Electropolymerization of polypyrrole on PFIL–PSS-modified electrodes without added support electrolytes

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Abstract

A novel polyelectrolyte-functionalized ionic liquid (PFIL)/poly(4-styrene sulfonate sodium) (PSS) modified electrode composed of the coaxial and coplanar working, reference and counter electrodes, was used to electropolymerize the polypyrrole. The PFIL/PSS was modified on the integrated electrode (IE) and connected by the working, reference and counter electrodes, resulting in an available charge transfer and lower Ohmic potential drop between the working and counter electrodes. Then polypyrrole (PPy) film was successfully prepared electrochemically without any participation of supporting electrolytes, only in a pyrrole monomer solution. The resulting PPy film in PFIL/PSS matrix exhibited a preferable electroactivity. Subsequently, influence of the modifications on the formation of PPy was further discussed. The results indicated that the synergetic cooperation of PFIL and PSS components accomplished such a successful electropolymerization of PPy.

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1. Introduction

The π-conjugated molecules such as polyaniline, polypyrrole and polythiophene belong to one of the most interesting classes of conducting materials. Since their discovery, they hold great promise for applications as electrochemical devices in fields of sensors, batteries, electrochromic devices, light emitting cells and supercapacitors, etc. [1–3]. Among them, polypyrrole is considered as an especially promising conducting polymer due to its relative ease of synthesis both chemically and electrochemically [4]. In the 1970s, Diaz and coworkers firstly synthesized conductive polypyrrole film via electropolymerization [5]. Due to the remarkable electric and optic properties, and favorable environmental stability, polypyrrole films received much attention and succeeded extensive applications in electrochemical sensor, semitransparent electrode, molecular electronic devices, anti-corrosion coating, etc. [6–13]. Furthermore, ionic liquids are fluid at room temperature, sometimes they were utilized both as electrolyte and solvents in the electrochemical preparations of conducting polymers [4,14]. Ionic liquids exhibit numerous advantages over conventional solvents due to their unique chemical and physicochemical properties, such as non-flammability, non-volatility and chemical stability [15–17]. In particular, the considerably high ionic conductivity (>10^{-4}\text{ s cm}^{-1}), broad electrochemical window (>4 V) and fast ion mobility (>10^{-14} \text{ m}^{2}\text{ s}^{-1}) [6] make it competent to play the roles of both solvent and electrolyte during the electropolymerization of conducting polymers.

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As presented in this work, a method for the electropolymerization of PPy without any added support electrolytes in pyrrole monomer solution was explored. A composite of polyelectrolyte-functionalized ionic liquid (PFIL) and poly (4-styrene sulfonate sodium) (PSS) was used as the electrode modifier, where polypyrrole can be polymerized electrochemically (as shown in Scheme 1).

Cyclic voltammetric measurements revealed that the obtained polypyrrole film has a preferable electroactivity. It is rarely reported that polypyrrole can be electrochemically prepared without any assistance of electrolyte in a pure pyrrole monomer solution.

2. Experimental

The PFIL is prepared according to our previous work [18]. Poly(4-styrene sulfonate sodium) (PSS, $M_{c,a} = 70,000$) was purchased from Aldrich Chemical Company. All aqueous solutions were prepared with double distilled water from a Millipore system (18.2 MΩ cm). The electrochemical measurements were carried out with a CHI 660 electrochemical workstation (CHI, USA).

The structure of the integrated electrode (IE) is shown in Scheme 2a and b. The working electrode was a glass carbon electrode ($d = 1$ mm), and coaxial Pt and Ag rings were used as the counter and quasi-reference electrodes, respectively. The cross-section of the three electrodes was a concentric circle and kept on a plane. The three electrodes were encapsulated with epoxy and assembled into an integrated electrode.

Prior to the modification, the IE electrode was polished with 1.0, 0.3, and 0.05 μm Al₂O₃ powder, washed ultrasonically, and dried under nitrogen. Then the polyelectrolyte aqueous solution was casted on the surface of IE and dried at room temperature.

Polypyrrole (PPy) film was electrochemically prepared by multiple potential cycling (50 cycles between $-1.0$ V and $1.0$ V vs. the Ag quasi-reference electrode) at a sweep rate of 100 mV/s in 0.1 M pyrrole monomer aqueous solution on the IE GC electrode. When the electropolymerization was accomplished, the PPy-coated electrode was subsequently removed from the monomer solution, and washed thoroughly with superpure water for several times. Electrochemical measurements of the resulting PPy film were succeeded in 1 M KNO₃ aqueous solution. All the experiments were performed at room temperature.

3. Results and discussion

Here, by using an integrated glassy carbon electrode and a PFIL/PSS modifying membrane which connected the working, reference and counter electrodes, electropolymerization of pyrrole can be successfully performed. By utilizing the PFIL/PSS membrane it resulted in an available

![Scheme 1. Scheme of preparation of PFIL–PSS (a) PFIL and (b) PFIL–PSS.](image1)

![Scheme 2. Illustration of the integrated glassy carbon electrode (a) top view, (b) section, and (c) electrochemical processes of the PFIL–PSS-modified electrode surface.](image2)
charge transfer and lower *Ohmic* potential drop between the working and counter electrodes. Different from conventional electropolymerization, the PFIL/PSS-modified IE resulted into unique polymerization of polypyrrole without the addition of any electrolytes in the solution.

In general, polyelectrolyte hydrogels could be easily immobilized onto the electrode substrate *via* various methods. The PFIL was a kind of hydrogels, thus, it could also form rather stable film on the electrode surface simply by casting, as we reported early [18]. The anion of PFIL, here is Cl, was exchanged by PSS *via* a direct mixing prior to the modification.

Scheme 2c illustrates the conformation of such an IE electrode with the immobilization of PFIL/PSS components and its mechanism of electrochemical process. A top view of the IE electrode exposes a GC rod in center of the electrode, which serves as the working electrode. The PFIL/PSS modified on the integrated electrode (IE) connected the working, reference and counter electrodes, resulting in an available charge transfer and lower *Ohmic* potential drop between the working and counter electrodes. The casting PFIL–PSS membrane on the IE electrode surface plays both the role of charge carrier and dopant of electropolymerized PPy. Thus, it is feasible for electropolymerization of PPy without further addition of any supporting electrolytes in this system.

Representative growth of PPy film was monitored by cyclic voltammetry (during −1.0 V to 1.0 V at a scanning rate of 100 mV/s), the resulting cyclic voltammogram during the electropolymerization on such a PFIL–PSS-modified IE electrode is shown in Fig. 1. Formation and growth of the polymer film can clearly be seen in this figure. With each successive scan, the peak current associated with both the characteristic anodic and cathodic waves of the PPy polymer increased and the maximum oxidation current of pyrrole monomer can be achieved at ca. 150 μA.

The above phenomena suggested the continuous deposition of PPy film in the PFIL/PSS matrix on subsequent potential scanning [13]. And the growth rate of PPy film on PFIL–PSS-modified IE electrode is found to be respectively uniform during the whole scanning process as well.

After electropolymerization, the PFIL/PSS-modified IE electrode with the electrodeposited PPy film was then characterized by cyclic voltammetry in pyrrole-free aqueous solution containing 1 M KNO₃ (as shown in Fig. 2). In order to distinguish the influence of PFIL/PSS modification on electrochemical behavior of the resulting PPy film, CV characterization of PFIL–PSS-modified IE electrode before the electrodeposition of PPy was also performed in the same solution. The result was also shown in Fig. 2.

It can be easily found in curve a in Fig. 2 (inset) that the CV of PFIL–PSS-modified IE electrode before the polymerization does not show any characteristic redox behavior of PPy. It is obviously seen that CV curve after the electrodeposition of PPy films (shown in curve b of Fig. 2) exhibits fairly well-defined oxidation–reduction waves at 0.15 V and −0.27 V, which are in great coincidence with previous report [19]. And it is notable that the maximum redox current almost reached ca. 200 μA, suggesting a favorable electroactivity of resulting PPy film and predominant electrodeposition of PPy in the PFIL/PSS matrix.

Comparing curve a with curve b, it can be confirmed that the PPy has been well deposited on the PFIL/PSS-modified electrode. And the PFIL/PSS membrane can play a role of charge carrier on surface of IE electrode instead of conventional electrolyte during the electropolymerization.

Moreover, influences of bare, PFIL- and PSS-modified IE electrodes on the electropolymerization of PPy were also investigated. As seen in Fig. 3, when a bare IE electrode was used, only a small current growth in CV curve a can be observed, and the maximum peak current is less than
A. The PFIL-modified IE electrode (curve b in Fig. 3) presented a similar result whose maximum peak current is only around 1.0 μA. While PSS itself was immobilized on the IE electrode (curve c in Fig. 3), a relatively high current growth was noticed. However, the maximum peak current is no more than 8.0 μA, and it is inappreciable to the result on PFIL–PSS co-modification.

Electrochemical behaviors of the resulting PPy films electrodeposited from the cases of different modifications were examined further by cyclic voltammetry in 1 M KNO₃ solution (shown in Fig. 4). It is found that an evident difference can be observed in curve a, b, c and d of Fig. 4. In another word, PPy film is much easier to be electrodeposited on PFIL–PSS-modified surface than those on bare, PFIL and PSS modifications.

The difference of electrodeposition of PPy films on various electrodes (bare, PFIL, PSS and PFIL/PSS) can be explained as follows: (i) It is the absence of supporting electrolytes in the monomer solution, which provides the necessary ions needed for electroneutrality during polymerization, that made it unsuccessful to trigger this polymerization under this open circuit system due to low conductivity of the solution (although the counter and working electrodes on the IE electrode is separated not too far). Finally, very low rate of electropolymerization resulted. (ii) PFIL is a kind of positively charged functionalized ionic liquids which can provide a high ionic conductivity and fast ion mobility during electropolymerization.

c. 0.6 μA. The PFIL-modified IE electrode (curve b in Fig. 3) presented a similar result whose maximum peak current is only around 1.0 μA. While PSS itself was immobilized on the IE electrode (curve c in Fig. 3), a relatively high current growth was noticed. However, the maximum peak current is no more than 8.0 μA, and it is inappreciable to the result on PFIL–PSS co-modification.

Due to the high conductivity of PFIL itself on the IE surface, the polymerization can be triggered on the working electrode. However, PFIL is positively charged species on the electrode, and the pyrrole radicals triggered from monomers are also positively charged. Then, the electrostatic repulsion restricts abundant triggering of pyrrole radicals on the surface of electrodes to deposit on the electrode surface [20], finally the electropolymerization is restricted. (iii) As depicted in the case (ii), the high conductivity of PFIL on the IE surface will undoubtedly result in the electrodeposition of PPy. In addition, the introduced big anion, PSS, with a quite low mobility will play a role as a counter ion of PFIL component in the film matrix. Then, during the polymerization, the electrostatic repulsion will be reduced and the negatively charged PSS can also act as the dopant of PPy, then, a high electropolymerization rate resulted. (iv) The enhanced electrodeposition of PPy should be originated from the synergistic effect of PFIL and PSS, the enrichment and solubility of PFIL towards species in the solution, here is pyrrole monomer, is helpful and predominant to electropolymerization of PPy, finally, an obvious PPy film was resulted on such a PFIL/PSS-modified substrate.

Furthermore, the stability of the PFIL–PSS membrane was examined too. Even after electropolymerization of PPy, it still shows quite great stability, no obvious desorption/loss can be observed after several cyclic potential scans.

4. Conclusion

In conclusion, PPy film was electrochemically prepared successfully on a PFIL–PSS-modified IE electrode with no added supporting electrolyte solution. Such a PFIL–PSS mixed modification shows a great enhancement on the electrodeposition of PPy. The results also indicate that the negatively charged surface is much favorable to the
electrodeposition, and ionic liquid component also plays a key role on the enrichment of monomers in the film matrix, which result in an enhanced electrodeposition of PPy. Similar way can be extended to the preparation of other conducting polymers. The resulting PFIL–PSS–PPy film shows potential applications in sensors, electrochromic devices, fuel cells, etc.

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