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Comparative study of electrochromic properties of polyaniline–polyacid layers prepared by spray– coating and drop–casting methods with adding carbon nanotubes

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The influence of the coating method (spray–coating or drop–casting onto horizontal substrate) on the electrochromic characteristics of the layers of water–soluble polyaniline–polyacid complex was investigated. It was shown that, in the case of adding single–wall nanotubes, the polyaniline–polyacid layers prepared by the scalable spray–coating technology demonstrate high coloration speed and electrochromic efficiency.

Keywords: polyaniline, electrochromism, polyacid, carbon nanotubes.

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Electrochromic materials find continuously growing application in the construction industry („smart windows" with variable light and heat transmittance), in the aircraft and automobile industry („smart windows" and variable–reflectivity rear–view mirrors), for adaptive camouflage. Among polymer electrochromic materials, one of the most promising ones is polyaniline (PANI), especially water–soluble compositions based on it [1]. Earlier we have developed a composition based on the water–soluble PANI complex with polyacid for applying solar cell functional layers by ink-jet printing [2,3]. However, this technique is more suitable for creating uniform thin layers necessary for organic electronics. To quickly produce large–scale electrochromic layers, it is preferable to use easier–to–perform methods like spray coating. The use of spray coating in fabricating electrochromic devices has been mentioned in literature mainly in connection with water–soluble polymer composition of poly(3,4–ethylenedioxithiophene) with polystyrene sulfonate [4–6] widely used in organic optoelectronics.

In producing PANI–based electrochromic layers, this technique was earlier applied with using as the spraying substance a suspension of the silicon oxide nanoparticles covered with PANI [7] or aqueous compositions obtained by the PANI enzymatic synthesis in the presence of gallic acid and polystyrene sulfonate [8].

In this work there were studied electrochromic characteristics of layers based on PANI complexes with another popular polyacid, namely, poly(2–acrilamido–2–metyl–1–propanesulfonic acid) (PAMPSA).

The water–soluble electrochromic composition was obtained by oxidation polymerization (with ammonia persulfate) of aniline in the PAMPSA aqueous solution similarly to the case of preparing ink-jet printing compositions [2] with the optimal PANI : PAMPSA ratio in the reaction mixture of 1 : 1.5. The electrochromic layers were applied from a solution 3.8 mg/ml in concentration onto optically transparent FTO electrodes ($SnO_2:F$) with resistance of $\sim 7\,\Omega/\Box$ by two methods: 1) drop casting onto a horizontal substrate with subsequent drying for 24 h at room temperature in the atmosphere saturated with water vapors (under a Petri dish with clearances); 2) spray coating onto a heated (to $\sim 70^\circ$C) horizontal substrate from the distance of 20 cm by using an aerograph.

To increase the electrochromic response rate, there were also prepared compositions to which single–wall carbon nanotubes (SWCNTs) were added in the amount of 2 to 4 mass% in the PANI–PAMPSA solid layer. The SWCNT aqueous suspension was prepared by ultrasonic processing (for 40 min) with subsequent centrifuging (6000 rpm, 1.5 h) for depositing large agglomerates. The SWCNT suspension was mixed with the PANI–PAMPSA solution in the required ratio and then processed with ultrasound (for 10 min). The following electrochromic layer samples were obtained: DC — drop casting; DCN-2 — drop casting with 2 mass% of SWCNTs; DCN-4 — dropcasting with 4 mass% of SWCNTs; S — spray, SN-2 and SN-4 — sprays with the SWCNT contents of 2 and 4 mass%, respectively.

The surface morphology of layers applied by spray coating was studied by atomic force microscopy (AFM) using AFM microscope Enviroscope with controller Nanoscope V (Bruker).

Electrochromic characteristics of the layers were measured in the 1M aqueous solution of HCl in a 2 cm spectrophotometric cuvette in which the working FTO electrode with the PANI–PAMPSA film, platinum counter–electrode and salt bridge into the bulk for the reference electrode (saturated silver chloride electrode SSCE) were fixed with a Teflon cover–holder. A potential in the form of three subsequent steps of -0.2 V

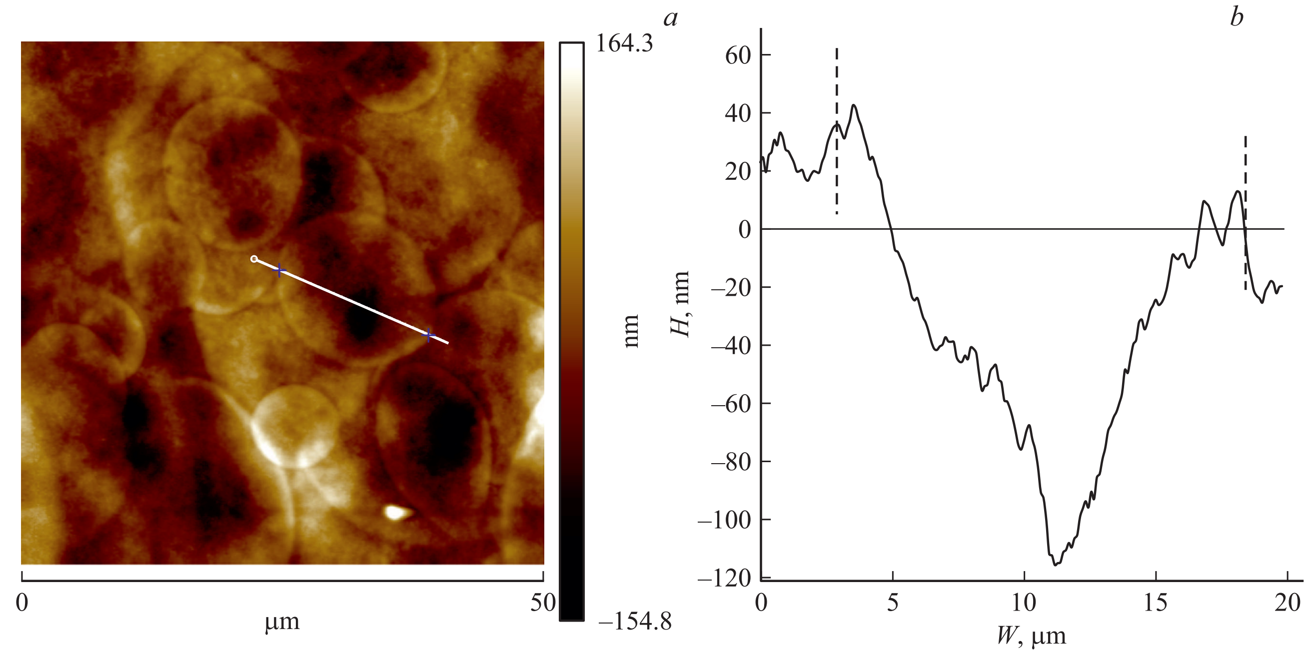

Figure 1. *a* — AFM image of an electrochromic layer based on the PANI−PAMPSA complex applied by the spray-coating method; *b* — the cross section profile along the bright line in panel *a*.

$(10\,\mathrm{s}) \rightarrow +0.8\,\mathrm{V}(10\,\mathrm{s}) \rightarrow -0.2\,\mathrm{V}(10\,\mathrm{s})$ (relative to SSCE) was fed to the working electrode by using a potentiostat/galvanostat HA-501G (Hokuto Denko), and transient currents were detected with digital oscilloscope Nicolet 2090. Transient curves of optical absorption were recorded at time intervals of 0.1 s with a scanning spectrophotometer Avantes 2048 at three wavelengths simultaneously (with averaging over the ±3 nm range): 755, 690 and 570 nm.

Fig. 1, *a* presents an AFM image of the electrochromic PANI−PAMPSA layer applied by spray coating. One can see that the layer consists mainly of round dried−up droplets; according to the cross section profile (Fig. 1, *b*) along the bright line, a dip is observed in the center of each of them. As shown below, such a heterogenic structure consisting of individual dried−up droplets can strongly affect the optical response rate.

Fig. 2 presents transient curves of optical absorption in the third cycle of coloration/decoloration and also curves of normalized optical absorption for the electrochromic layer coloration front at different wavelengths selected based on the results of analyzing the PANI spectra [9,10]: 755 nm — polaronic absorption of the emeraldine form; 570 nm — absorption of the PANI quinoid form. At 690 nm there is observed the maximal (Fig. 2, *a*) dynamic range of optical absorption variations which equals 1.0 ± 0.1 absorption units for all the samples. The transient curves exhibit at 755 nm (Fig. 2, *b*), after the absorption growth front, a decrease connected with the PANI polaronic form transformation into the quinoid form.

From the transient curves, times of reaching 90% of the dynamic range (CT 90% is the coloration time) were derived and listed in the table. Using the CT 90% value and integrating the transient current curves, the charge per unit electrode area necessary to reach 90% of the dynamic range was calculated. The ratio between the value corresponding to 90% of the dynamic range and the specific charge gives the electrochromic efficiency (CE 90% is the coloration efficiency). To compare electrochromic responses at different wavelengths, the normalized electrochromic efficiency (NCE 90%) calculated by normalizing the absorption values to the dynamic range for each spectral region was used.

As the table shows, the coloration speed and electrochromic efficiency of SWCNT−free layers applied by spray coating are essentially lower than those of layers obtained by drop casting.

Adding of SWCNTs expectedly increases the electrochromic efficiency of all the layers in the region of 690 nm; in the case of the SWCNT content of 4 mass%, the layer obtained by spray coating already dominates the drop−casting SWCNT−free layer with respect to this parameter. Adding of SWCNTs differently affects the response time and coloration efficiency NCE in different spectrum regions. In the 755 nm region of absorption of conductive polaronic fragments, the response time expectedly decreases while the electrochromic efficiency increases. In the 570 nm region (the semiconductor quinoid form), time of the film electrochromic reaction increases essentially. The response time at 570 nm in the DCN-4 sample is longer than in the DCN-2 sample. Similarly, the ratio between the NCE values at 755 and 570 nm decreases from 0.78 (DCN-2) to 0.69 (DCN-4), namely, adding of 2 mass% of SWCNTs improves

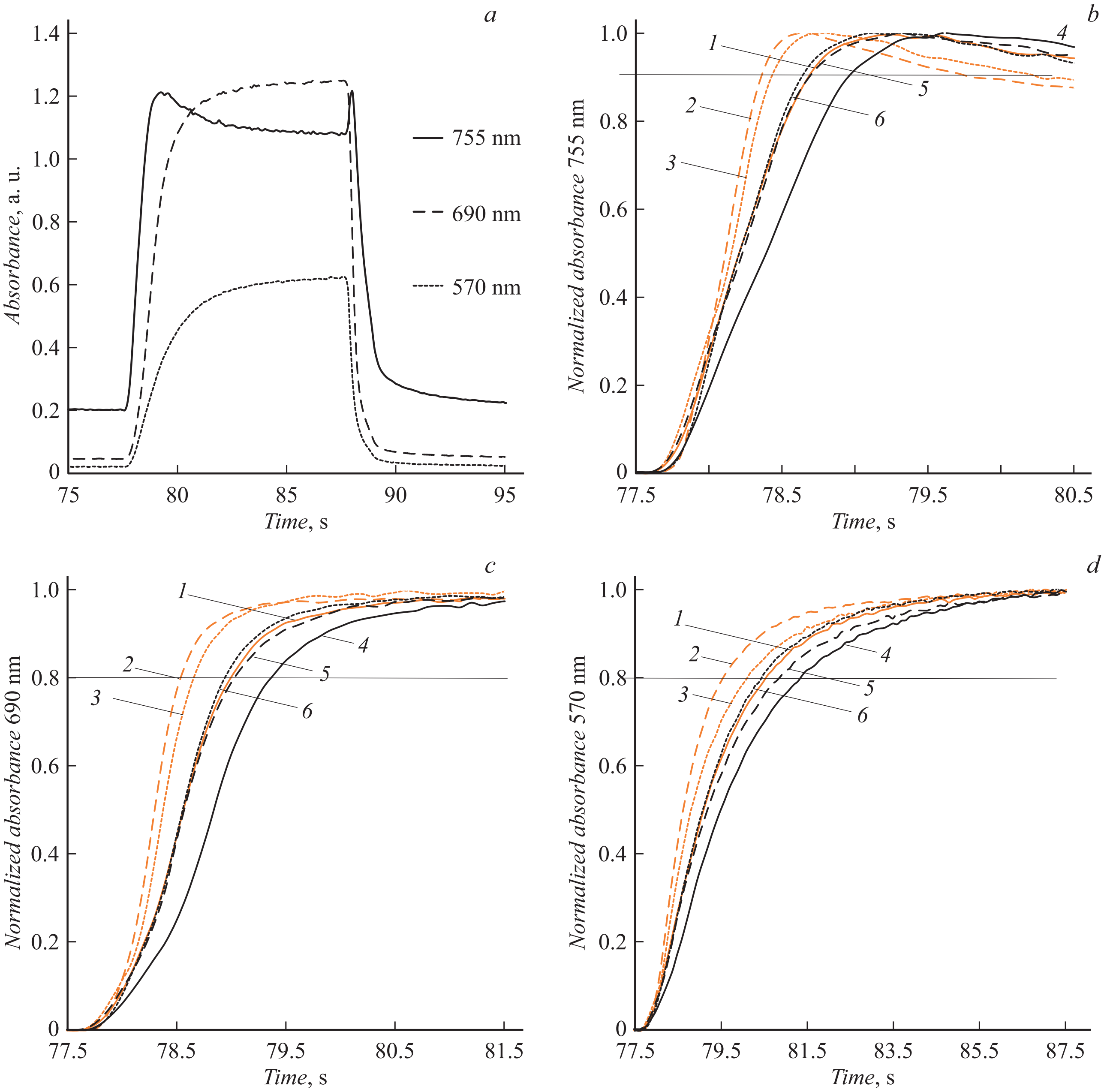

Figure 2. Transient curves of optical absorption (*a*) for the DC sample and normalized optical absorption at wavelengths of 755 (*b*), 690 (*c*) and 570 nm (*d*) in case a potential step of −0.2 V− + 0.8 V (SSCE) is fed in the third cycle of coloration/decoloration to samples DC (*1*), DCN-2 (*2*), DCN-4 (*3*), S (*4*), SN-2 (*5*), SN-4 (*6*).

the electrochromic response uniformity over the spectrum, while adding of more than 2 mass% impairs it.

Vice versa, almost no variations in the electrochromic response uniformity over the spectrum take place for the layers obtained by spray coating, only an increase in the electrochromic efficiency is observed.

These differences may be explained in the following way. Films produced by drop casting evolve slowly, and SWCNTs existing in them are able, due to mutual orientation, to form an analog of a spatial grid over which charge carriers are transported with high speed. This results in considerably higher values of electrochromic efficiency. In addition, slow drying−up of layers obtained by drop casting promotes optimal orientation of the PANI chains relative to SWCNTs. As a result, the speed of propagation of the second−stage oxidation front (emeraldine−pernigranilin) deep into the film increases, and the electrochromic response rate levels out over the spectrum. Adding of SWCNTs in amount larger than 2 mass% provides creation of charge−transport channels „bypass“ the electrochromic substance, and the current flow through them does not lead to coloration. Conversely, formation of such a spatial grid is low−probable in the

Electrochromic characteristics of the PANI–PAMPSA layers obtained by drop casting (DC) and spray coating (S) at different SWCNT contents (DCN, SN)

Sample	CT 90%, s			CE 90%, $cm^2 \cdot C^{-1}$ 690 nm	NCE 90%, $cm^2 \cdot C^{-1}$		
	755 nm	690 nm	570 nm		755 nm	690 nm	570 nm
DC	1.08	1.72	4.20	194	184	157 (0.85)	130 (0.71)
DCN-2	0.76	1.14	2.90	363	334	305 (0.91)	260 (0.78)
DCN-4	0.84	1.28	3.70	316	354	295 (0.83)	243 (0.69)
S	1.36	2.24	5.30	156	160	136 (0.85)	111 (0.69)
SN-2	1.08	1.82	4.70	176	174	144 (0.83)	116 (0.67)
SN-4	1.04	1.74	4.04	196	209	171 (0.82)	142 (0.68)

Note. The last two columns present the ratios between NCE 90% for 690 and 570 nm and NCE 90% for 755 nm.

layers obtained by spray coating on hot substances, and adding of SWCNTs with taking into account considerable heterogeneity of such layers (Fig. 1) enables only facilitation of the current transport between the boundaries of dried droplets.

Therefore, regardless of the fact that the PANI–PAMPSA electrochromic layers obtained by the easily scalable and technologically simple spray–coating method possess electrochromic efficiency lower than layers obtained by drop casting, their characteristics may be significantly improved by adding carbon nanotubes.

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Conflict of interests

The authors declare that they have no conflict of interests.

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