



Direct electrodeposition of micropatterned Prussian blue films on indium tin oxide/polyethylene terephthalate substrate by electrostatic field-assisted potentiostatic and pulse potentiostatic deposition methods

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ABSTRACT

Micropatterned Prussian blue (mPB) films are directly deposited onto indium tin oxide/polyethylene terephthalate (ITO/PET) conducting plastic substrates by electrostatic field-assisted potentiostatic and pulse potentiostatic deposition method in this study. A micropattern deposition selectivity, S , which is defined based on the film thickness ratio, is used to evaluate the quality of the mPB films. Adequate deposition parameters, such as the applying potential and the deposition time, are scrutinized for the preparation of mPB films with high S . Surface morphology and thickness of the mPB films are investigated using optical microscope, scanning electron microscope and a surface profiler. PB films with distinct micropattern structures can be successfully obtained by controlling the deposition parameters. Thin mPB films (thickness smaller than 100 nm) can be obtained by potentiostatic deposition with high S . Pulse potentiostatic deposition method is instead more suitable for the preparation of thicker mPB films (thickness up to 2 μm) and at the same time maintains high S . These electrodeposition methods might find its potential applications in preparing micropatterned functional materials on plastic conducting substrates for flexible electronic devices.

1. Introduction

Micropatterned functional materials and films have been extensively used in many research and application aspects, such as solar cells [1,2–3], sensors [4,5], or light emitting devices [6,7] etc. Methods of photoresist lithography [8], soft lithography [9], reactive wet stamping [10], templating [11], or aqueous chemical growth [12] have been employed for the preparation of micropatterns. These procedures usually consist of multiple steps and are relatively complicated. Recently, we have proposed and demonstrated a novel electrostatic field-assisted micropatterning method [13,14]. The procedure is briefly as follows: an electrostatic film with micropatterns was firstly attached onto the conductive side of an indium tin oxide (ITO) conducting glass through contact electrification and stayed for a period of time. Before the electrodeposition process the electrostatic film was removed, and a micropatterned electrostatic field was generated on the ITO surface. Such micropatterned electrostatic field could affect the electrodeposition rate and resulted in the direct formation of the micropattern film of the material being deposited.

Ferric hexacyanoferrate, which is also known as Prussian blue (PB), is a mixed valence compound [15] with blue color. PB is an

electrochromic material [16] can reversibly change its color between colorless and blue states under external bias. It has great potential in smart window applications [17]. PB also found its applications in H_2O_2 [18] or glucose [19] sensing. In our previous study, micropatterned PB (mPB) thin films with enhanced electrochromic properties [14] were successfully prepared on ITO conducting glass by the electrostatic field assisted electrodeposition method. In this study, the feasibility and suitable operating parameters of the electrostatic field-assisted deposition method for the direct electrodeposition of mPB films on indium tin oxide/polyethylene terephthalate (ITO/PET) conducting plastic substrate were investigated. The method for direct micropattern formation on conducting plastic substrate might find it potential in developing flexible electronic devices.

2. Experimental

Procedures for the electrodeposition of PB and mPB films are described as following: First, a micropatterned electrostatic film (mESF) was attached onto the ITO side of an ITO/PET substrate. Optical image of the mESF is shown in Fig. 1. It is a polyethylene (PE) film substrate on top of it with disc-shaped polyacrylate (PA) bumps array. Average

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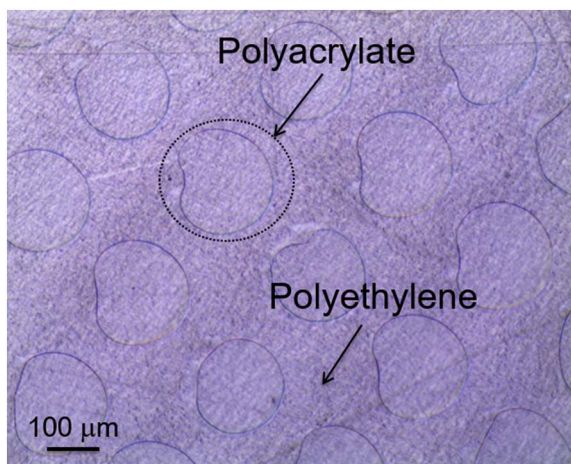


Fig. 1. Optical image of the micropatterned electrostatic film.

diameter and height of the PA bumps were 200 μm and 2 μm , respectively. Shortest distance between the centers of the two bumps was 300 μm . The ITO/PET was cleaned by sonication in dilute detergent solution, acetone and then de-ionized water (DIW) each for 5 min before the attachment of mESF. The mESF film stayed inflexibly on the substrate surface through contact electrification phenomena. The mESF-ITO/PET composite was stored in a digital desiccator for at least 7 days before use. The PB electrodeposition processes might be influenced if there were polymer residues left on the ITO surface. After the removal of the mESF, therefore, the ITO substrates were sonicated in an acetone bath for 5 min again and then dried by nitrogen flow before PB electrodeposition. The ITO/PET substrate that has been attached by mESF and removed before electrodeposition process was designated as ITO_{ES}/PET.

A conventional three-electrode electrochemical system was used for the electrodeposition of the PB and mPB films. The working electrode was the ITO/PET or ITO_{ES}/PET substrate (electrode area = 1.0 \times 1.0 cm^2), and a Ag/AgCl electrode and a Pt coil were served as the reference and counter electrodes. Potentiostatic [20] or pulse potentiostatic deposition [21] methods were employed for the electrodeposition of PB and mPB films. The plating solution was a de-aerated aqueous solution containing 10.0 mM FeCl₃, 10.0 mM K₃Fe(CN)₆ and 10.0 mM HCl. After the electrodeposition process, the obtained PB and mPB films were cleaned by DIW and stored in a digital desiccator for further experiments.

All electrochemical experiments were conducted using a CH Instruments CHI 760D Potentiostat/Galvanostat. Thickness of the PB and mPB films was measured by a surf-corder (ET3000, Kosaka Lab. Ltd.). A scanning electron microscope (S-2600H, Hitachi) was used to observe the surface morphology of the mPB films. All chemicals were used as received without further purification. ITO/PET (sheet resistance = 60 Ω/sq .) was purchased from Perm Top Co., Ltd. The potentials reported in this manuscript are all referenced to the Ag/AgCl reference electrode.

3. Results and discussion

Potentiostatic deposition method was firstly used to deposit PB films on the ITO/PET and ITO_{ES}/PET substrates. A deposition potential, E_d , was applied to the ITO/PET or ITO_{ES}/PET substrate in the plating solution for a period of deposition time, t_d , to obtain PB or mPB films. Open-circuit potential of the three-electrode system was about 0.9 V, and E_d , chosen for PB electrodeposition was 0.05, 0.25, 0.45, 0.65, 0.70, 0.75, 0.80 and 0.85 V.

The PB electrodeposition was a cathodic reaction (reduction), a more negative applying potential corresponded to a higher deposition driving force and therefore a faster PB growth rate. When ITO_{ES}/PET was used as the substrate, a mPB film can be directly created on it by the potentiostatic deposition process. Typical optical microscope images of the resulting mPB films on ITO_{ES}/PET are shown in Fig. 2. It can be seen that micropatterned PB films were indeed formed on the ITO_{ES}/PET surface by all of the potentials employed for the electrodeposition process. Fewer PB was deposited on the surface areas that had been attached by the PA bumps of the mESF (the areas inside the circles), and in contrast more PB was formed outside the circles. Average diameter of the circles was about 200 μm and which was the same as the size of the PA bumps on the mESF.

Fig. 3 shows the i - t curves of potentiostatic deposition of PB and mPB films at different E_d . The deposition current response would be larger if a more negative applying potential was used for the electrodeposition process. It was observed that the deposition current responses on ITO_{ES}/PET were all smaller than that on pristine ITO/PET substrate. Smaller deposition current response could relate to a smaller driving force for the deposition process, and which also suggested that fewer PB was deposited on ITO_{ES}/PET than on ITO/PET substrate.

Typical potentiostatic film deposition can be divided into nucleation and film growth two processes [22,23]. During nucleation process the current response increased with increasing deposition time to a maximum value, t_{max} , and started to decrease as the film growth process kicked in. Distinguishable current response maximum could be observed if E_d for the electrodeposition was more positive than 0.45 V. There was no distinguishable current peak can be determined if E_d was 0.05 V and 0.25 V, which should due to a very short nucleation period because of the use of large deposition driving force. Smaller deposition driving force could prolong the nucleation process and in this way allowed easier observation of t_{max} in i - t curves. If E_d was more positive than 0.70 V, as indicated by the arrows in Fig. 3(e)–(h), there will be two current response slope changes in the i - t curves. Such current response behaviors could be rationalized by the combination of two nucleation processes with different t_{max} involved during the electrodeposition process.

Table 1 listed the i - t curve peak time, t_{max} , of the PB potentiostatic deposition at different E_d on ITO/PET and ITO_{ES}/PET substrate (estimated from Fig. 3). As a more positive E_d was used for the PB electrodeposition, larger t_{max} could be observed on both ITO/PET and ITO_{ES}/PET substrates. It is deduced that the PB electrodeposition was proceeded at a slower speed on the areas that had been pretreated by attaching the PA bumps of the mESF than on the surface areas without such pretreatment. Therefore, the deposition current responses showed two detectable behavior changes in the i - t curves of E_d more positive than 0.07 V. These results suggested that a positive electrostatic field might be generated on the surface areas by contacting with the PA bumps for a period of time. Furthermore, such positive electrostatic field may persist during the PB electrodeposition process, which resulted in a diminution of the deposition driving force and therefore caused smaller deposition current responses.

It is interesting to know the ratio of the amount of PB deposited inside/outside of the circle areas in Fig. 2, which may refer to the selectivity of the micropattern electrodeposition. It is desired that more PB could be deposited outside than inside the circle areas, in this way a more distinct micropatterned PB film can be obtained. The micropattern deposition selectivity, S , of the micropattern electrodeposition was defined as follows:

$$S = \left(1 - \frac{T_{in}}{T_{out}} \right) \times 100\% = \left(\frac{\Delta T}{T_{out}} \right) \times 100\%$$

where T_{in} and T_{out} are the PB film thickness inside and outside the circle

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