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<th>Journal:</th>
<th><em>RSC Advances</em></th>
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<tr>
<td>Manuscript ID:</td>
<td>RA-ART-10-2015-021751.R1</td>
</tr>
<tr>
<td>Article Type:</td>
<td>Paper</td>
</tr>
<tr>
<td>Date Submitted by the Author:</td>
<td>20-Nov-2015</td>
</tr>
<tr>
<td>Complete List of Authors:</td>
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<tr>
<td>Subject area &amp; keyword:</td>
<td>Films/membranes &lt; Materials</td>
</tr>
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pH-Switchable Electroactive Composite Films of Carboxylated Multi-walled Carbon Nanotubes and Prussian Blue

Ying Tong, Yuanyuan Wang, Bowen Gao, Lei Su,* and Xueji Zhang,*

Here the combination of carboxylated multi-walled carbon nanotubes (CMWCNTs) and Prussian blue (PB) for fabricating pH-responsive electroactive composite thin films is reported. The as-prepared CMWCNT@PB composite films were found to change their electrochemical behaviors in response to the solution pH, including their cyclic voltammetric and the corresponding electrochromic behaviors. The electrochromic state of PB could be switched on and off by the solution pH. Furthermore, a linear relationship was found between the peak-to-peak potential separation of the cyclic voltammogram of PB and the solution pH, indicating that the composite film modified electrode might be useful for the development of novel pH sensors. The approach for the fabrication of pH-responsive electrochemical composite films demonstrated here should be generalizable to other redox nanomaterials.

On the other hand, carbon nanotubes (CNTs) are the typical one-dimensional nanocarbon materials that have had a profound impact on a wide range of applications. Recently, it has been known that the introduction of defects into CNTs or the doping of CNTs can be used to manipulate the electrical property of CNTs. The resultant CNTs (e.g., carboxylated CNTs) show the pH-sensitive electrical property, making them promising candidates for use as pH-responsive materials. However, despite their attractive pH-sensitive electrical property, the CNTs have received only limited attention as a kind of pH-responsive material for the design of modified electrodes.

In the present study, we report for the first time the use of carboxylated multi-walled carbon nanotubes (CMWCNTs) for fabricating pH-responsive electrochemical CMWCNT@PB composite thin films. Layer-by-layer (LBL) assembly method is used to deposite CMWCNTs multilayers onto an indium tin oxide (ITO) substrate electrode, followed by chemical deposition of PB layer. The electrochemical behaviors of the as-prepared CMWCNT@PB composite film modified electrode in response to the solution pH, including their cyclic voltammetric and the corresponding electrochromic behaviors, are studied.

1. Introduction

Stimuli-responsive materials, also known as “smart materials”, have attracted considerable research interest in recent years due to their enormous potential for many applications. Stimuli-responsive materials have also provided an opportunity to the controllable alternation of electrochemical reactions by using external stimuli. For instance, functionalization of electrode surfaces with stimuli-responsive materials in the form of self-assembled monolayers or polymeric thin films can produce switchable/tunable electrochemical properties controlled by external stimuli (e.g., heat, magnetic field, and pH). Many electrochemical reactions have been utilized in this way for developing novel electrochemical devices such as smart biosensors, switchable fuel cells and other novel electrochemical devices.

Prussian blue (PB) as the first known synthetic coordination polymers is a conventional pigment appearing in blue color and has been the subject of many applications including electrochemical sensors, ion batteries, and smart windows. Moreover, new and promising areas of application are still being explored. However, so far there have been very few reports on controllable alternation of the electrochemical reactions of PB by using external stimuli.

2. Experimental

2.1 Chemicals and materials

K$_3$Fe(CN)$_6$ was obtained from Sigma and used as received. Multi-walled CNTs (MWCNTs, 20-40 nm in diameter, 5-15 µm in length, purity > 97%) were purchased from Shenzhen Nanotech Port Co., Ltd. (China). All other chemicals of at least analytical reagent grade were obtained from Sinopharm Chemical Reagent Co., Ltd (Beijing, China). The electrolyte solution was prepared by using Britton-Robinson buffer solutions. In brief, 25 mL of a 0.4 M solution of...
H₂PO₄ and acetic acid were added to 75 mL of a mixture of KOH (1.0 M) and KCl (1.0 M). Buffer solutions of different pH were obtained by modifying the proportion between KOH and KCl.

2.2 Carboxylation of MWCNTs

MWCNTs were carboxylated using the well-known acid oxidation method. In brief, pristine nanotubes was firstly purified with 2 M nitric acid under stirring for 36 h. Then, the purified nanotubes were carboxylated using a mixture of concentrated H₂SO₄ and HNO₃ (v/v, 3:1) at 70°C for 4 h. Finally, the carboxylated MWCNTs were collected on a 220 nm pore filter membrane and washed up to neutral pH, followed by drying in vacuum at 60°C overnight.

2.3 Fabrication of films

Polycrystalline indium tin oxide (ITO) glass (Nippon Sheet Glass Co., Ltd., Japan) were cut into small pieces and then were treated with Piranha solution (7:3, vol/vol 96% H₂SO₄/30%H₂O₂) for 30 min. (CAUTION: piranha solutions are very aggressive, corrosive solutions, and appropriate safety precautions should be utilized including the use of acid resistant gloves and adequate shielding.) These treated ITO glasses were successively washed in acetone and deionized water under ultrasonication each for 10 min, and finally dried with nitrogen. Before use, the upper part of the ITO glass was covered with the double side tapes so that a square about 8 mm × 8 mm remained bare at the lower part of the ITO glass.

The MWCNT multilayers films were fabricated by alternately immersing the cleaned ITO substrates into an aqueous solution of positively charged poly(diallyldimethylammonium chloride) (PDDA) (Mw 400,000 ~ 500,000, 1 wt%) containing 0.5 M NaCl and a dispersion of negatively charged MWCNTs (1 mg mL⁻¹) for 20 min. After each immersing step the electrodes were carefully rinsed with deionized water to remove the excess of adsorption materials. The ITO covered with six or twelve bilayers of (PDDA/MWCNTs) with PDDA as the outmost layer, i.e., the MWCNT modified ITO electrodes, were used for further PB deposition.

The MWCNTs@PB modified electrodes were prepared by immersing the CMWCNT multilayers film modified electrodes into the freshly prepared mixture solution consisting of 10 mM FeCl₃·6H₂O, 10 mM K₃Fe(CN)₆, and 10 mM HCl for 20 min. Then, they were rinsed with 10 mM HCl and dried in an oven at 100°C for 2 h. For control experiments, a PB modified ITO electrode was prepared using a bare ITO electrode as the substrate according to this procedure. In addition, another PB modified ITO electrode was prepared according to a galvanostatic deposition procedure previously reported. In brief, a bare ITO electrode was immersed in a mixture solution consisting of 2 mM HCl, 2 mM K₃Fe(CN)₆, and 2 mM FeCl₃·6H₂O for galvanostatic deposition of PB by passing a current of 40 µA cm⁻² for 180 s. Then, they were rinsed with 10 mM HCl and dried in an oven at 100°C for 2 h.

2.4 Characterization of Films

For UV-vis absorption characterization, quartz slides were used instead of ITO substrates to fabricate the films. The layer deposition process was characterized by using UV-vis spectroscopy (SHIMADZU UV-1800, Japan). Surface morphology was characterized by using a field emission scanning electron microscopy (FE-SEM) (ZEISS Supra 55, German).

2.5 Measurements

Electrochemical measurements were performed with an Autolab potentiostat/galvanostat (PGSTAT302N, Metrohm, Switzerland) in an electrolytic cell with a three-electrode configuration. The modified electrodes were used as the working electrode, an Ag/AgCl (KCl-saturated) electrode as the reference electrode, and a platinum sheet as the counter electrode. Due to the well-known unstable property of PB in neutral and alkaline solutions, buffer solutions with pH values ranging from 2 to 6 were used in the electrochemical experiments. Before recording the voltammograms, all of the freshly prepared PB modified electrodes were cycled in 0.10 M KCl aqueous solution (pH 3.0) for 15 cycles around the PB±ES redox system for obtaining a stable voltammogram of soluble PB, K₂Fe(CN)_6/Fe(CN)_6^3-. During this process the insoluble PB, Fe₄Fe₆[Fe₃(CN)₆]_, formed via galvanostatic deposition can be converted to the soluble PB. Electrochemical impedance spectroscopy (EIS) measurements were carried out in the frequencies range between 10⁴ and 0.1 Hz and 5 mV of signal amplitude, and the stabilization potential was set to 0.2 V vs Ag/AgCl. The electrochemical process of the CMWCNTs@PB composite film modified electrode at potentials ranging from +0.60 to +0.10 V vs Ag/AgCl at pH 2 and 6 were videotaped, respectively, using a digital camera.

3. Results and Discussion

Fig. 1a shows the fabrication process of the CMWCNT@PB composite film modified electrode. Negatively charged CMWCNTs were firstly assembled with a strong electrolyte, i.e., positively charged poly(diallyldimethylammonium chloride) (PDDA), via the LBL self-assembly method. Then, a PB layer was deposited electrolessly on the CMWCNT multilayers to form the films of the
CMWCNT@PB composite. The obtained CMWCNT multilayers films showed a light grey color (inset of Fig. S1a, item ii). Fig. S1a shows the absorption intensity of around 730 nm, corresponding to characteristic S2a, item ii). The composite films also presented a broad absorption centered at around 730 nm corresponding to the characteristic CMWCNT@PB composite films showed a blue color (inset of Fig. S2a, item ii). The composite films also presented a broad absorption centered at around 730 nm corresponding to the characteristic C-N-Fe(III), randomly assembled networks. After PB deposition, the obtained SEM image shown in Fig. S1c indicates that the CMWCNT multilayers had the assembly growth of the CMWCNT layer was uniform spectroscopically.11 SEM image shown in Fig. S1c indicates that the CMWCNT multilayers had the randomly assembled networks. After PB deposition, the obtained CMWCNT@PB composite films showed a blue color (inset of Fig. S2a, item ii). The composite films also presented a broad absorption centered at around 730 nm corresponding to the characteristic mixed-valence charge-transfer absorbance of the polymeric Fe(II)-C-N-Fe(III), as shown in Fig. S2a. Further SEM characterization (Fig.S2b) also indicated that the CMWCNT layers were covered by the PB layer. The apparent thickness of the deposited PB layer with six bilayers was estimated to be ~100 nm according to the electron-generation electrical charge equation:

\[ L = \frac{N_A}{4F \Delta E} \]  

where \( Q \) represents the electrical charge, \( N_A \) the Avogadro's number, \( F \) the Faraday's constant and \( A \) the electrode area.

It is well-known that electrochromic PB is mainly operated between its oxidized form (PB state) and its reduced form (Prussian White state, also called as Everitt's salt (ES)), which correspond to its blue and colorless states, respectively.13 In addition, such electrochemical and electrochromic properties of PB are pH-independent. These properties of PB can be reflected from Fig.1b with the use of a bare ITO substrate electrode covered by electrolessly deposited PB with a thickness of ~3 nm. The deposited amount of PB on conductive glasses was usually very small, as reported previously.46 So, the galvanostatic deposition was used to prepare another PB modified ITO electrode with more PB amount corresponding to ~100 nm thickness calculated according to equation 1 for electrochemical and electrochromic studies, as shown in Fig. S3 and S4. From Fig. 1b and Fig. S3, it can be seen that the voltammetric behaviors of PB were essentially pH-insensitive, regardless of PB film thickness; from Fig. S4, the electrochemical behaviors of PB were also essentially pH-insensitive. For instance, at both pH 2 and pH 6, the potential cycling between +0.6 and +0.1 V vs Ag/AgCl could cause the common potential-dependent color changes between the blue color of the PB and the colorlessness of the ES.23 However, as shown in Fig. 1c, the CMWCNT@PB composite film modified electrode presented the pH-responsive cyclic voltammograms. As revealed, as the solution pH value increased, the electrochemical responses of the composite film modified electrode decreased, for instance, the values of the peak-to-peak potential separation, \( \Delta E \), and the half peak widths increased, and the peak current values decreased. These changes in the cyclic voltammograms are characteristic of the sluggish charge transfer kinetics, indicating that the increase of pH could induce the increase in the charge transfer resistance (vide infra). On the other hand, as the solution pH value decreased, the responses were restored, as shown in Fig. 1d. And as revealed, the changes in the \( I_{\text{pa}} \) and \( I_{\text{pc}} \) in response to pH were recyclable. Meanwhile, it was found that the change of the solution pH could alter the electrochromic behavior of the CMWCNT@PB composite film modified electrode. Fig. 2 shows the pictures of the electrolytic cell taken at different potentials applied to the composite film modified electrode. As revealed from Fig.2a, b, at pH 2, under the potential cycling from +0.6 to +0.1 V vs Ag/AgCl, the composite film modified electrode exhibited the common potential-dependent color changes between the blue color of the PB and the colorlessness of the ES.11 Note: the light grey was the color of the CMWCNT multilayers-coated ITO glass. However, at higher pH, the electrochromics of the composite film modified electrode was turned off. As revealed from Fig. 2c, d, at pH 6, under the same potential cycling conditions, the composite film modified electrode remained the blue color regardless of the changes in the external applied voltages. Electrochemical impedance spectroscopy (EIS) is a very useful tool in the study of charge transport processes in a film-modified electrode where the electroactive species is assumed to be fixed at the surface of the electrode.45 So EIS was performed to study the electrochemical behaviors of the CMWCNT@PB composite film modified electrode with six bilayers in response to pH. As shown in Fig. 3, at pH 2, the composite film modified electrode exhibited a small semicircle at high frequencies with a vertical branch at low frequencies in the complex impedance plane. The semicircle
corresponds to the charge transfer resistance, $R_{ct}$, at the CMWCNT|PB interface. With increasing pH, the semicircle became remarkably larger, indicating the increase in the charge transfer resistance at the CMWCNT|PB interface. For instance, at pH 6, the increase in the right intercept of the semicircle with the Z' axis was more than 1 kΩ, indicating remarkably sluggish electron transfer kinetics at the CMWCNT|PB interface, in accordance with the obtained voltammetric results (see Fig. 1c). In comparison, Fig. S5 shows the EIS of the PB modified ITO electrode. It can be seen that in the absence of CMWCNT the charge transfer resistance of PB was small, not more than 200 Ω. These results clearly indicate that the pH increase resulted in the increase in the charge transfer resistance at the CMWCNT|PB interface. It has been known that the carboxylation of CNTs can introduce the saturated sp² carbon centers which act as scattering sites to alter the electronic and transport properties of the nanotubes and that the scattering state of PB could be switched on and off by the solution pH. Meanwhile, a linear relationship was found between the $\Delta E$ and the solution pH, indicating that the composite film modified electrode might be useful for the development of novel pH sensors.

4. Conclusions

In conclusion, we have demonstrated the pH-responsive voltammetric and electrochromic behaviors of the composite films fabricated via combining the CMWCNTs and PB. The electrochromic state of PB could be switched on and off by the solution pH. However, such a linear relationship indicates that the composite film modified electrode might be useful for the development of novel pH sensors. On the other hand, although the potential application of the composite films could be limited by the instability of PB in nonacidic solutions at present, various methods for improvement of the stability of PB in nonacidic solutions are being developed worldwide, which will broaden the potential application of the composite films. In addition, the approach for the fabrication of pH-responsive electrochemical composite films demonstrated here should be generalizable to other redox nanomaterials.

Acknowledgements

The support from the National Natural Science Foundation of China (Grant No. 21775010, 21545012 and 21275017), the Project-sponsored by SRF for ROCS, SEM, and the grant from Beijing Municipal Science and Technology Commission (z131102002813058) is highly appreciated.

Notes and references


