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Layer-by-layer synthesis of nano Prussian blue electrochromic thin film modified electrodes

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A novel simple non-electrical fully controlled method has been developed for synthesis of modified electrodes by Prussian blue thin film on indium tin oxide substrates. The method comprises a tiny spot of silver as a sacrificed anode applied on one corner of the substrate by using layer-by-layer method for deposition nano Prussian blue thin film layers of electrodes (LBL/Ag), from a solution of equal concentrations of ferric chloride and potassium ferricyanide. The morphology of Prussian blue nanoparticles has been investigated by scanning electron microscopy and atomic force microscopy. The Prussian blue thin film thickness has been calculated. The Prussian blue film exhibits linear increase in the UV-vis light absorbance with the number of deposited layers, indicating that well organized lamellar systems are involved, which is consistent with the results based on the cyclic voltammetry measurements. These results show excellent electrochemical and reversible stable thin films, favorable for various applications such as electrochromic devices.

Chemically modified electrodes have received wide concern due to their clear advantages such as high stability over a wide range of solution composition, less prone to surface staining and low over potential at which the electron transfer process occurs, compared with indolent substrate electrodes.[1] At present, various inorganic materials including zeolites,[2] metal oxides,[3] transition metal nanoparticles[4] and transition metals hexacyanoferrates (MeHcF) have been used to fabricate the inorganic film modified electrode. Metals hexacyanoferrates (MeHcF) are important inorganic compounds that have been used for modification of electrode surface.[5] These compounds are fit to form stable crystalline structure films showing reversible redox processes without dissolution in solution.[6] These valuable properties of MHCFs attracted much attention due to their important role in various research areas as electrochemical sensors, solid state batteries, ion selective electrodes, electrophoresis detectors.[7] As a classical prototype of transition metal hexacyanoferrates, Prussian blue (PB) is one of the well studied materials, exhibiting interesting electrochemical,[8] electrochromic,[9] photophysical,[10] and magnetic properties.[11] These applications of PB modified electrodes are based on reversible redox characteristics (PB/PW and PB/PY transition) in appropriate potential ranges. Corresponding electrochemical processes are formulated as follows:[1]

$$\mathrm{KFe^{III}[Fe^{II}\,(CN)_6](PB) + K^+ + e^- \leftrightarrow K_2Fe^{III}[Fe^{II}(CN)_6](PW)} \quad \dots (1)$$

$$\mathrm{KFe^{III}[Fe^{II}(CN)_6](PB) \leftrightarrow Fe^{III}[Fe^{III}(CN)_6](PY) + K^+ + e^-} \quad \dots (2)$$

PB thin film modified electrodes are particularly attractive due to their ease of preparation by using a simple procedures: sol-gel method,[12] photochemical [13] and electrochemical deposition,[8] spin coating [14] and chemical non-electrical method.[15,16] However, among the above mentioned methods, few are suitable to fully control the film thickness and are difficult to prepare the PB-based ultra thin film using the conventional methods. The recently developed electrostatic layer-by-layer (LBL) self assembly method is believed to be the most power full methods for tailoring nanometer scale structured thin films and has been successfully applied to the structural organization of various charged species, including poly electrolytes, dyes, inorganic nanomaterials, DNA and enzyme.[17-23] It is eco-friendly in using aqueous solutions, under laboratory temperature. The LBL assembly method is based on sequential of oppositely charged species on a charged substrate.[24,25] Although types of chemical bonds may be involved in formation of multi layer thin films, the most common form of LBL deposition is based on ionic bonds between ionic species. Exposure of the charged substrate to a dilute aqueous ionic solution of opposite charge forms an ultra thin layer of the charged molecules on the substrate. The substrate is then rinsed with distilled water to wash the loosely bond molecules and immersed in the other dilute aqueous ionic solution with a charge opposite to the charge of the first ionic solution to form another ultra thin film on the existing, first, ultra thin film. This step is also followed by rinsing with distilled water. The two-layer system forms one bilayer. Repetition of these steps results in formation of thin film consisting of several bilayers.[26] In the present work we have assembled Prussian blue thin film modified electrode using a novel non-electrochemical way by applying a silver spot (Ag) on the substrate as a sacrificial anode and using layer-by-layer (LBL) method. The merit of this preparation method (LBL/Ag) is its simplicity, easiness, time saving and almost absolute control over thickness of the prepared nanofilm and hence, it can be considered as an important contribution in preparing such modified electrodes with their vast fields of applications i.e. electrochromic and electro catalytic devices.

Materials and Methods

Indium-tin oxide (ITO) conducting glass was chosen as a substrate (resistance: <150 ohm cm^{-2} Solaronix). Aqueous solutions of $FeCl_3.6H_2O$ and $K_3Fe(CN)_6.HCl$ were used for adjusting the solutions, while KCl was used as electrolyte in cyclic voltammetry. All chemicals were analytical grade from Merck and Riedel-De Haen, and used without further purification. Dottie silver paint (05003-AB China) was also used. Doubly distilled water was used throughout the experiments.

The electrochemical experiments were carried out using AMEL 7050 (potentiostate/galvanostat), in conjunction with a three-electrode system comprising a Ag/AgCl/KCl(saturated) as reference electrode, a platinum wire as an auxiliary electrode and PB thin film-modified /ITO (0.9×3) cm^2 as a working electrode. All the potentials given in this article are referred to the Ag/AgCl/KCl saturated electrode. UV-vis and FT-IR/ATR spectra were recorded on a Scinco PDA spectrophotometer and Jasco 4200 respectively. The morphology images were recorded on AFM Nano surf easy scan2 and SEM VEGA/TESCAN instrument. For investigating the electrochromic property, chronoamperometry was carried out with switching potential between –0.5 and +0.5 V for every 30 s step, in 0.2 *M* KCl as an electrolyte.

Deposition of PB thin films

The chemicals deposition was performed from two separated fresh solutions. One of the solutions was an aqueous 0.01 *M* $FeCl_3.6H_2O$, while the second solution was an aqueous 0.01 *M* $K_3Fe(CN)_6$ (pH = 2.76 adjusted with HCl). 0.1 *M* and 0.2 *M* KCl as an electrolyte for cycling voltammetric studies.

Prior to the deposition, the substrate (ITO/glass) was degreased by sonicated in aqueous detergent for 30 min (30 °C), well washed with water, ethanol and then water again. When dry, a small spot of silver paint was applied with a pasture pipette to give a thin spot of area ~ 0.01 cm^2 onto one corner of the ITO/glass electrode, and kept to dry. To prepare PB thin film, a clean spotted substrate immersed into one solution $FeCl_3.6H_2O$ for 30 s, followed by water rinsing for 5 s then immersed into the other solution $K_3Fe(CN)_6$ for 30 s (the exact length of time), then rinsed with water for 5 s. This cycle repeated several times to obtain the desired thickness of PB thin film (type A). After each cycle the substrate was dried by warm air. A noticeable blue color due to the formation of PB film on the substrate was noticed at the fourth cycle of the procedure, which became deeper on repeating the cycles. In the other way to prepare PB thin film, (Type B), a clean spotted substrate was immersed first into $K_3Fe(CN)_6$ solution for 30 s, followed by water rinsing for 5 s then immersed into $FeCl_3.6H_2O$ solution for 30 s, and the previous steps were repeat.

Results and Discussion

Spectroscopy studies

The growth of the multilayers of PB thin film (Type A and B) prepared by our LBL/Ag method was recorded by UV-vis absorption spectra for each cycle (layer). (Fig. 1a) shows the PB film (Type A) exhibit absorption around λ_{max}:720 nm due to the intervalence charge transfer (IVCT).The absorbance at λ_{max}: 720 nm increases with increasing number of cycling, indicating that the deposition of PB on the substrate has a constant rate. The linear increment of peak at 720 nm in (Fig. 1b) indicates that an approximately equal amount of PB for type A was deposited each cycle, which means all deposited layers have the same thickness. The absorbance in (Fig. 1c) increases linearly after 4 cycles, indicating quantitative formation of PB type B similarly. These results clearly indicate that the order of deposition of ionic or cationic solution on the substrate is very important not only at the adsorption of the ionic layer but also in the steady growth of the film. Further, the prepared blue film was characterized by FT-IR/ATR spectroscopy. The absorption band at 2072 cm^{-1} (Fig. 2) is attributed to the stretching

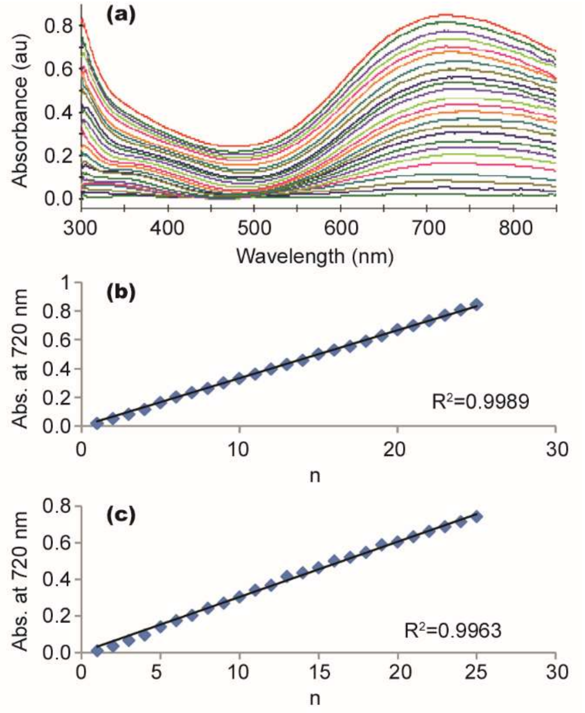

Fig. 1 — (a) UV-vis spectra of of PB thin film after deposition of 25 layers (type A). (b) Plot of absorbance of PB thin film (type A) at λ_{max} 720 nm against cyclic numbers. (c) Plot of absorbance of PB thin film (type B) at λ_{max} 720 nm against cyclic numbers.

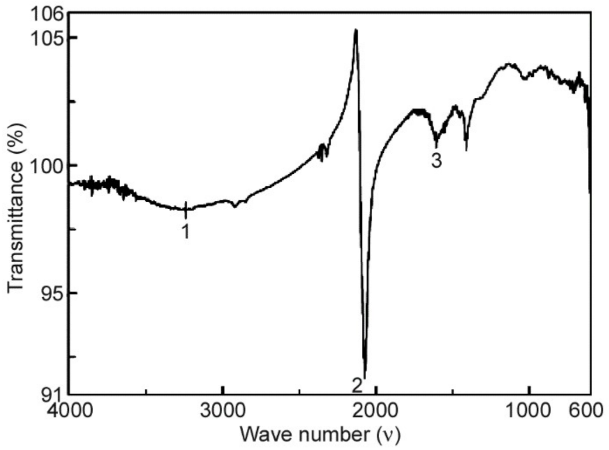

Fig. 2 — FT-IR spectra for PB deposited by LBL/Ag (*n* = 15 layers).

vibration of the (C=N) group in the cyanometallate lattice, as reported earlier.[27] The absorption band at 3237 cm^{-1} and 1605 cm^{-1} are assigned to the stretching and bending modes of interstitial water in PB lattice channel, respectively.[28] The propose mechanism of formation the thin film is as follows:

$$Ag + Cl^{-} \rightarrow AgCl + e^{-} \quad \ldots (3)$$

$$Fe^{3+} + e^{-} \rightarrow Fe^{2+} \quad \ldots (4)$$

$$3Fe^{2+} + 2Fe^{III}(CN)_6{}^{3-} \rightarrow Fe^{II}{}_3[Fe^{III}(CN(_6]_2 \quad \ldots (5)$$

Or according to an earlier report:[29]

$$7/2[\ Fe^{III}Fe^{II}(CN)_6] + e^{-} \rightarrow 3[(1/3Fe^{III})Fe^{III}[Fe^{II}(CN)_6]] \rightarrow Fe^{III}{}_4[Fe^{II}(CN)_6]_3 \quad \ldots (6)$$

Surface morphology

Figure 3 shows the surface morphology of the nano PB film before and after deposition (Fig. 3a) and (Fig. 3b) respectively (magnification 15.00KX) by scanning electron microscopy (SEM). As can be seen the electrode surface is covered uniformly with spherical semi-regular particles which have no cracks between PB particles. Also, the morphology of the prepared PB film was investigated by atomic force microscopy (AFM). The AFM study shows a homogeneous film and fully covered the ITO/glass base. Figure 4 shows images and Z-profiles of bilayers nanoparticles of a cleaned ITO/ glass substrate without PB thin film (Fig. 4a), PB thin film on ITO/ glass substrate deposited by LBL/Ag (*n*=15) method without cycling the film electrically (Fig. 4b) and PB thin film on ITO/ glass substrate deposited by LBL/Ag (*n*=15) method with cycling the film electrically in 1 *M* KCl for 20 cycles (Fig. 4c). Cycling the film by cyclic voltammetry (CV) method changed the horizontal distance and made it bigger and more changing of the lattice structure by insertion of K^+ into the PB lattice film changed the insoluble $Fe^{III}{}_4[Fe^{II}(CN)_6]_3$ PB to soluble PB $Fe^{III}K[Fe^{II}(CN)_6]$.

Electrochemistry of the PB films

PB thin film modified electrodes were stabilized by cyclic voltammetry around PB↔PW system at (0.55↔-0.1) V in 0.2 *M* KCl (pH=2.8 adjusted with dilute HCl) at scan rate 0.02 V s^{1} for 100 cycles as observed in Fig. 5(a). The anodic and cathodic peak current of PB thin (type B) (PB↔PW) rise with successive cycling and become more narrower and sharpener, until a stable voltammo gram appears after 15–20 cycles. This due to a partial transformation of insoluble PB into soluble PB.[30] Figure 5(a) shows the first and 20th, 40th, 60-100th cycles, while Fig. 5(b) shows the plot of anodic current peaks of PB thin film (Type B) against the electrocyclic numbers to investigate the film's stability. The PB thin film (type A) stabilized and gave good stability results. The successive cycling around the entire voltammogram from (–0.1↔1.1) V, for 10 cycles at 0.02 V s^{-1} in 0.2 *M* KCl (pH=2.8) shows an exceptionally stable PB thin film prepared by LBL/Ag method (*n*=15).

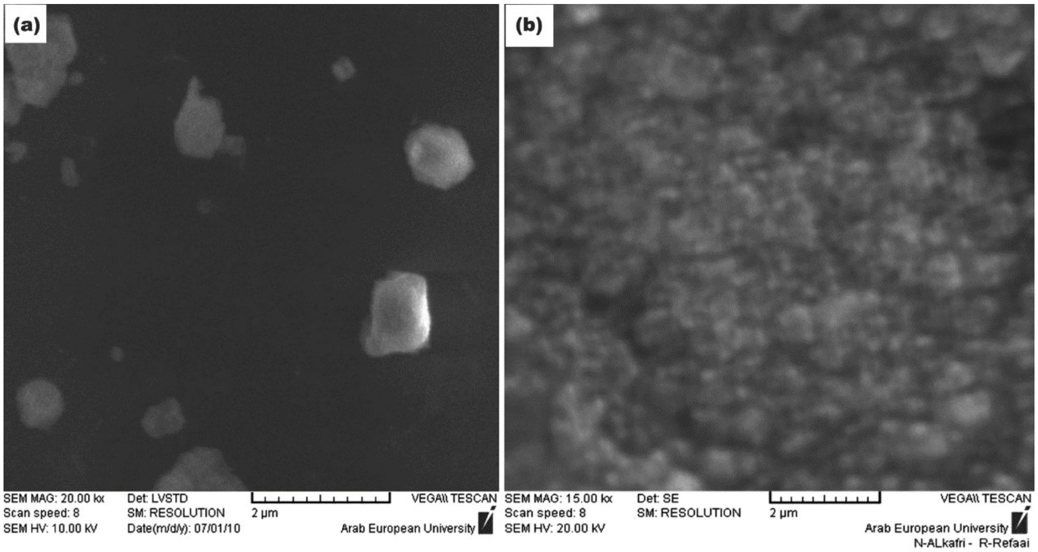

Fig. 3 — SEM images of (a) ITO/glass before and (b) after the deposition of PB thin films by LBL/Ag method.

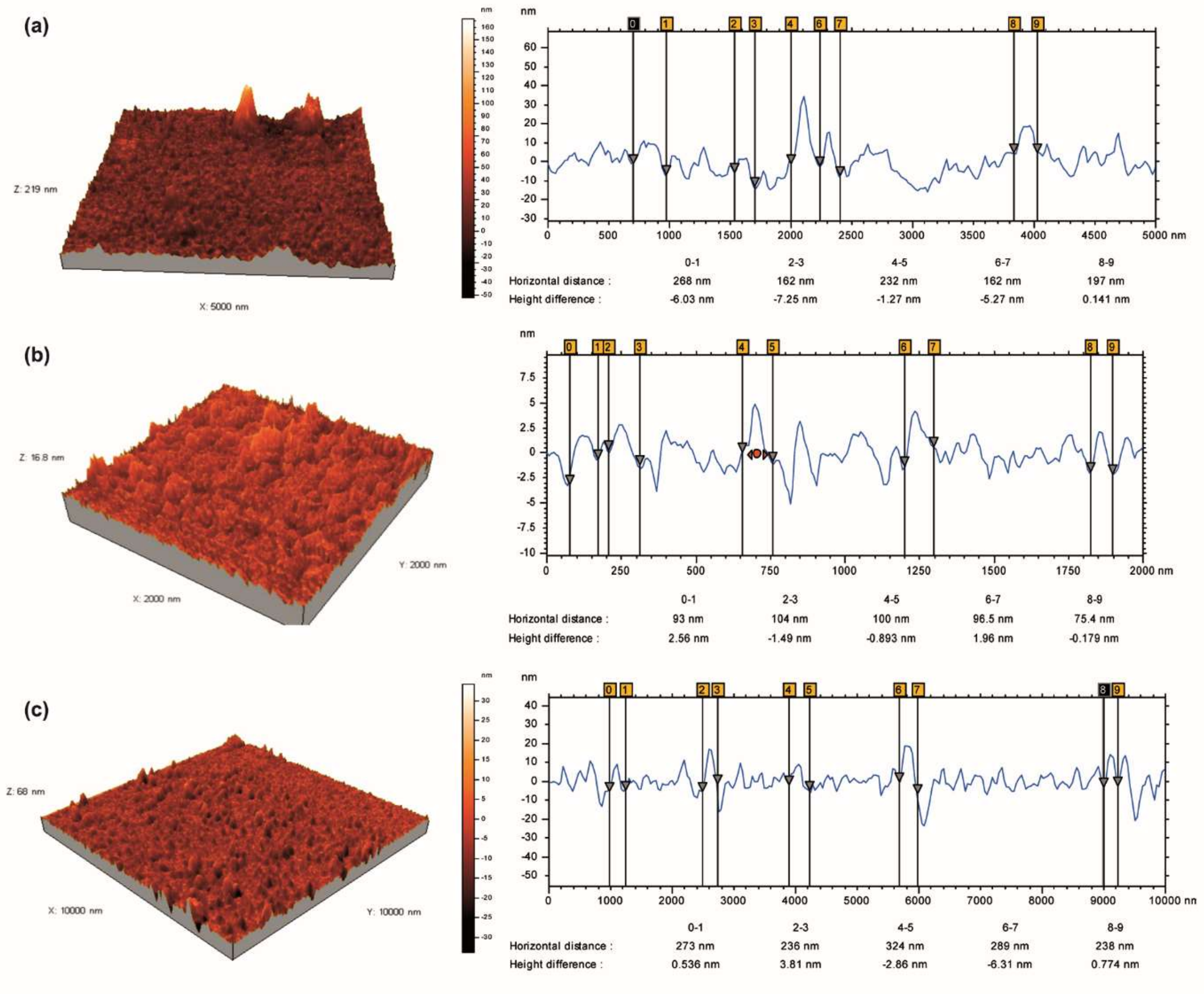

Fig. 4 — AFM images and and Z-profiles of bilayer nanoparticles. [(a) bare ITO/ glass substrate; (b) PB thin films on ITO/ glass substrate deposited by LBL/Ag (n = 15) method without cycling the film electrochemically; (c) film (b) and PB thin films on ITO/ glass substrate deposited by LBL/Ag (n = 15) method with electrochemical cycling of the film in 1 M KCl for 20 cycles, with scan rate: 0.02 V s^{-1} between –0.1 V and 0.5 V].

A typical cyclic voltammogram shows two couples of redox peaks located at around 0.232 V, due to the transformation between Prussian blue and Prussian white, while the couple of redox peaks located around 0.909 V is due to the transformation between Prussian blue and Prussian yellow (Fig. 5(c)). One can notice the difference sizes of the voltammograms of the two (PB↔PW) and (PB↔PY) systems. The latter is smaller than the former, since the soluble PB structure only contains $3Fe^{2+}$ sites for each $4Fe^{3+}$ site, as illustrated in an earlier report[31]. Besides, there are only $2K^{+}$ cations for each $3Fe^{2+}$. Then, not all Fe^{2+} oxidized may be balanced by expelling potassium cations and some chloride anions should be included. This fact causes two different Fe^{2+} sites within the structure. The experimental values of i_{ap}/i_{cp} (i_{ap} is the anodic peak current and i_{cp} is the cathodic peak current), and the peak potential separation $\triangle E = E_{cp} - E_{ap}$ (E_{cp} is the cathodic peak potential, and E_{ap} is the anodic peak potential) for the two systems are given in Table 1 According to the results, i_{ap}/i_{cp} values are close to unity, which means that film exhibits excellent reversibility, especially for the redox process of transformation of PB-PW. Figure 6(a) shows cyclic voltammograms

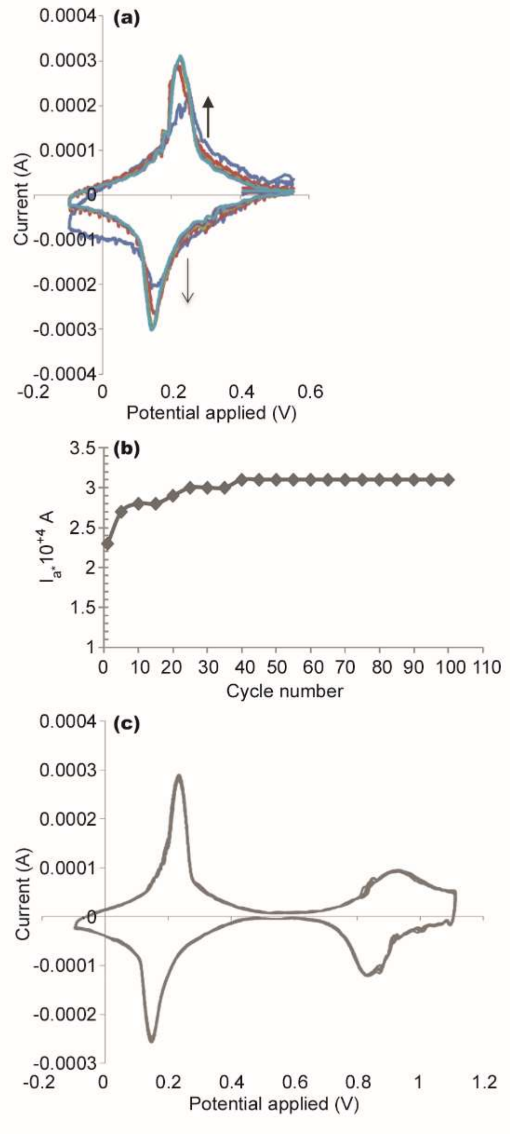

Fig. 5 — (a) Voltammogram of PB thin film deposited by LBL/Ag (*n* = 15) method, cycling in 0.2 *M* KCl (pH = 2.8) at a scan rate of 0.02 V s^{-1} for 100 cycles; applied voltage: 0.55↔–0.1 V. (b) Plot of anodic current peaks of PB thin film (type B) against the electro-cyclic numbers in 0.2 *M* KCl (pH= 2.8) at 0.02 V s^{-1} for 100 cycles. (c) Voltammogram of PB thin film deposited by LBL/Ag (*n* = 15) method, cycling in 0.2 *M* KCl at a scan rate of 20 mV s^{-1}. The applied voltage was set between –0.1 and 1.1 V.

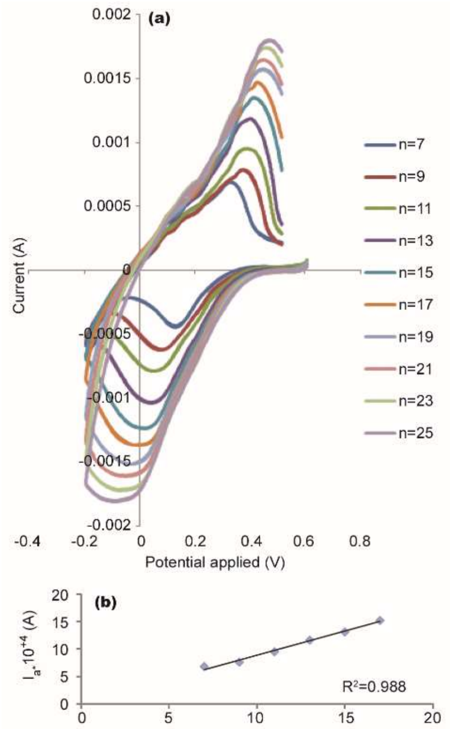

Fig. 6 — (a) Building up of PB thin film (type A) by cycling the odd number of deposition layers, starting from *n* = 7. (b) Plot of anodic current peak against the odd number building layers, starting from *n* = 7 of PB thin film by LBL/Ag (*n* = 17) method.

Table 1 — Experimental values for total charge, peak current , peak potential, i_{cp}/i_{ap} and $\triangle E = E_{cp}$-E_{ap}

System	Q×10^{3+} (C)	i_{ap}×10^{4+} (A)	-i_{pc}×10^{4+} (A)	i_{ap}/i_{cp}	E_{ap} (V)	E_{cp} (V)	$\triangle E$ (V)
PB↔PW	0.697	2.908	2.453	1.185	0.232	0.155	0.077
PB↔PY	0.499	0.953	1.208	0.788	0.909	0.847	0.062

recorded while building PB thin film (type A) by cycling the odd numbers of deposition layers, starting from $n = 7$. As shown in Fig. 6b, a linear increase of current to odd layer numbers was observed, confirming that similar amounts of PB was absorbed for each assembly. This is consistent with the results obtained based on the above spectral measurements of the LBL/Ag multilayers. In addition, the PB thin film can withstand exposure to air at room temperature for at least 8 months and remain unchanged, indicating the prepared PB thin film by LBL/Ag method is very stable in air without requiring further storing conditions.

Thin film thickness

The thin film thickness was measured by two methods. One from the equation ℓ (in cm) = $T\times$molar volume[32], where the molar volume is 677 cm^3/mole[33] and T is the surface coverage (mole/cm^2) as calculated from $Q = n\times A\times F\times T$, where Q is the total charge determined by integrating the area under voltammetric i-E, n is the number of electrons, A is the electrode geometrical surface area in cm^2, and F stands for Faraday. The other method to calculate the film thickness is the absorbance method by using the equation $A = \varepsilon\times C\times\ell$, where A is the absorbance, ε is the absorptive coefficient (6.6×10^6 cm^2/mole),[34] and C is the concentration of the solution deposition in mole/cm^3. The dependence of the nanofilm thickness on the deposition cycles is shown in Fig. 7. As shown, the deposition rate does not change by increasing the odd number layers of PB thin film deposition cycles.

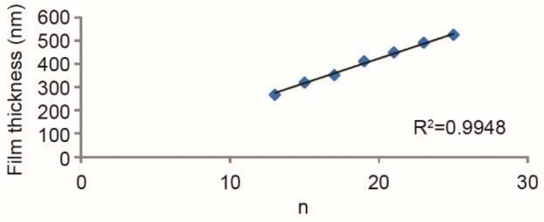

Fig. 7 — Film thickness of PB thin films versus the number of deposition cycles.

Optical properties

The final compound of the oxidation process, Prussian brown, is slightly soluble and therefore the application of the PB thin film in electrochromic devices is seen to be in the range between –0.9 and 0.4 V.[35] The chronoamperometry was carried out with switching potential between –0.5 V and +0.5 V for every 30 s step, in 0.2 *M* KCl. Figure 8a shows the corresponding current against time plot, by switching potential every 30 s step for 3 min. The thin film exhibits good stability by consequence switching. Figure 8(b) shows the UV-vis spectra of PB thin film type B before and after reducing it by –0.2 V for 30 s.

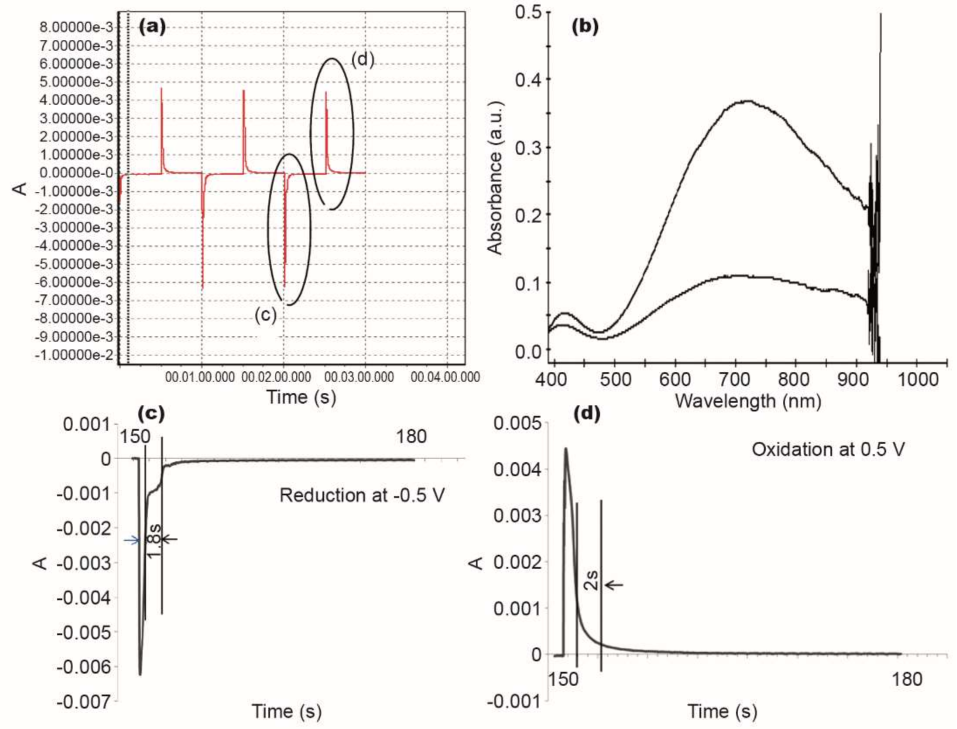

Fig. 8 — (a) Plot of current against time of PB thin film switching potential between –0.5 and +0.5 V for every 30 s step. (b) UV-vis spectra of PB thin film type B before and after reduction by –0.2 V for 30 s. (c and d) The zoomed in area in (a) for last time switching.

The time corresponding to full color change from blue to transparent is around 1.8 s (Fig. 8c) and to recolor is around 2 s (Fig. 8d).

Conclusions

Two types (A and B) of nano Prussian blue thin films modified electrodes can be successfully fabricated with nanometer thickness, by using LBL assembly method combined with sacrificial Ag anode (LBL/Ag). The assembly is shows linear correlation in film thickness (nm) and light absorbed layers (A better than B in the first four cycles only). Cyclic voltammogram shows that the film has excellent reversibility and stability, and is very stable in air for more than 8 months. Cycling the fabricated PB film enhances the morphology of film. The thin film also shows acceptable electrochromic properties. These thin films with such properties make this method very promising for preparing modified electrodes for vast applications.

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