



Hybrid electrochemical/electrochromic Cu(II) ion sensor prototype based on PANI/ITO-electrode



Megha A. Deshmukh^{a,b}, Mindaugas Gicevicius^a, Almira Ramanaviciene^c, Mahendra D. Shirsat^b, Roman Viter^{a,d}, Arunas Ramanavicius^{a,*}

^a Vilnius University, Faculty of Chemistry and Geoscience, Department of Physical Chemistry, Naugarduko St. 24, LT-03225, Vilnius, Lithuania

^b Dr. Babasaheb Ambedkar Marathwada University, Department of Physics, Intelligent Material Research Laboratory, Aurangabad, MS 431 004, India

^c Vilnius University, Faculty of Chemistry and Geoscience, Department of Analytical and Environmental Chemistry, Naugarduko St. 24, LT-03225, Vilnius, Lithuania

^d University of Latvia, Institute of Atomic Physics and Spectroscopy, 19, Raina Blvd., LV-1586 Riga, Latvia

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ABSTRACT

Conducting polymer polyaniline (PANI) based electrochromic films were electrochemically synthesized on indium tin oxide (ITO) covered glass electrodes and their electrochromic performances were investigated by spectroscopic methods before and after the incubation in Cu(II) ion containing aqueous solution. Chemical structure of synthesized PANI layer was evaluated by FTIR. The electrochromic performance of PANI film was determined by measuring of spectroscopic signals before and after the incubation of PANI film coated electrode in Cu(II) ion containing solution. During the change of potential, which was applied to PANI-modified electrode, the colour of PANI thin film turned from green to blue, dark blue, colorless and yellow dependently on the applied potential. Significant alteration of electrochromic effect was observed after the incubation of PANI/ITO-modified electrode in Cu(II) ion containing solution. It was also found that the PANI films exhibited highest optical contrast if potential profile of 0.200 mV vs Ag/AgCl_(3M KCl) was applied. Applicability of PANI/ITO-electrode for electrochromic effect based determination of Cu(II) ions was also evaluated. Investigated PANI/ITO-electrode response to Cu(II) ions indicates that PANI/ITO-electrodes can be used for both chronoamperometric and electrochromic detection of Cu(II) ions.

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1. Introduction

Water pollution is one of the major types of environmental pollutions. It is responsible for increasing health risk of humans and many aquatic animals. Heavy metal ions (HMI) viz. Pb(II), Cd(II), Cu(II), Hg(II) and Co(II) etc. are major water pollutants coming from the sewage of chemical industries. It is well known that Cu(II) is the most toxic element for the aquatic life particularly for fish. Dangerous level of Cu(II) ions also severely effects on the human health too, which leads to increase in blood pressure, adverse effect on respiratory system, liver damage, neurotoxicity, neurodegenerative diseases and acute hemolytic anemia [1–3]. Cu(II) ions also show their adverse effects on microorganisms and earthworms,

which indirectly interrupt the natural ecosystem and decomposition of organic matter may seriously slow down [4]. However usage and production of Cu(II) ions has been significantly increased from last decade, which inappropriately broadens the disposal of Cu(II)-containing waste water and spectra of Cu(II) in environment [5–7]. The adverse effects of Cu(II) ions manifest at fairly very low concentrations. Therefore, maximal permissible limit of Cu(II) ions is 1.0 ppm (0.9988 mg/L) [8].

Thus, there is a great demand for the selective and sensitive detection of Cu(II) ions, which are generated by various sources. A broad variety of organic and inorganic materials play an important role in the field of metal ion detection, because they could be applied to increase sensitivity and/or selectivity towards metal ions such as Cu(II) [9,10] Cd(II) [11] etc. Recently conducting polymers [12–14], carbon nanotubes [15,16] and metal oxides [17] have been explored to improve the detection of heavy metal ions. Conducting polymers are the most attractive materials due to their electrical and mechanical properties as well as environmental stability, low cost, ease of synthesis and due to their unique electric charge

* Corresponding author at: Vilnius University, Faculty of Chemistry and Geoscience, Department of Physical Chemistry, Naugarduko St. 24 LT-03225, Vilnius, Lithuania.

E-mail address: arunas.ramanavicius@chf.vu.lt (A. Ramanavicius).

transfer properties [18]. Their electrical and electrochemical properties could be easily tailored and controlled by doping of various materials and ions [19,20].

The tailoring of conducting polymer properties during electrochemical synthesis by manipulating various parameters such as potential, current, scan rate, time etc. is technologically advantageous possibility, which can be exploited in sensor and biosensor design [21]. Among the wide family of conducting polymers polyaniline (PANI), polythiophene (PTH) and polypyrrole (Ppy) are of greatest interest due to their high technological potential, which has been exploited in the designing of super capacitors, rechargeable batteries, corrosion prevention, sensors, solar cells and electrochromic devices [22–24]. However, among all conducting polymers PANI is one of the most prominent materials due to its excellent electrical, mechanical properties, easy synthesis and significant environmental stability.

In addition to various technological applications of PANI in some researches PANI-based electrochemical sensors dedicated for the determination of heavy metal ions (HMI) [25,26], have been reported. Such sensors potentially can replace liquid phase chromatography [27,28], solid phase chromatography [29–31], atomic absorption spectroscopy (AAS) [32–34], X-ray fluorescence [35,36], which are the most commonly used and expensive techniques for the analysis of HMI.

The monitoring of HMI is successfully performed by electrochemical techniques out of which one of the most widely preferred is stripping voltammetry [37–39]. However, even stripping voltammetry is long lasting and complex procedure, which is based on several technological steps [40]. The major disadvantage of stripping voltammetry is that in the analyte 'accumulation' step there is obvious possibility to accumulate or pre-concentrate such metal ions, which are not of interest. Moreover, metal ions, which have extensively large reduction potential, in most common cases may not be pre-concentrated by standard 'accumulation' step used in regular stripping voltammetry technique. Therefore, in such cases another electrochemical methods are required for the determination of heavy metal ion concentrations. One of such alternative methods is differential pulse voltammetry (DPV) [41].

Due to number of above listed limitations and shortcomings of existing detection techniques, new heavy metal detection methods and new materials suitable for these methods are of constant interest. Therefore, conducting polymers such as electrochemically synthesized PANI were also applied in the detection of heavy metal ions [42,43]. Among many conducting polymers PANI is considered as attractive electrochromic material due to its high colour contrast at multiple coloured states [22,44,45]. Reversible optical change of PANI appears due to electron transfer (redox) process or applied sufficient electrochemical voltage [46], therefore it is expected that PANI can act as an interesting electrochromic material suitable for optical sensing. PANI film frequently shows multiple changes in colour at its different redox states such as (i) leucoemeraldine, (ii) pernigraniline, (iii) emeraldine [47]. Typically, the colour of PANI depends on its optical absorption characteristics mainly attributed to polarons and bipolarons associated with the formation of quinoid units due to the oxidation/reduction-based transformation of aniline from amine to imine groups [48]. Most promisingly, the PANI/(metal complex)-based interfacial structures are showing very important features suitable for various scientific and technological interests [49,50]. However, according to best of our knowledge there are no reports on possible application of electrochromic effects of PANI in the determination of heavy metal ions. Hence, it is of considerable interest to evaluate principle sensitivity of PANI film towards Cu(II) ions and effect of Cu(II) ions to the electrochromic properties of synthesized PANI film.

The foremost aim of this study was to evaluate the effect of Cu(II) ions on the electrochromic and some electrochemical responses of PANI film deposited on indium tin oxide (ITO) substrate.

2. Experimental

2.1. Materials and methods

Aniline of reagent grade was purchased from Fluka (Germany) and used after filtration through 5 cm length column filled by Al_2O_3 in order to remove coloured impurities. H_2SO_4 and CuCl_2 were purchased from Carl Roth GmbH (Germany), phosphate buffer, pH 7.4, tablets and other chemicals were of reagent grade quality and used as received from Sigma-Aldrich (USA). Indium Tin Oxide (ITO) ITO-coated glass (surface resistivity 15–25 Ω/sq) was purchased from Sigma-Aldrich (Germany). Deionized water was used for preparation of all aqueous solutions.

2.2. Apparatus

Electrochemical measurements were performed with potentiostat/galvanostat Autolab PGSTAT128N controlled by NOVA 1.10 software, both from ECO-Chemie (Utrecht, Netherlands). All electrochemical measurements were carried out in three electrode cell system using ITO-coated glass as a working electrode, $\text{Ag}/\text{AgCl}/3\text{M KCl}$ electrode ($\text{Ag}/\text{AgCl}_{(3\text{MKCl})}$) as a reference electrode and platinum wire as a counter electrode.

FTIR measurements for the confirmation of chemical composition of PANI films and bonding of Cu(II) ions studies were carried out using FTIR-ATR spectrophotometer 'Frontier' from Perkin Elmer (Waltham, USA). Horizontal attenuated total reflectance at 65° angle was registered, 10 registration scans were performed at 1 cm^{-1} resolution. PANI layers deposited on ITO coated glass were investigated before and after incubation in 1 mM CuCl_2 solution.

Optical absorbance measurements were carried out using Ocean Optics USB4000 spectrophotometer from Ocean optics spectra (Dunedin, USA) controlled by Spectra Suite software. All measurements were carried out at room temperature. All electrochemical potential values were defined versus $\text{Ag}/\text{AgCl}_{(3\text{MKCl})}$ electrode.

2.3. Electrochemical synthesis

Solution containing 0.25 M aniline, 0.2 M sulphuric acid and 0.05 M K_2HPO_4 was used for the electrochemical synthesis of PANI. Before electrochemical synthesis the solution homogenized by stirring for 20 min. Electrochemical synthesis of PANI was performed by cycling the potential of the ITO glass working electrode between 0.1 V–1.0 V vs $\text{Ag}/\text{AgCl}_{(3\text{MKCl})}$ $\text{Ag}/\text{AgCl}_{(3\text{M KCl})}$ 10 times at a potential sweep rate of 0.1 V/s in the previously mentioned polymerization solution.

2.4. Electrochemical measurements

Cyclic voltammetry (CV) technique was used for primary electrochemical characterization of PANI modified ITO electrodes (PANI/ITO-electrodes) in the potential range from 0.1 to 1.0 V at the scan rate of 100 mV/s.

The DPV was performed prior and after the incubation of PANI/ITO-electrode in Cu(II) ions containing solution in order to observe the change of electrochemical properties Cu(II)-modified PANI/ITO-electrodes (Cu(II)/PANI/ITO-electrodes) caused by Cu(II) ions. Before heavy metal analysis PANI/ITO-electrode was incubated in the solution of 0.02 mM CuCl_2 , 0.2 M H_2SO_4 and 0.05 M K_2HPO_4 for 20 min under continuous stirring. After this Cu(II)/PANI/ITO-electrode was removed from the solution,

thoroughly rinsed with water and analysed again. For the differential pulse voltammetry (DPV) based analysis potentials of both PANI/ITO-electrode and Cu(II)/PANI/ITO-electrode were swept from -0.1 V to -0.4 V vs Ag/AgCl_(3MKCl) at the sweep rate of 100 mV/s. All measurements were performed in aqueous solution containing 0.05 M K₂HPO₄ and 0.2 M H₂SO₄.

2.5. Simultaneous electrochemical and electrochromic measurements

During this investigation we have simultaneously studied the electrochemical and electrochromic performances of PANI film before and after the incubation of ITO/PANI-electrode in solution 0.02 mM of CuCl₂, 0.2 M H₂SO₄ and 0.05 M K₂HPO₄. For these investigations the PANI/ITO- or modified Cu(II)/PANI/ITO-electrode was used as working electrode, Pt wire was used as counter electrode and Ag/AgCl_(3MKCl) as reference electrode. All electrodes were installed in specialized electrochemical/optical cell, which was placed in spectrophotometer quartz cuvette. The length of optical path in this cuvette was 1 cm and the beam passed the PANI/ITO-electrode at right angle. Two potential steps based pulse profile was applied in order to generate chronoamperometric and electrochromic responses of PANI/ITO- and Cu(II)/PANI/ITO-electrodes. Several potential pulse profiles with different low/high potential values ((i) 490/820 mV, (ii) 0.0/820 mV, (iii) 0.0/1000 mV, (iv) $-200/820$ mV, (v) 490/820 mV) were applied and electrochromic and chronoamperometric signals of PANI/ITO- and Cu(II)/PANI/ITO-electrodes were registered and evaluated in this investigation. Electrochromic and chronoamperometric signals were registered simultaneously.

For the evaluation of Cu(II) ions influence on PANI films, PANI/ITO-electrodes were incubated in the solution of 0.2 M H₂SO₄ and 0.05 M K₂HPO₄ containing 0.02 mM of CuCl₂ under continuous stirring for 20 min at room temperature. Colour changes of PANI/ITO-electrode and cyclic voltammograms were recorded simultaneously, potential was swept within -0.1 V and 1.4 V vs Ag/AgCl_(3MKCl) before and after incubation in Cu(II) ions containing solution.

Rough optical kinetics of PANI film was evaluated by calculating the time that was required to reach 95% of steady-state optical absorption, which was calculated as the arithmetic difference between lowest and highest optical transmittance states. The average time values of optical signals registered during five potential pulses of each applied pulse sequence were taken into account during above mentioned calculation.

3. Results and discussion

3.1. Electrochemical deposition of PANI layer on the ITO-based electrode

ITO coated substrates are the most widely used as electrode materials for the deposition of polymer films, because they offer an improved adhesion of conducting polymers and enhance electrochemical performance as well as life time of the optoelectronic devices [51]. During electrochemical synthesis of PANI on the surface of ITO electrode, typical oxidation and reduction peaks were observed at respective potentials of registered cyclic voltammograms. As the number of cycles has increased the current density has also increased, indicating the increase of electrochemically active surface area due to formation of electrically conducting PANI film over the ITO layer.

Dark green coloured coating was formed on the surface of ITO-based transferable working electrode during electrochemical synthesis, which confirms the successful synthesis of PANI film.

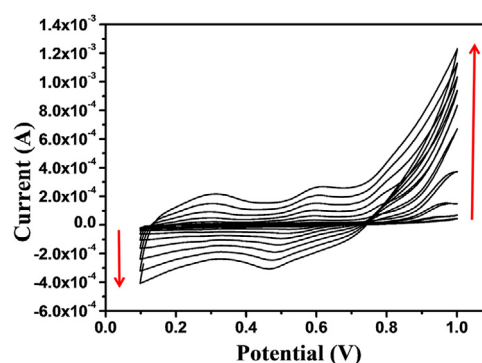


Fig. 1. Cyclic voltammograms registered during the formation of PANI film on ITO modified glass substrate at 0.1 V/s potential sweep rate, the potential was swept between 0.1 V–1.0 V vs Ag/AgCl_(3MKCl).

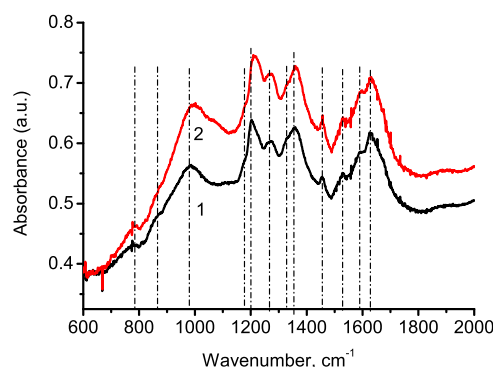


Fig. 2. Fourier transformation infrared (FTIR) spectrum of: (i) pristine PANI/ITO-electrode before incubation (curve 1) and (ii) after incubation (Cu(II)/PANI/ITO-electrode) (curve 2) in 0.02 mM solution of CuCl₂.

Fig. 1 represents cyclic voltammograms recorded during electrochemical deposition of PANI on ITO-modified glass substrate based electrode. After this procedure PANI/ITO-electrodes were rinsed thoroughly with water and dried for 24 h.

3.2. Fourier transformation infrared (FTIR) spectroscopic analysis of synthesized PANI films

Fig. 2 shows the FTIR absorbance spectra of: (i) pristine PANI/ITO-electrode before incubation in CuCl₂ solution (Fig. 2, curve 1) and (ii) Cu(II)/PANI/ITO-electrode after 20 min incubation in 0.02 mM solution of CuCl₂ (Fig. 2, curve 2). FTIR spectrum of pristine PANI/ITO-electrode has absorption peaks, centred at 785, 875, 984, 1202, 1211, 1272, 1325, 1356, 1454, 1525, 1585 and 1627 cm⁻¹, which could correspond to 1,4 substitution pattern of benzene ring, C–H bonding mode of aromatic rings (out of plane bending), C–H bonding mode of aromatic rings (in plane bending), HSO₄⁻ doping anions, C–H deformation mode, C–N stretching vibration of primary amine, C–N stretching of aromatic secondary amine, C–N stretching in the neighbourhood of a quinonoid ring, C=N stretching in aromatic ring, C=C stretching in quinoid ring, stretching mode of the N=Q=N quinoid rings and C–N stretching in aromatic amine, respectively [52–58].

After the incubation of Cu(II) the FTIR spectrum of Cu(II)/PANI/ITO-electrode has changed and following peaks were observed: 785, 880, 996, 1204, 1217, 1274, 1326, 1362, 1457, 1529, 1589 and 1631 cm⁻¹. Incubation of PANI/ITO-electrode in CuCl₂ resulted in increase of optical absorbance of Cu(II)/PANI/ITO-electrode. The peaks, related to quinoid rings appeared at the same positions. Significant decrease of the peak intensities was observed after incubation in CuCl₂ for peaks at 1204 and 1326 cm⁻¹, which

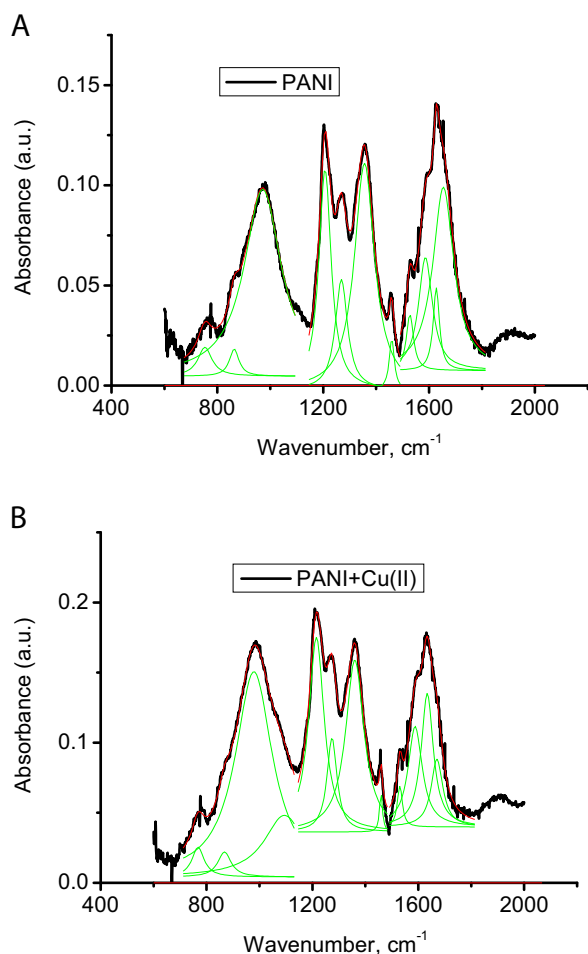


Fig. 3. Deconvolution of FTIR spectra of: (A) PANI film on PANI/ITO-electrode. (B) Cu(II)/PANI film on Cu(II)/PANI/ITO-electrode, which was formed after the incubation of PANI/ITO-electrode in 0.02 mM solution of CuCl_2 .

are related to doping by HSO_4^- ions and C–N stretching of aromatic secondary amine, respectively. Significant shifts towards higher wavenumbers for PANI peaks at 984, 1202 and 1274 cm^{-1} were induced by their interaction with Cu(II).

It was found that electrochemically fabricated PANI films in the presence of Cu(II) ion typically results in 6–30 cm^{-1} shift of 1589 cm^{-1} peak [58]. Interaction of PANI with other metal ions also resulted in FTIR peaks towards higher wavelengths due to forming of coordinate covalent bonds between PANI chains and metal ions [53,58]. We suppose that not significant changes of IR modes of quinoid rings are related to PANI film interaction with Cu(II) ions. Shift of peaks positions of amine groups in PANI molecule indicate forming of coordinate covalent bonds between PANI and Cu(II) ions. In addition partial deprotonation by the replacement of some protons of PANI by Cu(II) ions can influence some changes in FTIR spectra [58]. From this fact it can be predicted that the interaction of PANI with Cu(II) ions is related to partial deprotonation of imine and amine nitrogen atoms of PANI, then that deprotonated imine and amine nitrogen atoms are forming complexes with coordinating Cu(II) ions. Therefore, this effect also could have an influence to the change of the PANI electronic structure (Fig. 3).

3.3. Investigation of electrochromic effect

Fig. 4 shows cyclic voltammograms of PANI films: (i) pristine PANI/ITO-electrode before the treatment with Cu(II) ion containing solution (Fig. 4, curve 1), (ii) Cu(II)/PANI/ITO-electrode

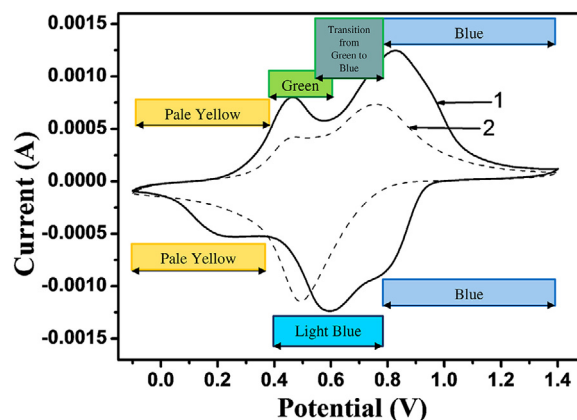


Fig. 4. CVs of: pristine PANI/ITO-electrode (solid line) and Cu(II)/PANI/ITO-electrode, which was formed by incubation of PANI/ITO-electrode (dash line) in 0.02 M solution of CuCl_2 .

(PANI/ITO-electrode after the incubation in Cu(II) containing solution) (Fig. 4, curve 2). In cyclic voltammogram of Cu(II) modified PANI/ITO-electrode two main oxidation peaks at about 0.46 V vs $\text{Ag}/\text{AgCl}_{(3\text{MKCl})}$ (green) and 0.82 V vs $\text{Ag}/\text{AgCl}_{(3\text{MKCl})}$ (blue) were observed. These two peaks are representing transitions from reduced leucoemeraldine form of PANI to partially oxidized emeraldine form and fully oxidized pernigraniline form, respectively. After the incubation of PANI/ITO-electrode in Cu(II) ions containing solution reduction peaks of cyclic voltammograms at 0.230 mV and 0.793 mV have significantly decreased, and only one reduction peak, which appeared at 0.487 mV vs $\text{Ag}/\text{AgCl}_{(3\text{MKCl})}$, was observed.

Observations of electrochromic effects of oxidized form of PANI film shows that colour of PANI film is changing from green (at 0.467 mV vs $\text{Ag}/\text{AgCl}_{(3\text{MKCl})}$) to blue (at 0.828 mV vs $\text{Ag}/\text{AgCl}_{(3\text{MKCl})}$) (Fig. 4), while the reduction peaks were observed at about 0.793 mV vs $\text{Ag}/\text{AgCl}_{(3\text{MKCl})}$, 0.588 mV vs $\text{Ag}/\text{AgCl}_{(3\text{MKCl})}$ and 0.230 V vs $\text{Ag}/\text{AgCl}_{(3\text{MKCl})}$ (Fig. 4) and the film was changing colour from blue to light blue and then to pale yellow, respectively. These changes are related to different absorbance of PANI film in visible region at above mentioned potentials. This effect was observed in both cases before and after the incubation of PANI/ITO-electrode in Cu(II) ions containing solution. The change in optical absorbance spectrum before the incubation of pristine PANI/ITO-electrode in Cu(II) ions containing solution originates from emerging polaron band, caused by applied potential.

The increase of optical transmittance of Cu(II)/PANI/ITO- compared to pristine PANI/ITO-electrode was observed. Therefore, in next part of the experiment, changes of optical transmittance of PANI/ITO- and Cu(II)/PANI/ITO-electrodes were registered at different potentials. Optical transmittance spectra of PANI/ITO-electrodes are shown in Fig. 5A. The increase of the applied potential decreases optical transmittance value of the PANI films. Adsorption/complexation of Cu(II) ions results the increase of the PANI film optical transmittance of Cu(II)/PANI/ITO-electrodes. From Fig. 5A it is clearly observed that PANI film after the incubation of PANI/ITO-electrode in Cu(II) ions containing solution (Cu(II)/PANI/ITO-electrode) shows the increase of optical transmittance compared to that of pristine PANI/ITO-electrode registered before the incubation of this electrode in Cu(II) containing solution.

Rough optical kinetics of PANI film was evaluated as it is described in experimental part and is presented in Fig. 6B1–B5. The response time for PANI/ITO was 2.05 s and for Cu(II)/PANI/ITO it was 1.85 s. The difference of response time reveals that copper ions have increased the rate of the optical response. This optical effect was greater in those potential-pulls phases during which

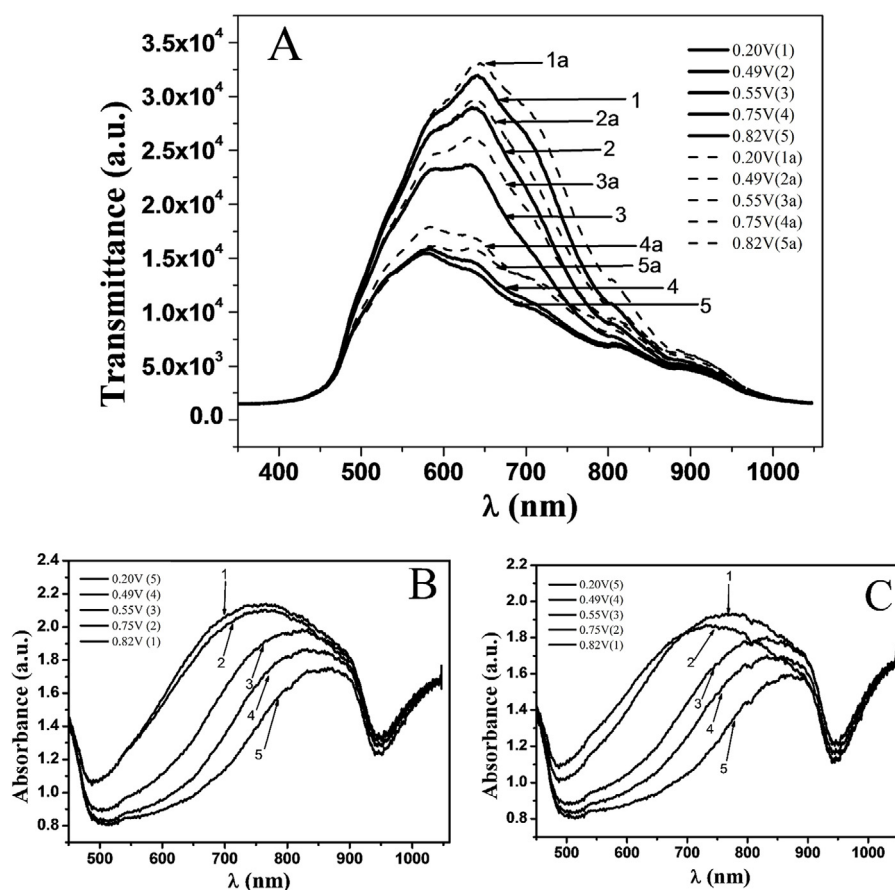


Fig. 5. Transmitted light intensity of PANI/ITO-electrode (dashed line) and Cu(II)/PANI/ITO-electrode (solid line) at different electrode potentials (A); Calculated absorbance spectra of PANI/ITO-electrode (B) and Cu(II)/PANI/ITO-electrode, which was formed by incubation of PANI/ITO-electrode in 0.02 M solution of CuCl₂ (C).

potentials decreased and it was less expressed in those phases during which potentials decreased. Considering that pristine PANI is less conducting therefore it could act as more significant barrier for electrons to enter to and get out from PANI surface during the redox reaction and consequently it slows down the switching of PANI optical signal during the rectangular potential pulse. On the other hand, the kinetics of optical response of PANI film, which was incubated in Cu(II) ions containing solution, confirmed different electrochromic behaviour compared with that of pristine PANI film, which was not incubated in Cu(II) ions containing solution. From above visible spectra it is clearly observed that after the incubation of PANI/ITO-electrode in Cu(II) ions containing solution the intensity of optical absorbance decreases (Fig. 5B,C). The most significant changes were observed when the negative potentials were applied to PANI/ITO-electrode. Above mentioned results confirm that Cu(II) ions significantly affect the optical absorbance of PANI film, which is registered at different potentials applied on PANI/ITO-electrode.

Absorbance spectra of PANI layers, which were calculated by subtraction of spectra of pristine ITO-electrode from that of the PANI/ITO-electrode at corresponding potentials, before and after the incubation in Cu(II) ion containing solutions are presented in Fig. 4B and C, respectively. Constant absorption band at 400–500 nm is accounted for $\pi \rightarrow \pi^*$ electronic transition. PANI layer initially showed wide absorption peak in the range of 500–950 nm related to excitonic benzenoid to quinoid transition. During electrochemical oxidation this peak shifts to shorter wavelength indicating the expansion of band gap of PANI film. The applied potential induced the increase of the absorbance value and the blue-shift of the peak. The absorbance value has saturated at

the applied potential of 750–820 mV vs Ag/AgCl_(3MKCl). Incubation of PANI/ITO-electrode in Cu(II) ions containing solution (Fig. 5C) resulted in the decrease of absorbance of PANI films. The decrease of absorbance dropped more significantly at higher values of the potentials applied to PANI/ITO-electrode.

In next part of the experiments changes of colour and optical absorbance of PANI film and chronoamperograms were registered simultaneously while rectangular potential pulses were applied to PANI/ITO-electrode before and after the incubation of the electrode in Cu(II) ions containing solution. Fig. 6 represents results observed during simultaneous chronoamperometric and optical transmittance measurements performed when rectangular potential pulses were applied to pristine PANI/ITO-electrode and Cu(II)/PANI/ITO-electrode. The highest optical transmittance of PANI films has been observed at about 600 nm. Simultaneously, the electrochromic effects of Cu(II)/PANI/ITO-electrodes and pristine PANI films and the reversibility of these effects were evaluated while applying number of sequences of repetitive rectangular potential steps. Each sequence consisted of 10 potential pulses, each pulse lasted for 10 s and working electrode potentials were changing in the range: (i) for the first sequence lower potential was set at 490 mV and higher potential was set at 820 mV, (ii) for the second sequence lower potential – at 0.0 mV and higher potential – at 820 mV, (iii) for the third sequence lower potential – at 0.0 mV, higher potential – at 1000 mV, (iv) for the fourth sequence lower potential – at –200 mV, higher potential – at 820 mV and (v) for the fifth sequence lower potential – at 490 mV, higher potential – at 820 mV. Note that the last sequence is similar to the first one, and it was performed in

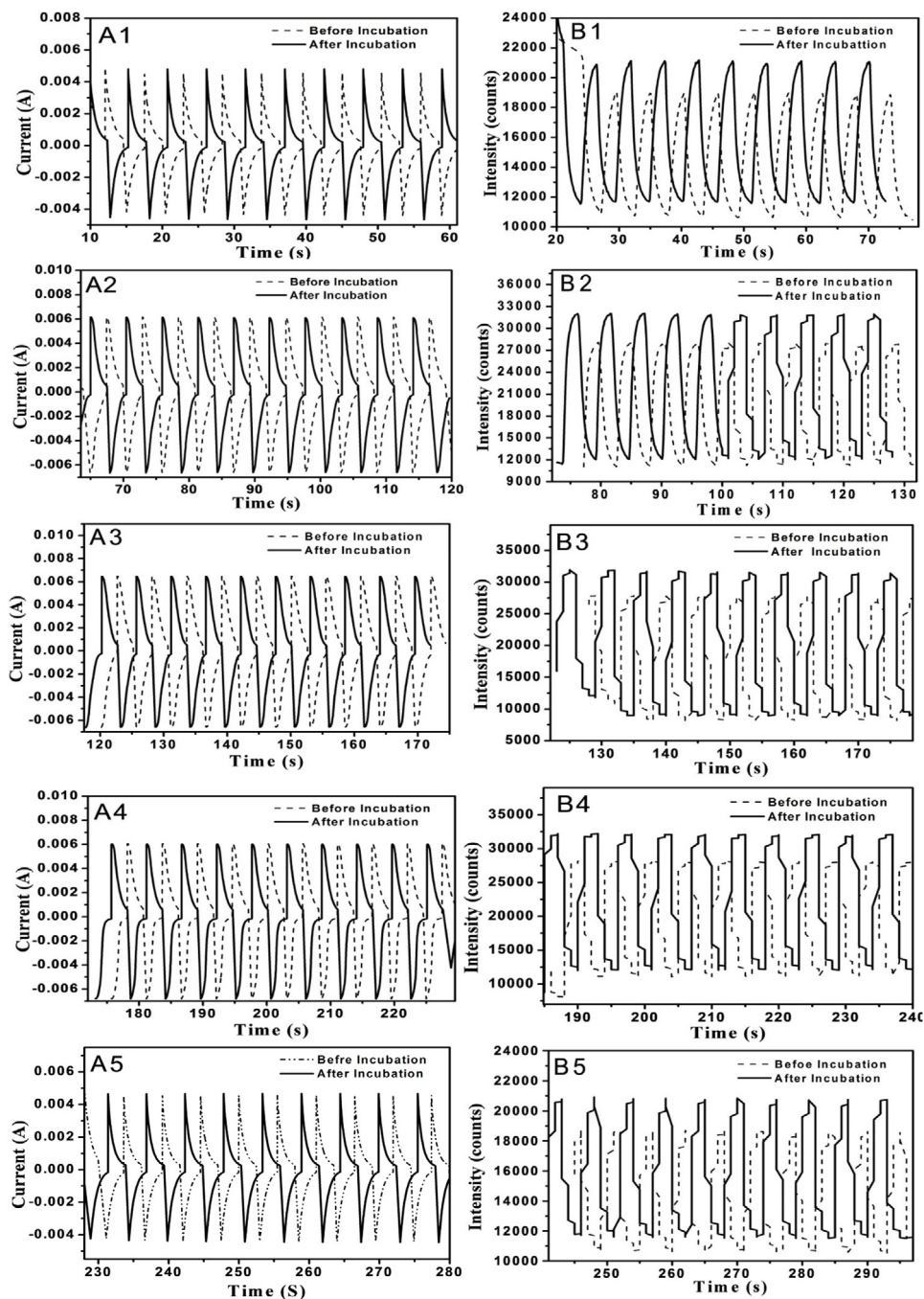


Fig. 6. Performance of PANI/ITO-electrode (dashed lines) and Cu(II)/PANI/ITO-electrode (solid lines), which was formed by the incubation of PANI/ITO-electrode in 0.02 M solution of CuCl_2 towards applied rectangular potential pulses; chronoamperometric signals (A1-A5) and optical absorbance (B1-B5) registered at 600 nm. Potentials of applied rectangular pulse profiles were fixed as: 490/820 mV (A1, B1), 0.00/820 mV (A2, B2), 0.00/1.00 V (A3, B3), -200/820 mV (A4, B4), 490/820 mV (A5, B5).

order to determine the reproducibility of the signals and stability of PANI film during here described electrochemical treatment.

After the incubation of PANI/ITO-electrode in Cu(II) ions containing solution optical transmittance of Cu(II)/PANI/ITO-electrode is increasing compared to that of pristine PANI/ITO-electrode, while chronoamperometric performance of the modified electrode remained unchanged. Such optical effect is related to the incorporation/complexation of Cu(II) ions within PANI layer. It is suggested that this interaction is based on the complexation between Cu(II) ions and deprotonated nitrogen atoms within amine/imine units in PANI layer. After five potential-pulse sequences the difference between the first and the last optical transmittance and chronoam-

perometric signals is lower than 10%. Thus it confirms that films show sufficient reproducibility after here applied electrochemical treatment by above mentioned repetitive sequences of rectangular potential pulses.

3.4. Differential pulse voltammetry of pristine PANI/ITO and Cu(II)/PANI/ITO-electrodes

Fig. 7 demonstrates differential pulse voltammograms of pristine PANI/ITO electrode and the same PANI/ITO-electrode after the incubation in solution containing 0.02 M of CuCl_2 . A current peak with a maximum at -250 mV vs $\text{Ag}/\text{AgCl}_{(3\text{MKCl})}$ was observed for

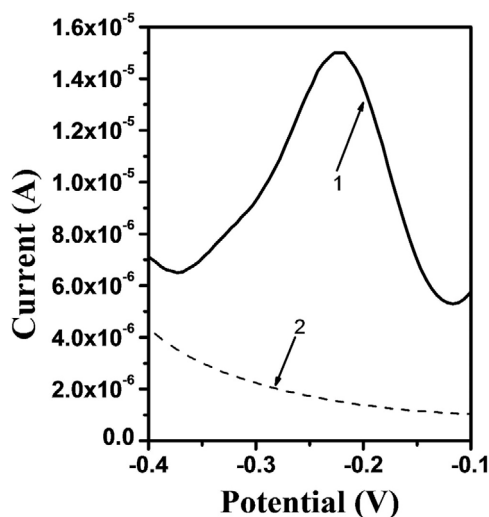


Fig. 7. Differential pulse voltammograms of pristine PANI/ITO-electrode (dashed line) and the same Cu(II)/PANI/ITO-electrode, which was formed by 30 min incubation of PANI/ITO-electrode in solution containing 0.02 mM of CuCl₂ ions (solid line).

Cu(II)/PANI/ITO-electrode, while the peak was absent for PANI/ITO-electrode before it was incubated in Cu(II) ions containing solution. The appearance of this peak clearly confirms the presence of copper ion species incorporated within the PANI layer.

4. Conclusions

Electrochromic PANI film was successfully synthesized on ITO-coated glass substrates by potential cycling. Synthesized PANI film exhibits electrochromic properties with well-defined electrochemical characteristics and sufficient reproducibility during repetitive current and optical absorbance measurements. PANI/ITO-electrode shows both electrochromic and electrochemical response towards Cu(II) ions in aqueous solutions. FTIR spectra confirmed the interaction of Cu(II) ions with PANI film. Differential pulse voltammetry showed that PANI/ITO-electrodes are sensitive to Cu(II) ions. Comparison between peak currents of chronoamperograms, which were recorded when rectangular potential pulses were applied to both types of electrodes, revealed most significant increase of Cu(II)/PANI/ITO-electrode current in comparison to that of pristine PANI/ITO-electrode. For registration of electrochromic responses of PANI/ITO-electrode towards Cu(II) ions the most suitable were potential profiles: 0.00/820 mV vs Ag/AgCl_(3MKCl), 0.00/1.00 V vs Ag/AgCl_(3MKCl), -200/820 mV vs Ag/AgCl_(3MKCl). Investigated PANI/ITO electrode response to presence of Cu(II) ions indicates that PANI/ITO-electrodes can be used for both chronoamperometric and electrochromic detection of Cu(II) ions.

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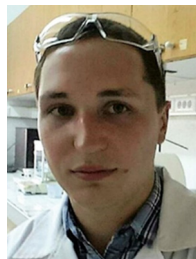
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Biographies



Megha A. Deshmukh currently pursuing her doctoral research in Physics at Dr. Babasaheb Ambedkar Marathwada University, Aurangabad (M.S.) INDIA. She has received her Master of Science degree in 2012 and then continued for research. Her area of interest includes electroanalytical chemistry, composite materials, materials engineering, nanostructured electrode materials and modified electrode surfaces and electrochemical sensors. She has worked on major research project leading to electrochemical sensors, funded by DST SERB and supported by Dr. Babasaheb Ambedkar Marathwada University, Aurangabad (M.S.) INDIA. She is awardee of ERSUMS MUNDUS Euphartes programme for one year at Department of Physical Chemistry, Vilnius University, Vilnius, Lithuania.



Mindaugas Gicevicius is currently a senior student at Vilnius University, Vilnius, Lithuania. Having been involved in research early on in chemistry studies, his current research interests lie within the fields of conductive polymers, electrochromism and sensors.



Prof. Dr. Almira Ramanaviciene is a head of Nanotechnas – Centre for Nanotechnology and Materials Science at the Faculty of Chemistry and Geoscience of Vilnius University, and is head of a biosensor research group at State Research Institute Centre for Innovative Medicine, Lithuania. She received her PhD degree in biomedicine in 2002 from the Institute of Immunology of Vilnius University. In 2008 she completed habilitation procedure in Physical Sciences at Vilnius University. Prof. Dr. Almira Ramanaviciene has comprehensive experience in biosensors and immunosensor development using electrochemical, optical and acoustic signal transducers. She served as expert-evaluator in FP7 program and recently she serves as expert in H2020 program founded by European Commission.



Prof. Dr. Mahendra D. Shirsat is a Professor at Department of Physics, Director at Deen Dayal Upadhyay Kaushal Kendra & RUSA – Center for Advanced Sensor Technology, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad (MS) India. He has completed his Bachelors (B.Sc.), Masters (M.Sc.) and Ph. D. in Physics from Dr. Babasaheb Ambedkar Marathwada University, Aurangabad (MS) India. He has completed Master of Computer Applications (MCA) from IGNOU, New Delhi India. He has completed Post-Doctoral studies at Department of Chemical and Environmental Engineering, University of California, Riverside USA. His area of research includes Functional Materials for Sensors and Optoelectronics Applications which includes nanostructured materials (viz. single walled carbon nanotubes(SWNTs), organic conducting polymers(OCP), porphyrins, phthalocyanine, metal nanoparticles etc.) for Chemiresistive and ChemFET sensing modalities to detect air contaminant (viz. NH_3 , NO , CO , H_2S , Benzene, Xylene etc.) and NLO Material Crystals for optoelectronics applications.



Dr. Roman Viter is a Senior researcher at Institute of Atomic physics and Spectroscopy, University of Latvia, Riga, Latvia. In 2011 he obtained PhD degree in Physics. Recent scientific interests: metal oxides nanostructures (deposition, characterization and applications), structure and optical characterization of novel photonic nanostructures, organic semiconductors and hybrid structures for sensors, optical fiber sensors, semiconductor and surface physics, biosensors and medical applications. He is an active participant of EU funded projects within H2020, Erasmus Mundus, ERA-Net programs and COST actions. Dr Viter is a participant of bilateral projects France-Latvia and Latvia-Ukraine targeted to fabrication of novel nanostructures for optical biosensors for medical applications.



Prof. Habil. Dr. Arunas Ramanavicius is a professor at Vilnius University, Vilnius, Lithuania. He is a head of Department of Physical Chemistry at Vilnius University. He is also leading the laboratory of NanoTechnology at Research Center of Physical Sciences and Technologies. Prof. Arunas Ramanavicius is a member of Lithuanian Academy of sciences. In 1998 he received PhD degree and in 2002 doctor habilitus degree from Vilnius University. Prof. A. Ramanavicius is serving as expert-evaluator in EU-FP7 program coordinated by European Commission and he is technical advisor of many foundations located in European and non-European countries. He has research interests in various aspects of nanotechnology, bionanotechnology, nanomaterials, biosensors, bioelectronics, biofuel cells and MEMS based analytical devices. He is a national coordinator of several nanotechnology related COST actions.