoelectrochemical behavior of the copper sulfides modified PPy using the simple SILAR procedure.

2. Experimental

Polypyrrole was synthesized galvanostatically with current density of 1 mA cm⁻² from electrolyte containing 0.1 M pyrrole (Aldrich p.a., previously distilled under reduced pressure) and 0.5 M NaNO₃ (p.a. Merck) acidified to pH ~3 with 0.1 M HNO₃, onto the plane (1 cm × 2 cm, A = 2 cm²) glassy carbon electrode with polymerization charges of 0.3 mA h cm⁻². To avoid PPy degradation synthesis was performed at ~5 °C. During electropolymerization, electrode potentials were ~0.75–0.7 V. Before SILAR and/or PPy polymerization, electrode was mechanically polished with fine emery papers (2/0, 3/0 and 4/0, respectively) and degreased in acetone in an ultrasonic bath. Solutions contained 50 mM of Cu(NO₃)₂ and 0.1 M Na₂S were used for the SILAR, either on the pure glassy carbon electrode or PPy covered. SILAR procedure consisted of five successive cycles in metal ion precursor solution during 60 s, followed by reaction with sulfide solution for 60 s (180 s last cycle), rinsed with distilled water between cycles.

All the photoelectrochemical experiments were conducted in the electrolyte contained 0.5 M NaNO₃, 0.2 M thiourea and 25 mM Na₂S (p.a. Merck) prepared using double distilled water. As the main sulfide (HS⁻) source, the thiourea was chosen due better stability compared to pure polysulfide solutions [1], and high degradation potentials [23]. For PPy synthesis and photoelectrochemical experiments two compartment glass cells, with working compartment volume of 100 cm³, were used, connected to the reference electrode compartment *via* Lugin capillary. The Pt plate 2 cm² in the same solution as a counter, and saturated calomel electrode as the reference electrode, connected with the cell reference electrode compartment using agar–agar NaNO₃ salt bridge to avoid contamination with sulfides, were used. Before photopotentiostatic experiments, electrode potential was held in the dark, until steady state current was reached, typically 300–600 s.

The homemade dark chamber equipped with an electromagnet controlled blind, and fan cooler was used. The light sources was 300 W Osram-Vitalux lamp, with light intensity of 0.34 Sun. Experiments were performed using Gamry PC3 potentiostat/galvanostat. Optical micrographs were obtained with an optical microscope Olympus CX41 connected to PC. The chemical composition of the as prepared copper sulfide sample was analyzed using an energy dispersive spectrometer (EDS) Isis 3.2, with a SiLi X-ray detector (Oxford Instruments, UK) connected to the scanning electron microscope (JEOL 5800 JSM, Japan) and a computer multi-channel analyzer.

3. Results and discussion

3.1. Photoelectrochemical behavior of polypyrrole

Fig. 1 shows cyclic voltammogram of PPy in the solution contained 0.5 M NaNO₃, 0.2 M thiourea and 25 mM Na₂S at pH ~12. In a separate experiments (not shown) it was observed that irreversible degradation of the PPy occurred above ~0.15 V, hereafter in all further experiments the anodic potential was limited to 0 V. From the shape of the cyclic voltammogram, it can be concluded that *p*-doping with either nitrate or sulfide ions

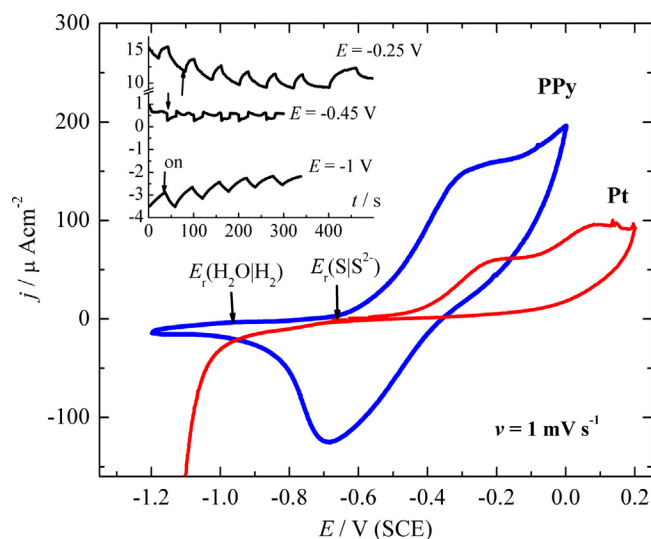
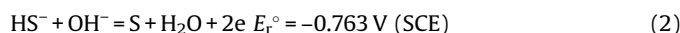


Fig. 1. Cyclic voltammograms of the PPy and Pt in solution contained 0.5 M NaNO₃, 0.2 M thiourea and 25 mM Na₂S at pH ~12. Inset: potentiostatic response of the PPy electrode at different potentials under dark and illumination conditions.

occurred in the potential range of -0.7 to -0.1 V, while dedoping in -0.35 to -1.1 V.

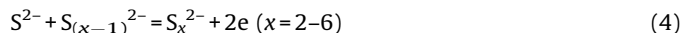
With the experiments using pure platinum it was determined that reversible potential in the solution had the value of -0.62 V. The oxidation of HS⁻ or S²⁻ to S₂²⁻ occurred above potentials of -0.6 V. It was also observed (not shown) that oxidation of the thiourea dissociation products, e.g. CH₂N₂, occurred above ~0.35 V. Standard potentials for dominant reaction in the solution are [24]:



and:



But it should keep in mind that mechanism of those reactions, are more complex, and occurred through the formation of polysulfide, according to the overall reaction [25]:



The thermodynamic potential for the hydrogen evolution reaction of -0.963 V, was calculated.

The photoelectrochemical behavior of the PPy was investigated under potentiostatic control, and results are shown in the inset in Fig. 1. At the negative potentials e.g. -1.1 V the PPy exhibited slight activity with a cathodic photocurrent of ~0.5 μA cm⁻². At potential of -0.45 V negligible activity with overshooting was observed, suggesting the presence of some unknown surface states [26]. At more positive potentials e.g. -0.25 V, PPy shows better activity, with stable anodic photocurrent of ~4.5 μA cm⁻². Such behavior is in agreement with data reported by Miquelino et al. [27].

The band gap structure of PPy is well established in the literature [28,29]. Theoretical band gap energy, *E_g*, of the pristine PPy is 3.2 eV, while increase of the doping level, e.g. in our case potential, reduce the band gap due to formation of the polarons and bipolarons states. The highest occupied molecular orbital, HOMO, is reported to be positioned at -4.75 to -5.0 eV with respect to the vacuum level [13,30–33]. In a slightly doped state of the polymer, lowest unoccupied molecular orbital, LUMO, is reported at approximately -2.45 eV (*E_g* = 2.5 eV) with respect to vacuum [33]. In doped PPy, additional energy levels and bands are formed in the energy gap, which are polaronic and bipolaronic nature. Bipolaronic band for highly doped PPy is at approximately -3.3 eV acting as a conduction band. As a result, doping induces

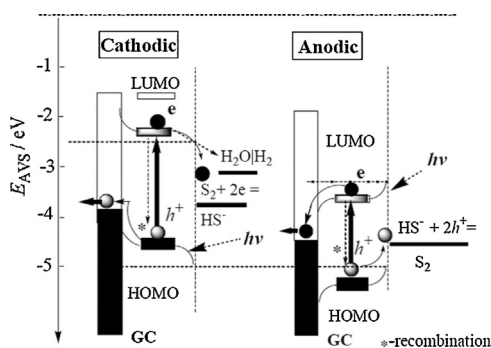


Fig. 2. Schematic presentation of PPy band gap structure during illumination at cathodic and anodic polarization.

reduction in the band gap of polymer, $E_g = 1.7$ eV, by moving the conduction band down into energy. Therefore, based on these considerations in Fig. 2 the structure of PPy band gap and plausible photoelectrochemical reactions during cathodic and anodic polarization are represented.

In contact with electrolyte an equilibrium between the Fermi levels of the redox species and PPy occurred, inducing the formation of depletion layer and Fermi level alignment. During cathodic polarization and under illumination, electron–hole pairs are generated in PPy. It should be noted that without the presence of a donor or acceptor, electron–hole pairs are not well separated, forming a short living excitons state. Because, the LUMO of the PPy is positioned at lower energy than both Fermi levels of the possible redox in the solution, transfer of the electrons either to molecular sulfur or water occurred. The holes were transferred to the Fermi level of glassy carbon. Simultaneously, recombination of the excited electrons with holes occurred as well, producing relatively small cathodic photocurrent. During anodic polarization, generated holes from HOMO levels were transferred to the Fermi level of

the sulfide redox, generating anodic photocurrent. Better alignment between PPy LUMO and Fermi level of the glassy carbon allowed faster electron transfer, and the smaller possibility of electron–hole recombination, resulting in a higher and more stable anodic photocurrent.

3.2. Photoelectrochemical behavior of the copper sulfide and modified polypyrrole

Fig. 3(a)–(c) shows optical micrographs of as synthesized polypyrrole, copper sulfide, and copper sulfide modified polypyrrole. Polypyrrole, Fig. 3a does not have any typical morphological characteristics. Some cavities on the surfaces are the results of the oxygen evolution reaction, which occurred at a limited rate during synthesis under relatively high anodic potentials of ~ 0.75 V. Copper sulfide deposits on the glassy carbon electrode, Fig. 3b, has an irregular porous film structure. Copper sulfide deposited onto polypyrrole, Fig. 3c have porous, but much finer, dendritic like structure with an average dendrite length of ~ 20 μm . The EDX spectrum of the as synthesized Cu_{2-x}S is shown in Fig. 3d. The elemental composition ratio of Cu:S was 2:1, revealed that pure Cu_2S phase were synthesized by the current synthetic route.

Cyclic voltammograms of the investigated materials in the dark are shown in Fig. 4. For the pure Cu_{2-x}S electrode in the anodic direction at -0.97 V very sharp peak, followed by a broad peak in the potential range of -0.9 to -0.7 V could be associated with the phase transformations of the copper sulfide [21]. Namely, during the synthesis of the copper-deficient sulfides at the potentials of -1.2 , -0.6 , and 0 V, the $\text{Cu}_{1.97}\text{S}$, $\text{Cu}_{1.8}\text{S}$, and CuS were produced, respectively. Therefore, in our cases similar phase transformation could occur. At negative potentials, e.g. lower than -1 V, Cu_2S phase was dominant. Increasing anodic potentials the following overall solid-state surface reactions could occur [34]:

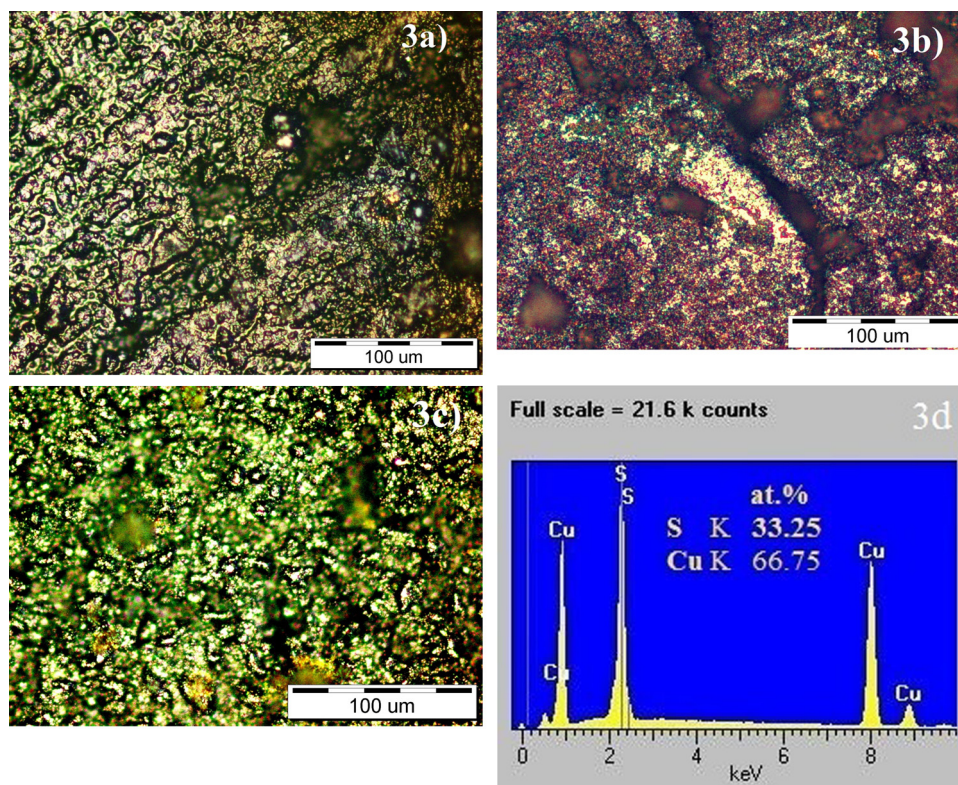


Fig. 3. Optical micrographs of as synthesized (a) polypyrrole, (b) Cu_{2-x}S , and (c) Cu_{2-x}S modified polypyrrole. (d) EDX spectra of pristine copper sulfide.

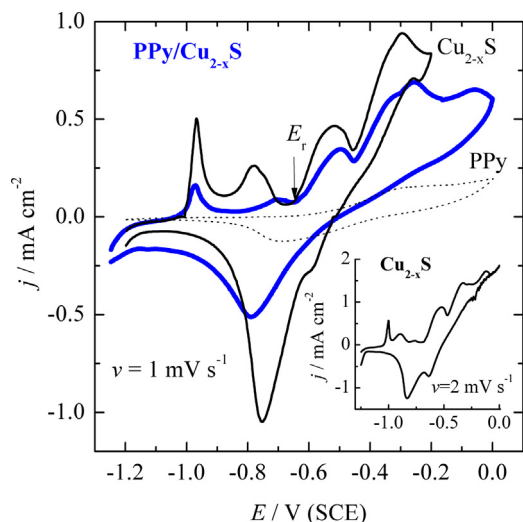
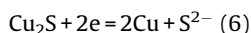


Fig. 4. Cyclic voltammograms of the Cu_{2-x}S , $\text{PPy-Cu}_{2-x}\text{S}$ and pure PPy, deposited onto a glassy carbon electrode in the dark. Inset: cyclic voltammogram of Cu_{2-x}S with increased anodic potential limit.

At the potential higher than reversible ($E_r = -0.64\text{ V}$), different oxidation reactions of the solution sulfide species occurred, Eqs. (2)–(4), as well as the further oxidation of copper sulfide substrate [25]. Above -0.2 V instability of the system was observed, as it can be seen in the inset in Fig. 4. In cathodic direction, one shoulder positioned at -0.6 V , and huge peak with the maximum at -0.75 V were observed.

On the contrary, Cu_{2-x}S modified polypyrrole electrode had a much smaller peak at -0.97 V , disappearance of the followed broad peak, and better stability above -0.2 V . The smaller cathodic peak and the absence of the shoulder positioned at -0.6 V could indicate better oxidation stability of the deposited Cu_{2-x}S onto PPy. This could be attributed to the possible electronic interactions between polypyrrole and copper sulfide.

Potentiostatic photoelectrochemical measurements were performed in cathodic and anodic region. It should be noted that stable photoactivity was not observed in the potential range of approximately -0.9 to -0.4 V . For the pure Cu_{2-x}S at sufficiently negative potentials e.g. greater than -1.2 V , photoactivity was observed, Fig. 5a, but the photoresponse was very slow and irreproducible. Such behavior could be connected to the Cu_{2-x}S phase transformation. Namely, the reversible standard potential for the reaction [35]:



is -1.133 V (SCE), therefore at more negative potentials, reduction of Cu_2S phase to the photoinactive metallic copper phase is thermodynamically possible. The dark current density of $-120\ \mu\text{A cm}^{-2}$ at -1.25 V could be associated with electrochemical hydrogen evolution and sulfur reduction reactions. Observed photocurrent density of $\sim 5\text{--}10\ \mu\text{A cm}^{-2}$ could be connected to the simultaneous scattered electron transfer from conducting band of the remaining Cu_2S phase to both water and dissolved sulfur molecules. At more positive potentials, e.g. greater than -1.2 V , much better photoactivity was observed, with faster photoresponse. This increased photoactivity could be connected to the substrate phase transformation, observed as a sharp peak at approximately -1 V , see Fig. 4, and only sulfur reduction reaction, due to the kinetic limitation of the hydrogen evolution reaction. Córdova et al. [36] observed similar decrease in photoactivity of well defined Cu_2S phase in sulfide contained solution, which was

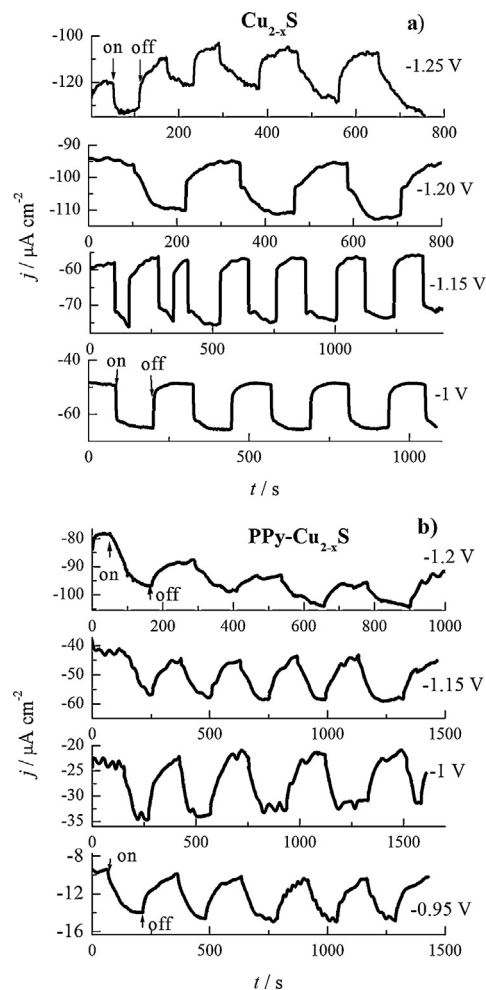


Fig. 5. The dependence of the current density over time for different constant cathodic potentials under dark and illumination (a) pure Cu_{2-x}S and (b) Cu_{2-x}S modified polypyrrole electrodes.

also explained by Cu_2S reduction reaction. For the Cu_{2-x}S modified polypyrrole, Fig. 5b, the same magnitude of the photocurrent density was observed, but photoresponse was slower, indicating some additional charge transfer reactions, most probably recombination of the hole–electron pairs.

At the anodic polarization, Cu_{2-x}S electrode exhibited anodic photoresponse, Fig. 6a. But it was observed that in the dark, steady state current density could not be reached even after 600 s, indicating formation of the holes (probably due to the thermal excitation), and self-oxidation. On the contrary, for Cu_{2-x}S modified polypyrrole much higher dark steady state currents, in the range of few hundred microamperes were observed, Fig. 6b. The stable photocurrent density of $\sim 30\text{--}100\ \mu\text{A cm}^{-2}$ was almost five times higher than in the case of pure Cu_{2-x}S electrode.

Fig. 7 shows summarized dependence of the steady state photocurrent density on the applied potentials, in comparison to the cyclic voltammograms of the investigated materials. It is evident that during cathodic polarization up to -1.15 V , both materials had similar photoactivity. Below -1.2 V decreased activity could be connected to phase transformation of Cu_2S , and in addition, for $\text{PPy-Cu}_2\text{S}$ decrease of the PPy conductivity, widening of the PPy band gap to 3.2 eV and absorption of only UV light. On the contrary, in anodic direction, $\text{PPy-Cu}_{2-x}\text{S}$ possesses much better activity, then pure Cu_{2-x}S , in the reaction of photoelectrochemical oxidation of sulfide.

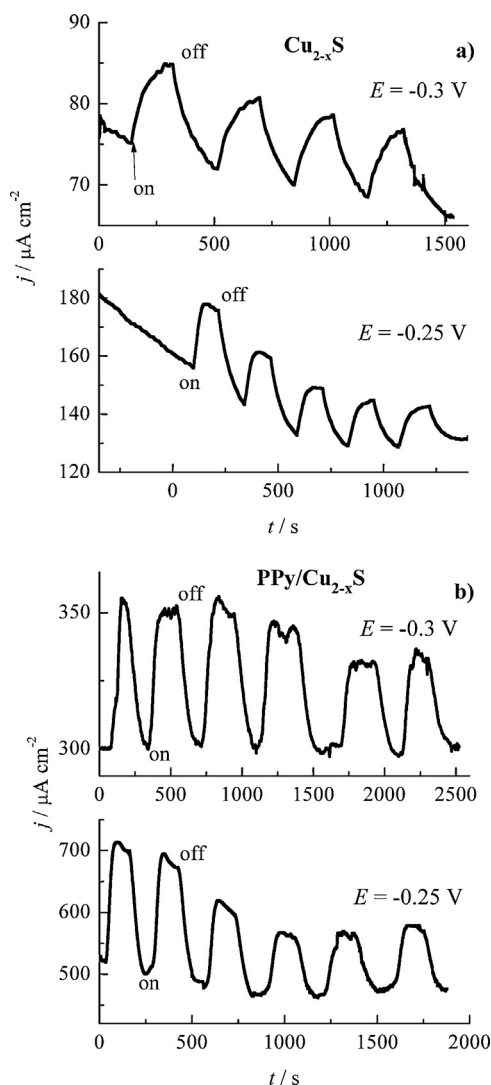


Fig. 6. The dependence of the current density over time for different constant anodic potentials under dark and illumination (a) pure Cu_{2-x}S and (b) Cu_{2-x}S modified polypyrrole electrodes.

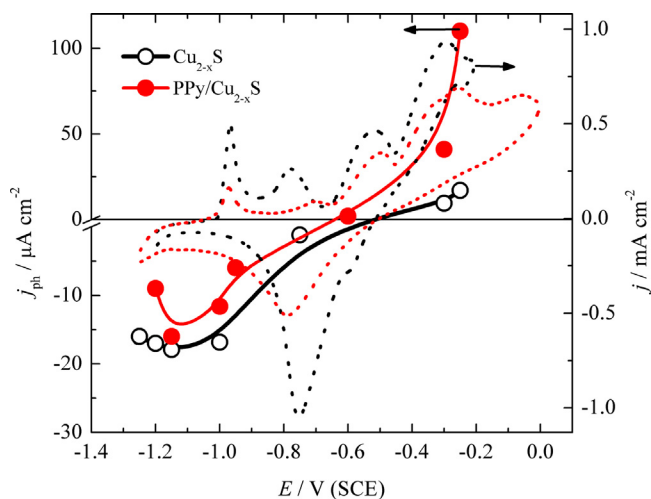


Fig. 7. Dependence of the steady state photocurrent on applied potentials, in comparison with the cyclic voltammograms of the investigated materials.

3.3. Possible charge transfer reactions

The band gap structure of the PPy was elaborated in Section 3.1. The band gap energy of Cu_{2-x}S phases exhibited stoichiometry dependence. An increase in the band gap occurred with an increase of the x value in the bulk copper sulfide, with some data scattering depending on the reports: $E_g = 1.2$ eV for Cu_2S , 1.35 eV for $\text{Cu}_{1.96}\text{S}$, 1.75 eV for $\text{Cu}_{1.8}\text{S}$, 2.11 eV for $\text{Cu}_{1.75}\text{S}$ and 2.2 eV for CuS [20,21]. In covellite, CuS , the valency of copper is still debated, but some recent studies shown that practically in all copper sulfides valence is around +1 [37]. Gadgil et al. [20] have shown that the valence band (VB) energy of -5.3 ± 0.1 eV had not changed as the phases of the bulk Cu_{2-x}S changed from chalcocite to djurleite, only the conducting band (CB) energy level changed. Because in practically all Cu_{2-x}S phases copper has a valency of approximately +1 the same position for VB at -5.3 ± 0.1 eV could be assumed, in the first approximation, for all phases. Position of conduction band for different x values in Cu_{2-x}S was estimated by addition of the band gap energies to the valence energy band. Based on these considerations in Fig. 8, possible energy band gap diagram for the bulk materials is shown. The positions of band energies are shown against absolute vacuum and corresponding reference electrode scale taking into account that $E_{\text{SCE}}=0$ is equivalent to -4.68 eV [38]. Polypyrrole and Cu_{2-x}S are both considered as a p-type semiconductors [14,37], and the Fermi levels could be positioned at ~ 0.05 – 0.25 eV above PPy HOMO and Cu_{2-x}S valence band [3]. Fermi levels of the redox species in the solution corresponds to their reversible potentials. The work function, Φ , for the Pt was assumed to be -5.4 eV [39], and for glassy carbon at approximately -4.5 eV [40].

Based on the proposed band diagram in Fig. 8, the approximate structure of the band gap and charge transfer reactions of Cu_{2-x}S modified PPy under cathodic and anodic bias are schematically presented in Fig. 9b. Owing to the porous structure of the Cu_{2-x}S film, formation of the electron–hole pairs can occur simultaneously in both materials. Under the cathodic bias electrons from CB could be recombined, either with holes on PPy HOMO, or with holes from Cu_{2-x}S VB. At sufficiently negative potentials excited electrons from PPy LUMO or Cu_{2-x}S CB, can be involved in reduction of the water or sulfur molecules, depending on hole–electron recombination path. At less negative cathodic potentials, due to the thermodynamic limitations of the hydrogen evolution reaction, only reduction of sulfur molecules can occur. Simultaneously, holes that are not recombined can be transferred to the Fermi level of the glassy carbon. Under anodic bias, Fig. 9b,

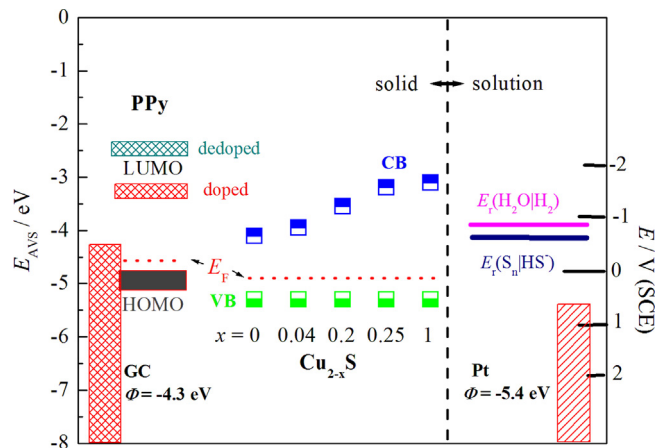


Fig. 8. Proposed energy band diagram of the photoelectrochemical cell considering bulk materials (positions of valence (VB) and conduction (CB) bands of Cu_{2-x}S for different x values; E_F – Fermi level, Φ – work function).

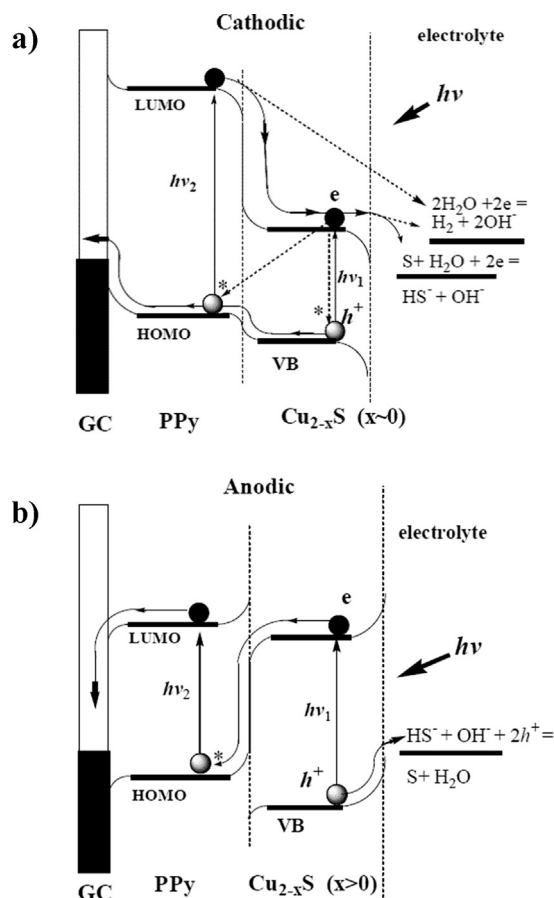


Fig. 9. The approximative structure of the charge transfer reactions of Cu_{2-x}S modified PPy under illumination for (a) cathodic and (b) anodic bias.

due to the better energy alignment, fast recombination of the electrons from Cu_{2-x}S CB with holes on the PPy HOMO occur. Because holes from Cu_{2-x}S VB cannot be sufficiently fast recombined, average effective life and diffusion length is probably much higher than in pure Cu_{2-x}S . Consequently, holes easily oxidize HS^- , instead of adjacent Cu_{2-x}S in the reaction of photocorrosion.

4. Conclusions

The Cu_{2-x}S was successfully deposited onto PPy using simple successive ion-layer adsorption and reaction procedure. It was observed that under cathodic polarization and illumination the pure Cu_{2-x}S and Cu_{2-x}S modified PPy shows similar behavior. On the contrary, under anodic polarization, significant improvement in photactivity of Cu_{2-x}S modified PPy was achieved. Such behavior was explained by recombination of electrons from Cu_{2-x}S conducting band with the holes of the PPy LUMO, resulting in the increased effective life and diffusion length of the Cu_{2-x}S holes, which easily oxidize HS^- , instead of adjacent Cu_{2-x}S in the reaction of photocorrosion.

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