

## Electrochemiluminescent Properties of Organic Films with Incorporated Carbon Nanotubes

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This work describes the study of the electrochemical and electrochemiluminescent properties of electrodes modified by films of polyvinyl alcohol containing luminophor tris-bipyridine ruthenium and carbon nanotubes. Studied electrode structures showed good applicability for the development of nanotechnological ECL-sensors intended for the assay in aqueous mediums.

**Keywords:** Electrogenerated chemiluminescence, Sensor, Carbon nanotubes, Modified electrode, Assay.

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### 1. INTRODUCTION

Method of electrogenerated chemiluminescence (ECL) finds wide application in the analysis for the detection of substances in liquid media [1]. Biology, medicine, ecology, pharmacy, etc. are the main fields of application of this method. The ECL phenomenon represents chemiluminescence, in which reagents arise during the electrolysis process of the solution. Thus, the main analytical signal in the given method is the light emitted due to non-optical excitation that significantly increases the signal/noise ratio and analysis sensitivity. This analysis method is also attractive in view of its high selectivity, realization simplicity, and expressivity [2].

Simultaneously with the growth of popularity of the ECL analysis method, the tendency of transition from usage of high volume laboratory instruments to diminutive analytical devices – sensors – is observed in analytics. For the electrochemical and ECL analysis, it is prospective to produce electrodes of such sensors as layered structures, whose surface is modified by some functional film which contains components (reagents) necessary to perform the quantitative analysis of liquid media [3, 4].

Use of polymer matrices with incorporated carbon nanotubes (CNT) is one of the challenging techniques for producing functional coatings for electrochemical and ECL analysis. In matrix, CNT act as conductors through which charge passes from the electrode surface to the oxidizable/restorable components of the solution during the electrolysis process. Catalytic activity of CNT with respect to the compositions, which do not possess electrochemical activity on traditional electrode materials, is well-known. One more advantage of the electrodes modified by CNT is the lower capacitive current in comparison with usual electrodes that increases the signal/noise ratio at electrochemical detection of analytes. Thus, development and investigation of detector electrode elements, whose surface is modified with the use of modern nanotechnologies, for electrochemical and ECL sensors with high metrological characteristics is a rather actual problem.

The aim of the present work is in the creation and investigation of electrochemical and ECL properties of

detector elements of sensors modified by organic films of polyvinyl alcohol (PVA) with incorporated CNT and organic luminophor tris-bipyridine complex of ruthenium ( $\text{Ru}(\text{bpy})_3^{2+}$ ).

### 2. MATERIALS AND INVESTIGATION METHODS

For the film formation on the electrode surface, the centrifugation method was used. The method consists in the following: solution of film-forming components was deposited on the surface of rotating substrate where it spread by thin layer with further volatilization of the solvent and film formation.

Electrochemical and ECL properties of the films on the surface of plane glassy carbon (SU-2000) electrodes of the sizes of  $15 \times 25$  mm were studied in the present work. Films consisted of film-forming matrix of PVA, CNT, and molecules of water-soluble organic luminophor  $\text{Ru}(\text{bpy})_3^{2+}$ . Ruthenium complex  $\text{Ru}(\text{bpy})_3^{2+}$  used in the work possesses high stability of properties in liquid media and can emit ECL with high quantum efficiency.

To prepare solution of film-forming matrix, 15 mg of PVA (molecular weight is  $M_w \approx 100.000$ ) was dissolved in 2 ml of the mixture of bidistilled water and dimethyl formamide in the volume ratio of 1:1. Mixture was kept at the temperature of  $90^\circ\text{C}$  during 2 hours, then it was cooled to the temperature of  $4^\circ\text{C}$  in refrigerator, and was kept again during 12 hours.

To prepare films of PVA/  $\text{Ru}(\text{bpy})_3^{2+}$  structure without CNT, 5 mg of ruthenium complex  $[\text{Ru}(\text{bpy})_3^{2+}]\text{Cl}_2$  were added to the obtained in such a way solution and mixed at room temperature during 5 min.

To prepare films with CNT, 2 mg of CNT and 5 mg of ruthenium complex  $[\text{Ru}(\text{bpy})_3^{2+}]\text{Cl}_2$  were added to the obtained PVA solution (2 ml), and then they were mixed at room temperature during 1 hour.

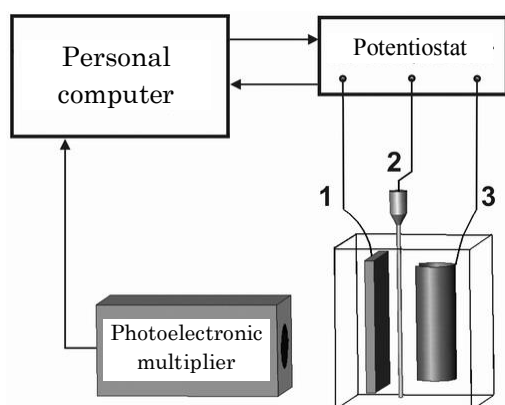
Deposition on the substrate was carried out by the centrifugation method. To this end, 50  $\mu\text{l}$  of solution were deposited on glassy carbon substrate which was rotated with the speed of 3000 rpm during 60 s. After deposition the substrates with the film were kept at the temperature of  $80^\circ\text{C}$  during 1 hour.

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For ECL excitation, the following coreactants were added to the solution: the well-known in the field of aqueous ECL tripropylamine (TPA) and new coreactant sodium tetraphenylborate (STPB) studied earlier in the laboratory of Analytic optochemotronics [5] which works within anodic potential range.  $\text{NaClO}_4$  solution (0,1 M) was used as the supporting electrolyte.

All investigations of the electrochemical and ECL properties of modified electrodes were performed by the method of cyclic voltammetry at the potential scan rate of 100 mV/s on the firmware complex "ELAN-3d" developed in the laboratory of Analytic optochemotronics [6]. In Fig. 1 we show the scheme of the measurement module of the complex.



**Fig. 1** – Scheme of the measurement module of the complex "ELAN-3d": 1 – modified working electrode; 2 – reference electrode; 3 – auxiliary electrode

The substrate modified by the film is placed to the rectangular quartz cell in such a way that the side covered by the film is directed toward the external face of the cell behind which the window of photoelectronic multiplier is situated. The auxiliary electrode represents a platinum foil convoluted in the form of cylinder for the increase in the working surface. Non-modified surfaces of the glassy-carbon substrate were covered by paraffin and window of the area of 50 mm<sup>2</sup> was left uncovered in the working surface.

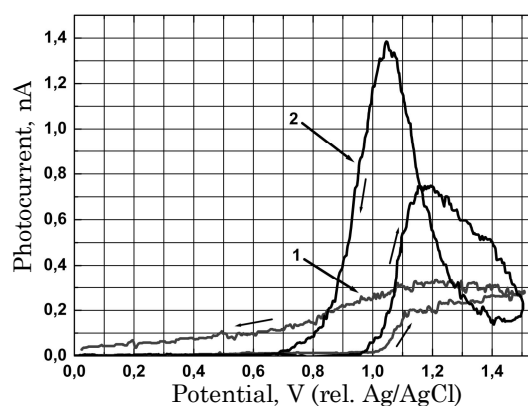
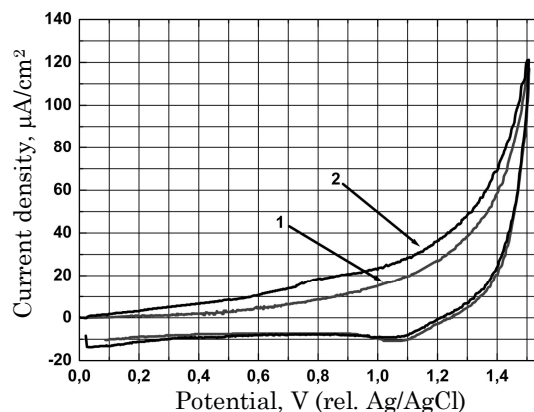
Solution volume in the cell by using polyethylene capillary is connected with the saturated silver chloride reference electrode, relative to which all potentials in the work are measured.

### 3. ANALYSIS OF THE OBTAINED RESULTS

In Fig. 2 we present the investigation results of the electrochemical and ECL behavior of electrodes modified by luminophor  $\text{Ru}(\text{bpy})_3^{2+}$  in PVA matrix in the anodic potential range.

The same results for electrodes modified by luminophor  $\text{Ru}(\text{bpy})_3^{2+}$  in PVA matrix with addition of CNT are illustrated in Fig. 3.

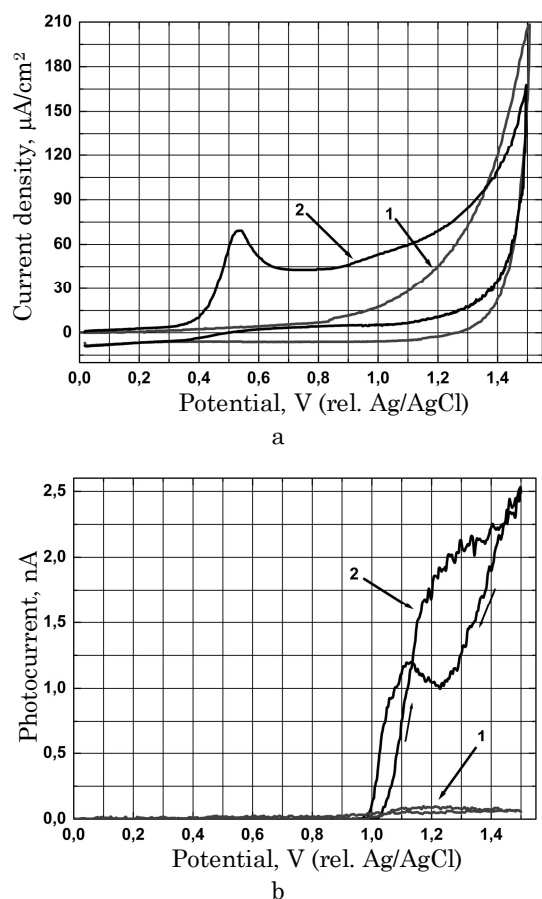
As seen from the comparison of the results of two investigations, with addition of CNT to PVA matrix the background discharge current of the solvent (curve 1 in Fig. 2a and Fig. 3a) increases almost 2 times. Probably, this is conditioned by the increase in the film conductivity due to the charge transfer along CNT which have sufficiently high lateral electroconductivity.



**Fig. 2** – Cyclic voltammetry (a) and ECL response (b) of glassy-carbon electrodes modified by  $\text{Ru}(\text{bpy})_3^{2+}$  in PVA matrix in water without addition of coreactant (1) and with addition of 0,1 mM of TPA (2). 0,1 M  $\text{NaClO}_4$  is the supporting electrolyte

It also follows from the comparison of Fig. 2a and Fig. 3a that electrochemical oxidation wave of STPB is clearly seen at the potential of 0,55 V (Fig. 3a, curve 2), while oxidation waves of TPA are almost not visible (see Fig. 2a, curve 2). Such behavior can have double explanation. First of all, this is the influence on the film conductivity of CNT themselves. Just CNT provide high oxidation current of STPB coreactant in Fig. 3a. Also this behavior can be connected with the structure of PVA matrix in different conditions. Taking into account the fact that PVA is partially dissolved in water turning into gelatinous film, one cannot exclude a strong influence on its structure of solution pH which in this case can be significantly shifted toward alkaline region due to the presence of TPA. At the same time, STPB almost does not influence the given parameter of the solution.

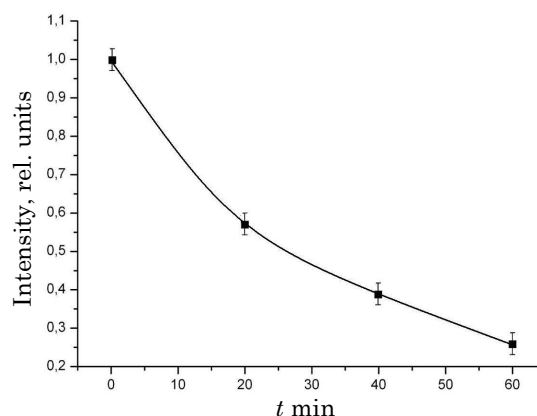
Analysis of the ECL response of the studied films shows sufficient similarity of the processes in both cases. Emission of ECL starts at the potential of about 1 V after beginning of oxidation of luminophor  $\text{Ru}(\text{bpy})_3^{2+}$ . In the second case, maximum ECL intensity is roughly 1,5 times higher, but one cannot conclude definitely if this is conditioned just by the presence of CNT in the film. We have to note that the backward ECL wave in Fig. 2b (curve 2) is considerably shifted in the potential with respect to the forward one and has a higher intensity. This can indirectly confirm the low rate of the processes in the films in the absence of CNT there.



**Fig. 3** – Cyclic voltammetry (a) and ECL response (b) of glassy-carbon electrodes modified by  $\text{Ru}(\text{bpy})_3^{2+}$  with CNT in PVA matrix in water without addition of coreactant (1) and with addition of 0,13 mM of STPB (2). 0,1 M  $\text{NaClO}_4$  is the supporting electrolyte

It is also evident that with addition to the solution of TPA and STPB coreactants, there is a 5-fold increase (Fig. 2b) and a 20-fold increase (Fig. 3b), respectively, in the ECL intensity with respect to the background emission, while change of the electrochemical current in the first case is insignificant, and in the second one – it is about 15 times. That is, application of the electrochemical analysis for the determination of TPA using the developed electrode structures is utterly difficult, while the ECL method allows to confidently detect both compounds in the solution with sufficiently low detection limit.

To determine the stability of the proposed type of the films for creation of ECL sensors, investigation of the influence of the aqueous medium on the temporal stability of the luminescent properties of the films of PVA/CNT/ $\text{Ru}(\text{bpy})_3^{2+}$  structure is also performed. To this end, dependence of the photoluminescence intensity of the film of such composition on the exposure time in water at the temperature of 24 °C was studied. Decrease in the photoluminescence intensity within the emission band of  $\text{Ru}(\text{bpy})_3^{2+}$  complex was discovered. Kinetics of the photoluminescence intensity at the wavelength of the emission maximum  $\lambda_{\text{Lum}} = 600$  nm with excitation in the maximum of the absorption band at the wavelength of  $\lambda_{\text{Ex}} = 450$  nm is represented in Fig. 4.



**Fig. 4** – Kinetics of the photoluminescence intensity of the  $[\text{Ru}(\text{bpy})_3]^{2+}$  complex in PVA/CNT/ $\text{Ru}(\text{bpy})_3^{2+}$  film at the film treatment in the aqueous medium at the temperature of 24 °C

As seen from Fig. 4, there is a 3,5-4-fold decrease in the photoluminescence intensity after exposure of PVA/CNT/ $\text{Ru}(\text{bpy})_3^{2+}$  film in the aqueous medium during 60 minutes. Taking into account the fact that  $\text{Ru}(\text{bpy})_3^{2+}$  complex is well water-soluble, the dependence shown in Fig. 4 implies a rather weak chemical bond between electrochemiluminophor and polymer PVA matrix with CNT. Thus, swelling of PVA film occurs in water, then one can observe transformation of this film to gelatinous structure and washing-out of luminophor  $\text{Ru}(\text{bpy})_3^{2+}$  to the aqueous phase. Considering the duration of the procedure of the ECL analysis itself (several minutes), such kinetics of luminophor washing-out from the surface of sensor electrode is quite satisfactory.

#### 4. CONCLUSIONS

Electrochemical and ECL properties of electrodes modified by organic PVA films with incorporated CNT and organic luminophor  $\text{Ru}(\text{bpy})_3^{2+}$  were obtained and investigated in the present work. Difference in kinetics of the charge transfer through the films in the presence and in the absence of CNT is discovered. Obtained results of the ECL investigations also demonstrate that such structures can be applied for detection in solution of different substances which are coreactants for ECL excitation. In particular, ECL emission in the presence in solution of 0,1 mM of TPA exceeds 5 times the level of background signal, and 20 times – in the presence of 0,13 mM of STPB.

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