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Nanostructured Prussian Blue–polypyrrole composite coatings with electrochromic properties

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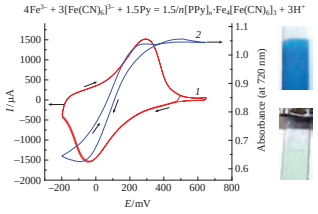
The Prussian Blue–polypyrrole (PB/PPy) composite materials were obtained by a chemical redox process in a mixed solution of iron(III), hexacyanoferrate(III) and pyrrole with a nitrate supporting electrolyte. The morphology of the composites (as a sedimented powder or a film on the ITO-glass electrode surface) varied depending on the composition of synthetic solution.



Prussian Blue (PB), $Fe^{III}_4[Fe^{II}(CN)_6]_3$, as a film on electrode surface is an electroactive material due to its redox transformations to both oxidized (Prussian Green) and reduced (Prussian White, PW) forms depending on electrode potential.[1–3] The electrodeposition of PB on the electrode surface coated with an organic layer was used to extend the stability period of such modified electrodes for electrochromic and sensor applications.[4–7] An alternative method to enhance the stability of PB-containing films is based on the deposition of a PB/polymer composite *via* a chemical (redox-reaction) procedure.[8,9]

We studied the dependence of the redox and electrochromic properties of composite PB/polypyrrole (PB/PPy) films on synthesis conditions and characterized the structural and morphological properties of these films in order to optimize the synthesis procedure and to reach a high-stability electrochemical (electrochromic) response of such modified electrodes.

Similarly to a previously described procedure,[8] blue PB/PPy composites were generated *via* a one-pot one-step redox reaction between an oxidizer [an equimolar mixture of iron(III) and ferricyanide salts] and a reducing agent [pyrrole (Py) taken in excess] in their mixed dilute aqueous solution with the addition of a nitrate background electrolyte. The Fe^{3+}:$[Fe^{III}(CN)_6]^{3-}$:Py molar ratios in the reaction mixture were 1:1:5, 1:1:10, 1:1:1 and 1:1:2.†

Both Fe^{III} and $Fe^{III}[Fe^{III}(CN)_6]$ can oxidize pyrrole in mixed solution with the simultaneous generation of PB and PPy in the form of the PB/PPy composite, $1.5/n\,[Py]_n{\cdot}Fe^{III}_4[Fe^{II}(CN)_6]_3$:

$$4\,Fe^{3+} + 3\,[Fe^{III}(CN)_6]^{3-} + 1.5\,Py = PB/PPy + 3\,H^+, \quad (1)$$

$$4\,Fe^{III}[Fe^{III}(CN)_6] + 1.5\,Py = PB/PPy + [Fe^{III}(CN)_6]^{3-} + 3\,H^+. \quad (1')$$

The (spectro)electrochemical measurements were performed in a deoxygenated single-compartment three-electrode quartz cell (10 mm).‡

Pure PB films were electrodeposited on the surface of ITO-glass electrode in potentiostatic mode (0.55 V for 100 s) in the aqueous solution of 10 mM $Fe(NO_3)_3$ + 10 mM $K_3[Fe(CN)_6]$ with 0.1 M HNO_3 + 0.1 M KNO_3 as a supporting electrolyte. Moreover, pure PB and PPy films were formed on the electrode surface *via* double-pulse potential polarization mode[10] from a solution with the same concentrations as in 1:1:10 synthetic solution. The thickness of composite and pure component films was ~150–200 nm.

The morphology of PB/PPy films on the ITO-glass electrode surface was characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM).§ For composites formed in solution with high Py content, the adhesion of film to

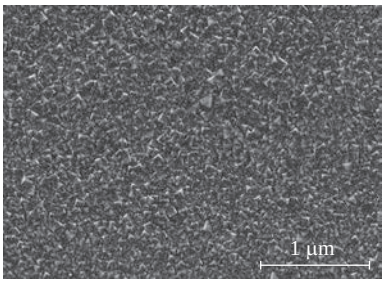


Figure 1 SEM image of PB/PPy composite film on ITO support.

† $Fe(NO_3)_3{\cdot}9H_2O$ (p.a., Carl Roth GmbH) was used in nitrate medium combined with $K_3[Fe(CN)_6]$ (p.a., Carl Roth GmbH) reagent and distilled pyrrole monomer (98+%, Alfa Aesar). The reaction was carried out at 20±1 °C. To modify the electrode surface with PB/PPy film, the ITO-glass electrode was placed in the reaction mixture for 48 h. Then, it was rinsed thoroughly with distilled water.

‡ (Spectro)electrochemical measurements were performed under potential control by PI-50 Pro (Elins); coiled Pt wire was used as counter electrode and SCE (Jenway) as reference electrode. All potentials are given *versus* SCE. Kinetic absorbance measurements (at 720 nm, registration time, 1 s) were carried out on a Lightwave II (Biochrom) spectrophotometer.

§ JEOL JSM-6400F and field-emission gun scanning electron microscope (FEG-SEM) JEOL JSM 6500F instruments at 15 or 20 kV accelerating voltage and Jeol JEM-2100 TEM with LaB6 source operating at an accelerating voltage of 200 kV were used for SEM and TEM measurements.

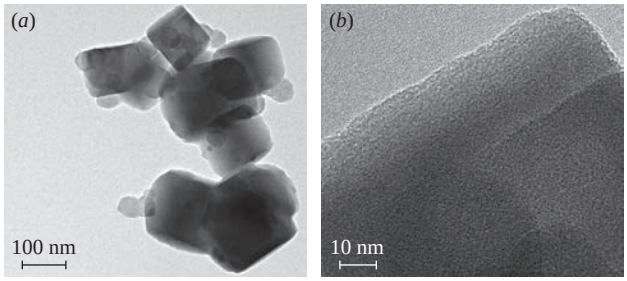


Figure 2 (*a*) TEM and (*b*) HR-TEM images of PB/PPy composites.

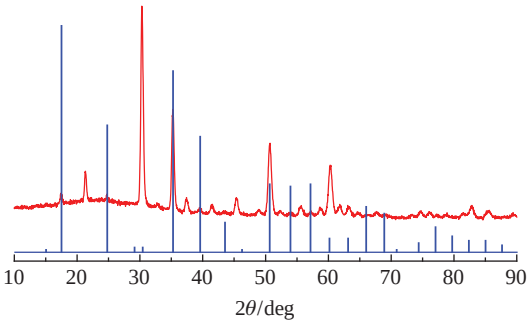


Figure 3 XRD spectrum of a PB/PPy composite film on ITO-glass surface, in comparison with peaks of pure PB crystals (bars, JCPDF 052-1907). Other peaks in the XRD spectrum correspond to the ITO substrate.

electrode surface is higher because of PPy good adhesion and distribution of PB particles between PPy globules is more uniform than for composites formed in solution with high content of iron(III) salts. The SEM image (Figure 1) of the PB/PPy composite film obtained from 1:1:10 synthetic mixture demonstrates morphology of a very uniform and compact layer. The TEM images (Figure 2) reveal that PB/PPy is composed of rectangular PB elements about 100 nm in dimension.

The PB crystalline structure in films was confirmed by SAED and XRD (Figure 3) techniques.¶ The size of PB crystalline fragments estimated from the XRD peak at 17° (<200>) was about 28 nm.

Stability of the electrochromic response of PB/PPy films on ITO-glass substrate was tested by a spectroelectrochemical procedure (in contact with background nitrate solution). Redox transformation PB/PW inside these films is accompanied by a color change from blue to almost colorless (Figure 4). The repetition of potentiodynamic polarization leads to progressive synchronic diminution of both the redox charge in CV curves (scan rate, 100 mV s^{-1}; potential range, –0.200 V and +0.650 V) and the absorbance at 720 nm wavelength. Calculation of color/redox transformation degradation/stability degree of film *via* diminution of redox charge from CV or *via* decrease in absorbance from spectra gives similar results. Figure 5 demonstrates the stability of PB/PPy films formed from various mixed solutions in comparison with that for the pure PB film calculated *via* redox-charge changes. It is clear that the stability of composite films is ten times greater than that of a pure PB film (independent of its formation procedure). A comparison of composite film stability with the stability of pure PB and pure PPy films formed in solution with the same concentration of reagents as in mixed solution allowed us to conclude that the electrochromic signal degradation occured due to the instability of the PB component in film in PW state. Decrease in stability of pure PPy film is much lower than that for pure PB (~30% in 600 cycles). Stability of PB/PPy composite formed in solution with high Py content is

¶ XRD spectra were recorded on a CPS 120 INEL diffractometer with monochromated CuKα radiation at 40 mA and 40 kV.

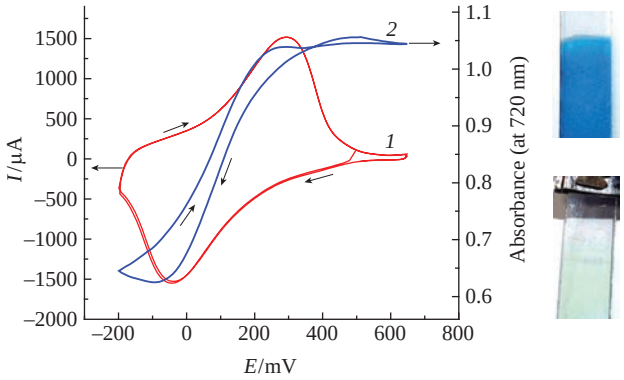


Figure 4 Spectroelectrochemical measurements of PB/PW transformation in a PB/PPy film deposited from solution with $Fe^{III}(NO_3)_3$:$K_3[Fe^{III}(CN)_6]$:Py molar ratio 1:1:10 on the ITO-glass electrode. (*1*) CV response of the film (100 mV s^{-1}); (*2*) absorbance changes (at 720 nm) in the course of this CV potential variation. Photos demonstrate the colors of the composite film in its reduced (–0.145 V) and oxidized (+0.500 V) states.

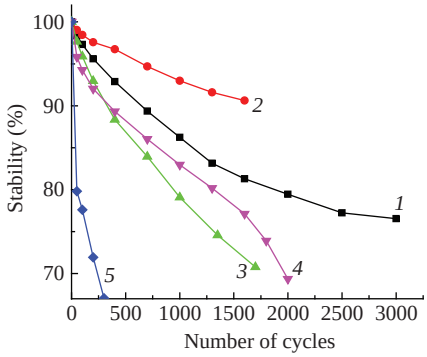


Figure 5 Stability degree variation of the composite PB/PPy films deposited from solutions with $Fe^{III}(NO_3)_3$:$K_3[Fe^{III}(CN)_6]$:Py molar ratios of: (*1*) 1:1:5, (*2*) 1:1:10, (*3*) 1:1:1, (*4*) 1:1:2 and (*5*) a pure PB film on the ITO-glass electrode.

the highest. This film has better morphology (Figures 1 and 2) and better adhesion to the electrode surface. Thus, we can conclude that this composite film is a more promising material for electrochromic devices.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2016.03.011.

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