

Electropolymerization of Pyrrole in Ionic Liquid Microemulsion

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ABSTRACT: The direct electropolymerization of pyrrole in [BMIM]PF₆ microemulsion was investigated for the first time. The H₂O/TX-100/[BMIM]PF₆ (W/IL), bicontinuous (BC), [BMIM]PF₆/TX-100/H₂O (IL/W) subregions can be used as electrolytes for pyrrole electropolymerization. The use of IL microemulsion remarkably reduces the amount of IL. Furthermore, electrochemical measurements indicated that W/IL microemulsion was the optimal medium and its polymerization rate was the fastest. Compared with molecular solvent system (0.25 mol L⁻¹ [BMIM]PF₆/

acetonitrile) and neat [BMIM]PF₆, the resultant films electrodeposited in W/IL microemulsion possessed excellent electrochemical activity and uniform morphology. All the results indicated that the H₂O/TX-100/[BMIM]PF₆ microemulsion as electrolyte medium is the most suitable for electropolymerization of pyrrole. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 2342–2347, 2012

Key words: ionic liquid; microemulsion; electropolymerization; conducting polymer; polypyrrole

INTRODUCTION

Inherently conducting polymers (ICPs) as promising organic materials have been extensively studied with growing interest, which not only display electrical, electronic, magnetic, and optical properties similar to metals, but also have mechanical properties and low density of a polymer.¹ As an especially promising ICP, polypyrrole (PPy) was investigated actively during the last two decades. Because of highly conducting, environmentally stable and relatively easy to synthesize, PPy has been widely used in biological sensors,^{2,3} light emitting diodes,⁴ advanced battery systems,⁵ and electromechanical actuators.⁶

Traditionally, PPy films were prepared by electrochemical polymerization of pyrrole in an electrolyte/molecular solvent system. The properties of the resultant PPy films were closely related to the nature of the dopant counter-ions and solvent.⁷ Nowadays, room temperature ionic liquids (RTILs) are air and

water stable salts,⁸ which also have been used as electrolyte for the electropolymerization of pyrrole. The as-prepared films displayed significantly higher conductivity and better mechanical behaviour than those prepared in conventional solvent systems.^{9–11} In a word, the use of RTIL both as the growth medium and a supporting electrolyte led to significantly altered film morphologies and improved electrochemical activities. Although the popularity of the air and moisture stable RTILs has raised steadily, the high cost of RTILs confined their applications.

Microemulsions are transparent, isotropic, and thermodynamically stable dispersions of two immiscible liquids stabilized by a surfactant and occasionally a cosurfactant.¹² To expand the application of RTILs and microemulsion, a new concept relating to IL-based microemulsions was put forward.^{13,14} Similar to traditional microemulsion, the IL-based microemulsions were also classified as three types. For 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM]PF₆), non-ionic surfactant TX-100 and water system, water-in-[BMIM]PF₆ (W/IL), bicontinuous (BC), and [BMIM]PF₆-in-water (IL/W) subregions were identified.¹⁵ In view of economic and environmental problems, these new versatile ionic liquid microemulsion media were used for electrodeposition, catalysis, and fabrication nanomaterials.^{16–19} By the aid of good conductivity and special microstructure, ionic liquid microemulsion possesses transcendent applications in electrosynthesis.^{20,21} Further-

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more, compared with neat IL, this kind of IL microemulsion significantly reduces the amount of IL.

However, the categories of ionic liquid microemulsion have obvious effects on the rate of electropolymerization and properties of polymer films.²¹ In our work, we investigated the electropolymerization of pyrrole in [BMIM]PF₆ microemulsion (W/IL, BC, and IL/W). In the process of electropolymerization, [BMIM]PF₆ serves both as dopant and supporting electrolyte, and PF₆⁻ anion enters into the conjugated backbone of PPy films. Series of comparative experiments showed that the H₂O/TX-100/[BMIM]PF₆ microemulsion was optimal medium for the electropolymerization of pyrrole. The electrochemical properties and morphology of as-prepared PPy films were investigated.

EXPERIMENTAL

Material

The ionic liquid [BMIM]PF₆ was prepared according to previous literature,²² and dried under vacuum at 70°C for 12 h before use. Its purity was checked by AgNO₃ test, ¹H- and ³¹P-NMR, and cyclic voltammetry.²³ The pyrrole monomer was purchased from Shanghai Chemical Reagent Factory (China), distilled under reduced pressure and stored at -4°C prior to use. Surfactant TX-100 (chemical pure grade, Sinopharm Chemical Reagent) and acetonitrile (CH₃CN, HPLC grade, Sinopharm Chemical Reagent) were used directly without further purification. Water used in the experiments was deionized (DI), double distilled prior to use. All experiments were carried out at room temperature.

Electropolymerization

Prior to each experiment, the glassy carbon electrode was polished to a mirror finish using alumina powder and then was ultrasonicated in ethanol and double distilled water for 5 min successively. PPy films were grown potentiostatically in pure [BMIM]PF₆, 0.25 mol L⁻¹ [BMIM]PF₆/acetonitrile and H₂O/TX-100/[BMIM]PF₆ microemulsion. For the three electrolytes mentioned above, the parameters of pyrrole electropolymerization are as follows: the monomer concentration is 0.25 mol L⁻¹ and the polymerization potential is 1.0 V, 0.9 V, and 0.9 V respectively. The slightly higher potential used in pure [BMIM]PF₆ reflected the increased IR drop in the medium due to its higher viscosity. The amount of polymer was controlled by the deposited charge (0.1 C). All the measurements were performed under a nitrogen atmosphere to avoid the effect of oxygen. After polymerization, the polymer was washed carefully with acetonitrile and water. Finally, the resultant films

were characterized after they were dried in vacuum at 60°C for 12 h. Note that during electrochemical polymerization and examination, there was no deposit at all in the monomer-free IL microemulsions, indicating that the electrolyte systems and the electrode were electrochemically inert.

Characterization

The morphologies of the films were studied by HITACHI S-4800 scanning electron microscopy (SEM) at an accelerating voltage of 5 kV. The chemical analysis was obtained by energy dispersive X-ray spectroscopy (EDS) microanalyzer mounted on the HITACHI S-4800.

Electrochemical polymerization and examination were carried out with a CHI model 660C electrochemical workstation (Shanghai Chenhua Instrument Factory, China), using glassy carbon (GC, *S* = 0.07065 cm²) or PPy films modified GC electrode as working electrode, a platinum coil counter electrode and a Ag wire pseudo-reference electrode, which was not calibrated.²⁴ All potentials were measured versus the pseudo-reference electrode.

RESULTS AND DISCUSSION

Anodic polarization curves of pyrrole

Three types of IL microemulsions were prepared as previous reported.¹⁵ The anodic polarization measurements of pyrrole were performed in three types of IL microemulsions and neat IL, as shown in Figure 1. It is obvious that for W/IL microemulsion, the oxidation onset potential of pyrrole was moderate (0.68 V) and the current density of polymerization

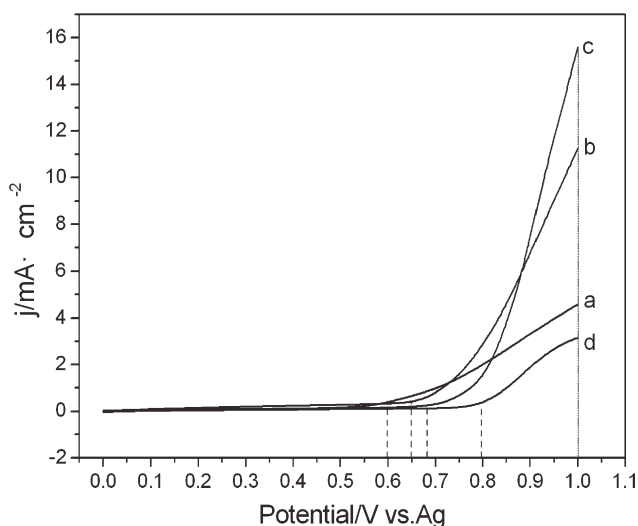


Figure 1 Anodic polarization curves of 0.25 mol L⁻¹ pyrrole in IL/W (a), BC (b), W/IL (c), and IL (d). Scan rate: 50 mV s⁻¹.

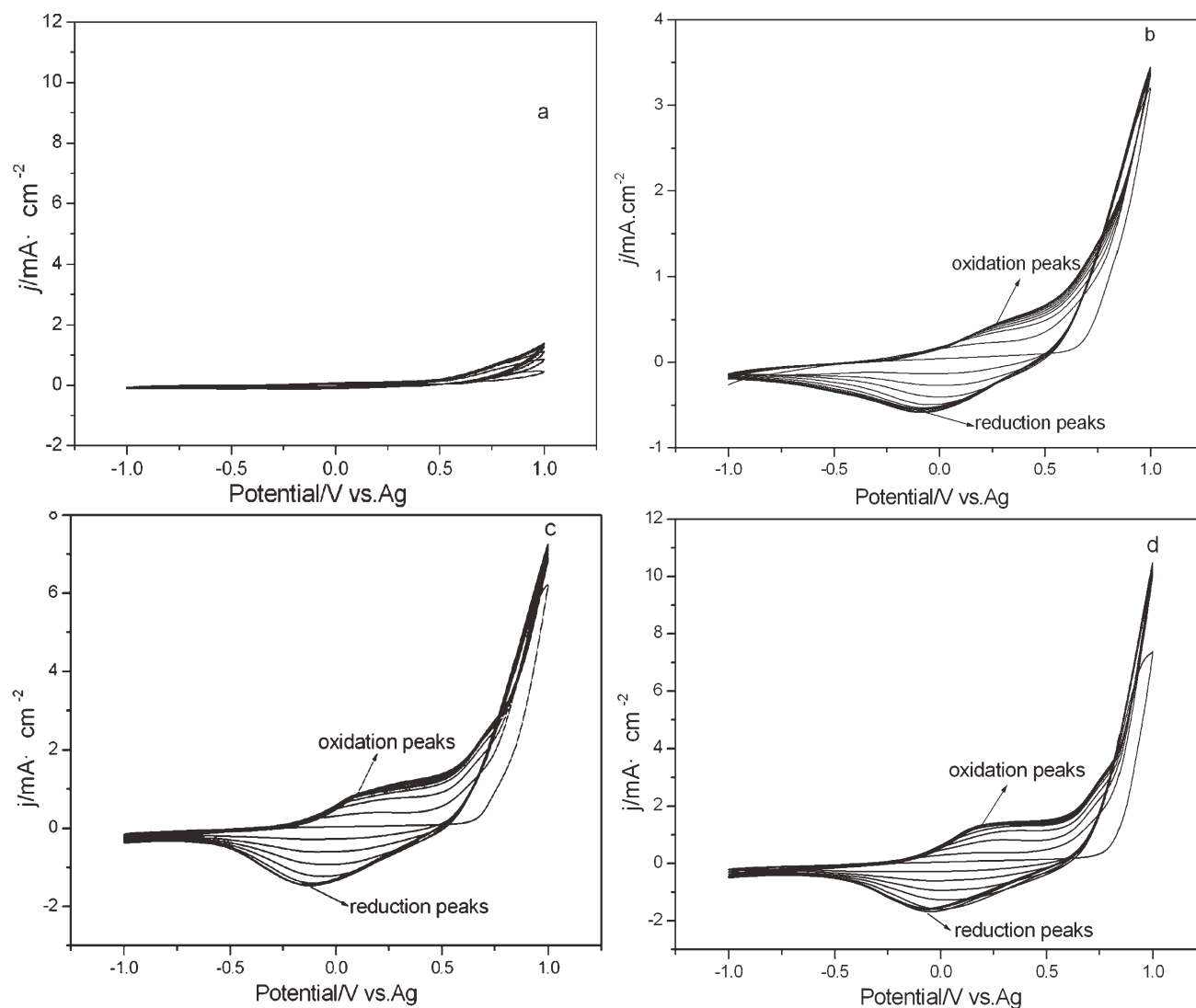


Figure 2 Cyclic voltammograms of 0.25 mol L⁻¹ pyrrole in IL (a), IL/W (b), BC (c), and W/IL (d). Scan rate: 50 mV s⁻¹.

was the largest [Fig. 1(c)]. After polymerization, black PPy films on the GC electrode were clearly observed. It was clear that the electropolymerization of pyrrole can be completed easily in W/IL microemulsion. As for IL/W microemulsion [Fig. 1(a)], the oxidation onset potential of pyrrole was 0.6 V lower than that in both BC microemulsion (0.65 V) and neat IL (0.8 V) as shown in Figure 1(b,d). However, much lower current density was presented when pyrrole was polymerized in IL/W microemulsion. The electropolymerization was inhibited by large surfactant concentration in IL/W microemulsion due to surfactant adsorption.^{15,25} The lowest current density was attributed to higher viscosity of IL when pyrrole was electropolymerized in neat [BMIM]PF₆ at room temperature [Fig. 1(d)]. The different oxidation onset potential of pyrrole in these four media might be attributed to their different microstructure. Further, the apparent concentration is the same, but the real concentration distribution of pyr-

role might differ due to the different structure of the microemulsions, which also affect the onset potential. Therefore, among the four electrolytes, W/IL microemulsion is the most suitable medium for electropolymerization of pyrrole. Similar results would be obtained in the following cyclic voltammetry measurements.

Cyclic voltammograms of pyrrole

Comparison of the growth cycles recorded during the electropolymerization of pyrrole in neat IL and those recorded during film growth in three types of IL microemulsions is shown in Figure 2. It records successive 10 cyclic voltammograms (CVs) of pyrrole in the four electrolytes. In IL or IL/W microemulsion, redox peak currents did not obviously increase, and thus, a little polymer film formed on the surface of the working electrode [Fig. 2(a,b)]. As for W/IL microemulsion [Fig. 2(d)], such a CV is similar to

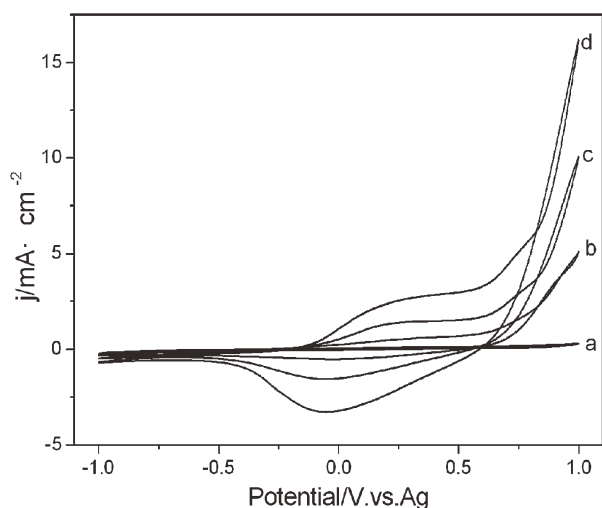


Figure 3 Cyclic voltammograms in W/IL microemulsion at different pyrrole monomer concentrations of 0.05 mol L⁻¹ (a), 0.15 mol L⁻¹ (b), 0.25 mol L⁻¹ (c), and 0.35 mol L⁻¹ (d). Scan rate: 50 mV s⁻¹.

that of pyrrole electropolymerization in 1-ethyl-3-methylimidazolium trifluoromethanesulfonate (EMICF₃SO₃) reported by Kei Sekiguchi et al.¹⁰ Redox peak currents increased upon sequential cycles, suggesting that more and more polymer films formed on the working electrode. Comparing the CVs of pyrrole in the four media, the defined peaks and the largest current density are presented in W/IL microemulsion, implying that the formation of PPy film was the easiest and the polymerization rate was the fastest. On the basis of the discussions above, the following work was focused on the electropolymerization of pyrrole in W/IL microemulsion.

The effect of monomer concentration

It was worth mentioning that the monomer concentration affected the electropolymerization. Figure 3 records the tenth cycle in W/IL microemulsion at different pyrrole monomer concentrations (0.05, 0.15, 0.25, and 0.35 mol L⁻¹) from -1.0 V to 1.0 V. With the increase of monomer concentration, the redox peak currents increased. Although defined redox peaks and the largest peak currents existed at the condition of high concentration pyrrole in Figure 3(d) (0.35 mol L⁻¹), the microemulsion became a little feculent, and it never belongs to the definition of "microemulsion".²¹ Therefore, we choose 0.25 mol L⁻¹ pyrrole as the optimum concentration for the electropolymerization of pyrrole in W/IL microemulsion.

The electrochemistry of PPy films

Recently, electrolyte/molecular solvent system or pure ionic liquid was used as electrolyte for the elec-

tropolymerization of pyrrole. However, according to the discussions above, the H₂O/TX-100/[BMIM]PF₆ microemulsion can be considered as an effective medium for the electropolymerization of pyrrole at the condition of 0.25 mol L⁻¹ monomer concentration. To investigate the predominance of the H₂O/TX-100/[BMIM]PF₆ microemulsion as electrolyte, we also electrosynthesized PPy films in electrolyte/molecular solvent system (0.25 mol L⁻¹ [BMIM]PF₆/acetonitrile) and pure ionic liquid ([BMIM]PF₆). After electropolymerization, the working electrode with PPy films attached was removed from the three media, rinsed with a little acetonitrile, and the electrochemical properties of the films were assessed. Surprisingly, the electrochemical responses of the films when cycled in a conventional solvent system were dramatically different.

The considerable increase in capacitance of the PPy films is of particular interest, since PPy and other ICP materials have recently been found in redox supercapacitors application.²⁶ Figure 4 presents the post-polymerization cyclic voltammograms of PPy films. It is clear that the PPy films prepared in H₂O/TX-100/[BMIM]PF₆ microemulsion [Fig. 4(b)] are much more electrochemically active than those prepared in the conventional [BMIM]PF₆/CH₃CN solvent system [Fig. 4(c)] and neat [BMIM]PF₆ [Fig. 4(a)] under equal deposited charge. The peak current of the anodic wave of the PPy films grown in H₂O/TX-100/[BMIM]PF₆ microemulsion (1.2 mA) is about three times of the films obtained in neat [BMIM]PF₆ (0.4 mA). Therefore, the H₂O/TX-100/[BMIM]PF₆ microemulsion as an electrolyte for pyrrole electropolymerization was useful to improve the electrochemical activity and capacity of PPy films.

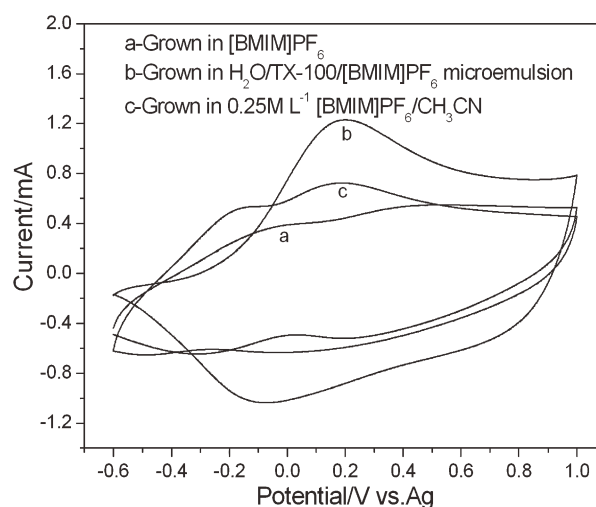


Figure 4 Comparison of the electrochemical activity of the PPy films in 0.25 mol L⁻¹ [BMIM]PF₆/CH₃CN solution. Scan rate: 50 mV s⁻¹.

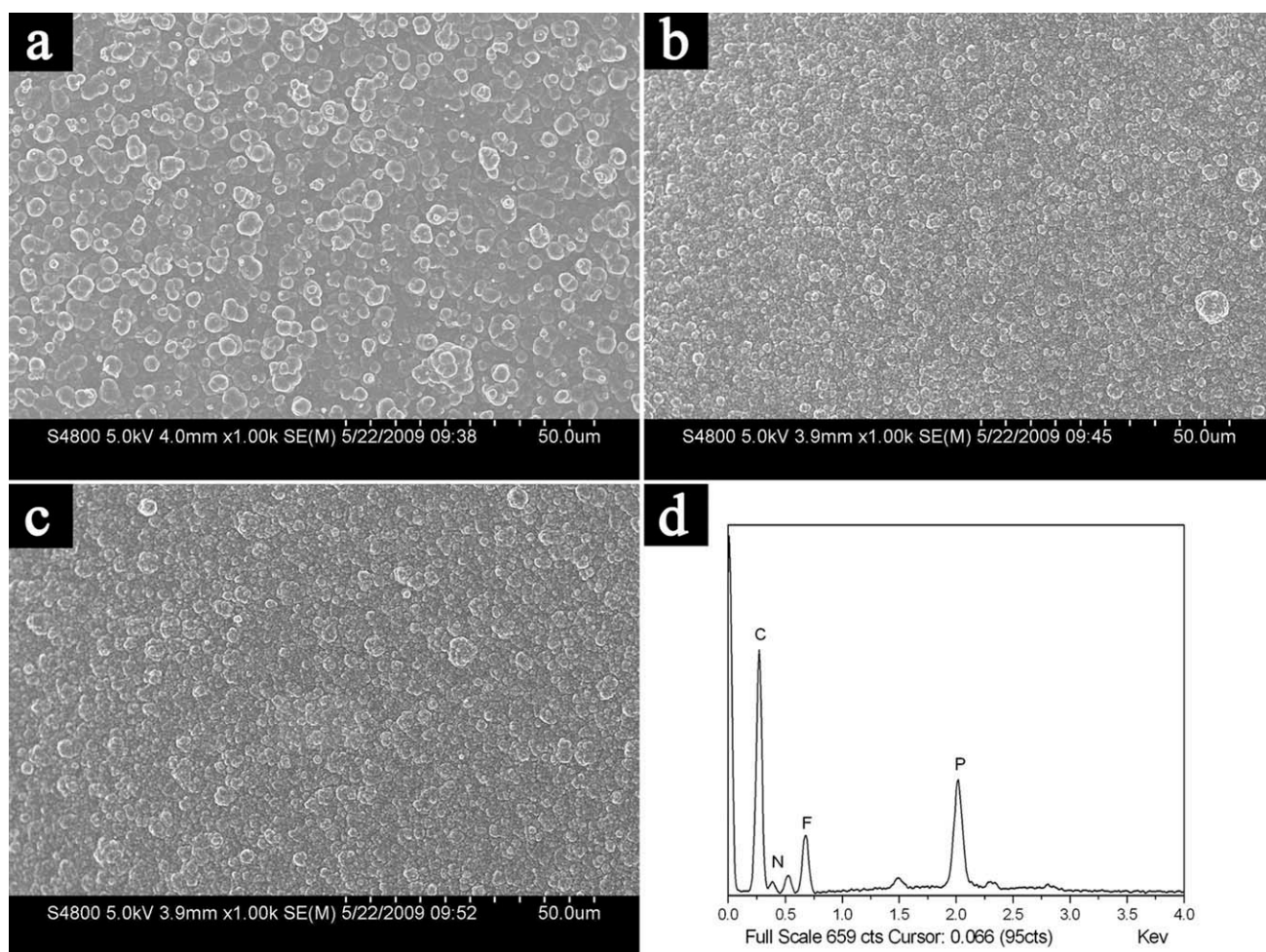


Figure 5 SEM images of as-formed PPy films obtained in neat [BMIM]PF₆ (a), H₂O/TX-100/[BMIM]PF₆ microemulsion (b), 0.25 mol L⁻¹ [BMIM]PF₆/CH₃CN (c) and the EDS of PPy films deposited in H₂O/TX-100/[BMIM]PF₆ microemulsion (d).

The morphology of PPy films

The surface morphologies of PPy films synthesized in 0.25 mol L⁻¹ [BMIM]PF₆/CH₃CN solvent system, neat [BMIM]PF₆ and H₂O/TX-100/[BMIM]PF₆ microemulsion were observed by SEM. As shown in Figure 5, the microballs located densely, covering the whole surface of the working electrode. However, the mean size of microballs grown in H₂O/TX-100/[BMIM]PF₆ microemulsion is 0.1 μm [Fig. 5(b)], which are smaller and more uniform than those in neat [BMIM]PF₆ (5 μm) or [BMIM]PF₆/CH₃CN solvent system (2 μm) as shown in Figure 5(a,c). Here, the smooth film prepared in the H₂O/TX-100/[BMIM]PF₆ microemulsion are mainly due to the homogenous microstructure of microemulsion. When the pyrrole monomer was added into the ionic liquid microemulsion, it was emulsified to tiny droplet due to the effect of TX-100.²⁷ At the beginning of electrodeposition, the emulsifiable droplet collided with the working electrode simultaneously, which made identical velocity of nucleation and

growth in the process of electrochemical synthesis of PPy films. Consequently, the H₂O/TX-100/[BMIM]PF₆ microemulsion was suitable for electrochemical synthesis of PPy films. The EDS of PPy films electrodeposited in H₂O/TX-100/[BMIM]PF₆ microemulsion is shown in Figure 5(d). The phosphorus and fluorine elements were from PF₆⁻ group. Hence, the PF₆⁻ anion serving as dopant entered into the conjugated structure when PPy films were electrochemically synthesized in H₂O/TX-100/[BMIM]PF₆ microemulsion.²⁸

CONCLUSIONS

In summary, the electropolymerization behavior of PPy in H₂O/TX-100/[BMIM]PF₆ (W/IL), bicontinuous (BC), [BMIM]PF₆/TX-100/H₂O (IL/W) microemulsions and [BMIM]PF₆ were studied and compared. The results indicate that the electropolymerization in W/IL microemulsion shows a relatively negative onset potential (0.68 V vs. Ag) and the largest current density. The as-prepared PPy

film was composed of dense microball with uniform size (0.1 μm). The use of W/IL microemulsion remarkably reduces the amount of IL. Simultaneously, compared with conventional molecular solvent system, W/IL microemulsion as an electrolyte for electropolymerization of pyrrole is effective to control the morphology, improve polymerization rate and electrochemical activity of the films. The successful electrosynthesis of PPy films in ionic liquid microemulsion develops a versatile medium for conducting polymers preparation.

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