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Water/ionic liquid/organic three-phase interfacial synthesis of coral-like polypyrrole toward enhanced electrochemical capacitance

Linrui Hou [a], Changzhou Yuan [a,*], Diankai Li [a], Long Yang [a], Laifa Shen [b], Fang Zhang [b], Xiaogang Zhang [b,**]

[a] Anhui Key Laboratory of Metal Materials and Processing, School of materials Science & Engineering, Anhui University of technology, Ma'anshan, 243002, PR China
[b] College of Material Science & Engineering, Nanjing University of Aeronautics and Astronautics, Nanjing, 210016, PR China

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ABSTRACT

Two interfacial synthesis strategies are proposed to synthesize polypyrrole samples for electrochemical capacitors (ECs). In contrast to water/organic two-phase route, unique water/ionic liquid (IL)/organic three-phase interface strategy is first performed to prepare coral-like polypyrrole with even better electrochemical capacitance, where 1-Ethyl-3-methylimidazolium tetrafluoroborate IL, as a "buffering zone", is set between the water and organic phases to control the morphology and micro-structure of the polypyrrole phase during polymerization. The polypyrrole synthesized by three-phase interfacial route owns more ordered structure, less charge transfer resistance and better electronic conductivity, compared with two-phase method, and delivers larger specific capacitance, higher rate performance and better electrochemical stability at large current densities in 3 M KCl aqueous electrolyte.

1. Introduction

Electrochemical capacitors (ECs), due to their greater power density than batteries and larger energy density than conventional capacitors, are widely investigated presently [1,2]. They not only enable electric vehicles but also provide back-up for wind and solar energy, which are both essential to meet the challenge of global warming and the finite nature of fossil fuels. Now much effort has been devoted to increase their energy and power density meanwhile, as well as using environmentally friendly materials with low cost. Particularly, conducting polymers (CPs) have been considered as one of the most potential electrode materials for ECs application. Among various CPs, polypyrrole (PPy) is an especially practical material for ECs thanks to its high electronic conductivity, long-term environmental stability, environmental friendliness and relative easy synthesis process [2–7].

For electroactive PPy, a key point to obtain a high and stable specific capacitance (SC) at high rates lies in a pregnant design of the electroactive region [3–7]. For instance, the overoxidation and more $-CH_2-$ formation at its rings during the polymerization should be avoided, and its ordered structure and good electronic conductivity must be guaranteed meanwhile. They greatly influence the electrochemical capacitance of the PPy electrode. Of note, these factors are firmly dependent upon the polymerization process. Therefore, it is of great significance to explore a facile but efficient way to control the PPy polymerization. Recently, an organic-aqueous soft interface has been established as an alternative useful approach to conventional homogeneous synthesis [8–10]. Two-phase interface polymerization was performed commonly [10], unfortunately, three-phase interface synthesis has been scarcely reported up to now.

In this work, water/ionic liquid (IL)/organic three-phase interface route was first used to synthesize coral-like PPy sample, where 1-Ethyl-3-methylimidazolium tetrafluoroborate ([Emim]BF_4) IL was set between organic and aqueous phases and played a great role of "buffering zone" to control the PPy polymerization process. In comparison with the two-phase route, coral-like PPy synthesized by the three-phase strategy possessed more ordered structure, less charge transfer resistance and better electronic conductivity, and delivered larger SC, higher rate behavior and better electrochemical stability in 3 M KCl aqueous solution.

2. Experimental

2.1. Interfacial synthesis and characterization of the PPy samples

[Emim]BF_4 IL and pyrrole monomer were purchased from Aldrich. The typical three-phase synthesis was described as follows. 0.23 mL pyrrole monomer was added into 6 mL $CHCl_3$ to form organic phase, then 7 mL [Emim]BF_4 IL was set between 7 mL $FeCl_3$ aqueous solution (0.5 M) and the $CHCl_3$ phase. After

* Corresponding author. Tel.: +86 555 2311871; fax: +86 555 2311570.
** Corresponding author. Tel.: +86 025 52112902; fax: +86 025 52112626.
E-mail addresses: ayuancz@163.com (C. Yuan), azhangxg@163.com (X. Zhang).

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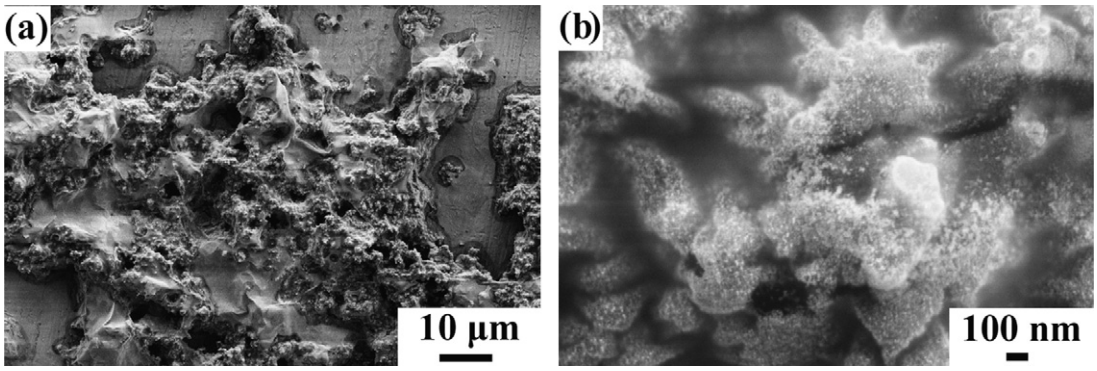

Fig. 1. FESEM images of the as-synthesized TH-PPy sample.

5 days, the PPy sample was collected, washed and dried at 40 °C in vacuum. For comparison, the two-phase route was also performed, which was same as the three-phase method as mentioned above just with exception of IL phase. The PPy samples synthesized by two-phase and three-phase methods are donated as TW-PPy and TH-PPy, respectively. The samples were examined by powder X-ray diffraction (XRD) (Max 18 XCE), field-emission scanning electron microscope (FESEM, JEOL-6300F), Fourier transform infrared (FT-IR) spectra (360 Nicolet AVATAR FT-IR) and the Brunauer–Emmett–Teller (BET) surface area of the samples was obtained with a Micromeritics ASAP 2010 analyzer. The BET method was used to calculate the specific surface area (SSA) of the samples.

2.2. Electrochemical tests

Electrochemical performance of the PPy samples was evaluated in 3 M KCl aqueous solution by cyclic voltammetry (CV), chronopotentiometry (CP) and electrochemical impedance spectroscopy (EIS) tests, which were performed on CHI660C electrochemical workstation at room temperature. Working electrodes were prepared by mixed the electroactive materials with acetylene black (AB) and polytetrafluoroethylene (PTFE) with the weight ratio of 5:1.5:0.5, which was smeared onto the pretreated graphite substrates [9,11]. A platinum plate (ca. 1 cm^2) and a saturated calomel electrode (SCE) were used as the counter electrode and reference electrode, respectively.

3. Results and discussion

3.1. Morphology and structure analysis of the as-synthesized PPy samples

Fig. 1 presents the FESEM images of the as-prepared TH-PPy sample. Clearly, the TH-PPy sample exhibits loosed coral reef-like morphology, as seen from Fig. 1a. The higher-magnification FESEM image (Fig. 1b) shows that the as-synthesized TH-PPy possesses a typical emanative coral-like nanostructure. Notably, the PPy synthesized by the two-phase route displays a mixture of microspheres and micro sheets, as shown in Fig. 2a and b, just without the IL phase during the polymerization. And the higher-magnification FESEM presented in Fig. 2c demonstrates that the size of the PPy microspheres is ranged from 1 to 2 μm. It demonstrates that the existence of the [Emim]BF_4 IL layer greatly influences the PPy polymerization process indeed, which results in the distinct morphologies and micro-structures of the PPy samples.

XRD analysis was performed to evaluate the alignment and orientation of the synthesized PPy samples. Fig. 3 shows the XRD diffraction patterns of the TH-PPy and TW-PPy samples, respectively. Typical diffraction patterns shown in Fig. 3 clearly indicate that both of the TH-PPy and TW-PPy samples are mainly amorphous structure. Of note, the sharper peaks at 19.1°, 26.2° and 29.2° of the TH-PPy, as indicated by the red ellipses, illustrate that the alignment and orientation of TH-PPy molecular chain are more regular than those of the TW-PPy [4,7,12]. Specifically, the peaks at 2θ of 19.1° and 26.2° should be attributed to pyrrole-counterion or intercounterion interaction scattering and arise from PPy chains close to the interplanar van der Waals distance for aromatic groups, respectively. And the high angle peak at $2\theta = 29.2°$ indicates order in the polymer backbone.

FT-IR spectra of the TH-PPy and the TW-PPy samples are shown in Fig. 4, respectively. The characteristic peaks ranged from 700 to 2000 cm^{-1} of the TH-PPy and the TW-PPy samples are similar to each other, indicating the two PPy samples have the same conjugated structure [7,13]. However, the TH-PPy presents very weak absorption bands in the region of 2830–2980 cm^{-1}, compared to the TW-PPy sample, which means the less $–CH_2–$ groups in TH-PPy matrix [7,13]. Therefore, it is confirmed that the [Emim]BF_4 IL can regulate and control the PPy polymerization, due to its great role of "buffering zone", which makes the TH-PPy sample own more ordered structure and produces less nonconducting oligomers $–CH_2–$ groups existing in the TH-PPy matrix. Notably, the less $–CH_2–$ groups in the TH-PPy sample favor for the enhancement of its electronic conductivity, which can be further verified by the following EIS plots. Consequently, the more ordered structure and higher electronic conductivity of the TH-PPy should greatly benefit for its more desirable electrochemical performance.

3.2. Electrochemical properties of the as-prepared PPy samples

Fig. 5a depicts the CV curves of the TH-PPy electrode at different scanning rates from 2 to 20 mV/s in 3 M KCl aqueous solution. The electrochemical response currents on the positive sweep of the TH-PPy electrode are nearly mirror-image symmetric to their corresponding counterparts on the negative sweep with respect to the zero-current line in the given potential range from −0.8 to 0.5 V (vs. SCE) at all the scanning rates, indicating their good characteristic supercapacitive feature. Moreover, even when the scanning rate increases to a scan rate of 20 mV/s, the electrochemical response current of the TH-PPy electrode subsequently increases while the CV shape changes little and still keeps quasi-rectangular in shape, indicating its good rate performance. In contrast, the CV plots for the TW-PPy electrode at various scanning rates are also depicted in Fig. 5b. Obviously, the TW-PPy electrode displays good electrochemical capacitance within the electrochemical window between −0.7 and 0.6 V (vs. SCE). However, electrochemical response currents of the TW-PPy are much less than those of the TH-PPy at all the