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Research paper

Electrochemical synthesis of conductive, superhydrophobic and adhesive polypyrrole-polydopamine nanowires

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ABSTRACT

Polypyrrole-polydopamine (PPy-PDA) films with nanowire morphologies were synthesized by a simple one-step electrochemical method using sodium dodecyl benzene sulfonate (SDBS) as dopant. Compared to the PPy films and PPy-PDA films synthesized with other dopants, the SDBS-doped PPy-PDA nanowire films exhibited greatly enhanced adhesion force to the electrodes. In addition, the conductivities of the resultant PPy-PDA nanowire films were also significantly improved by three times compared to that of the PPy film. More interestingly, the PPy-PDA nanowire films displayed sticky superhydrophobicity. Water drop could adhere to the films tightly even when the films were turned upside down. These attractive properties, plus the simple and rapid synthetic method, offer a possibility for the PPy-PDA nanowire films being used as universal electrode modified materials for various applications.

1. Introduction

Recently, polypyrrole-polydopamine (PPy-PDA) has emerged as a new functional material and attracted both scientific and industrial attention [1–4]. The reason is straightforward: PDA and PPy are two important polymers that have been studied extensively during past two decades due to their actual and potential applications in numerous active fields such as batteries, supercapacitors, organic electronics, surface science and biomedical science [5–14]. The combination of the advantages of the two polymers apparently affords the PPy-PDA some attractive properties that are not available when either PDA or PPy was used alone. For example, PDA can offer PPy-PDA excellent chemical modification performance and enhanced adhesion property, and PPy can render PPy-PDA good electrical conductivity.

On the other hand, the synthesis and application of nanostructured PPy and PDA have become a focus of attention in recent years because of their superior properties compared to their non-nanostructured counterparts. So far, numerous nanostructured PPy and PDA have been synthesized by either chemical or electrochemical methods [10,11,15–17]. As for the PPy-PDA, chemical method used by Zhang et al. could produce nanostructured PPy-PDA with enhanced adhesion and conductivity compared to the pure PPy after a relatively long reaction time (~18 h) using ammonium persulfate as oxidant [1–3]. However, the chemically prepared PPy-PDA was formed mainly in bulk solution and therefore the sophisticated filtration and compression process were required to obtain PPy-PDA film. Very recently, Kim et al. electrochemically polymerized PPy-PDA film directly on the ITO electrode in phosphate-buffered saline (PBS, pH 6) in a short time (300 s) without the need of further post-processing steps [4]. The obtained film also exhibited enhanced adhesion and electrical conductivity, thus making it a desirable material to modify surface properties of electrodes. But unfortunately, the morphology of such electrochemically prepared film was normal compact structure, instead of nanostructure.

In the present study, we successfully synthesized nanostructured PPy-PDA film with wire-like morphology on the titanium electrode by an electrochemical method using sodium dodecyl benzene sulfonate (SDBS) as dopant. In addition, the effects of dopants on the morphologies of PPy-PDA films and adhesion force between the PPy-PDA film and the titanium electrode were investigated. Besides SDBS, other four kinds of often-used dopants, NaCl, $LiClO_4$, sodium p-toluenesulfonate (TosNa) and phosphate-buffered saline (PBS, pH 6) were also selected in the present work to electrochemical synthesis of doped PPy-PDA. We found that only SDBS could induce the formation of nanostructured PPy-PDA and the best adhesion force were obtained between the SDBS-doped PPy-PDA nanowire film and the titanium electrode. More interestingly, the surface of the SDBS-doped PPy-PDA nanowire film

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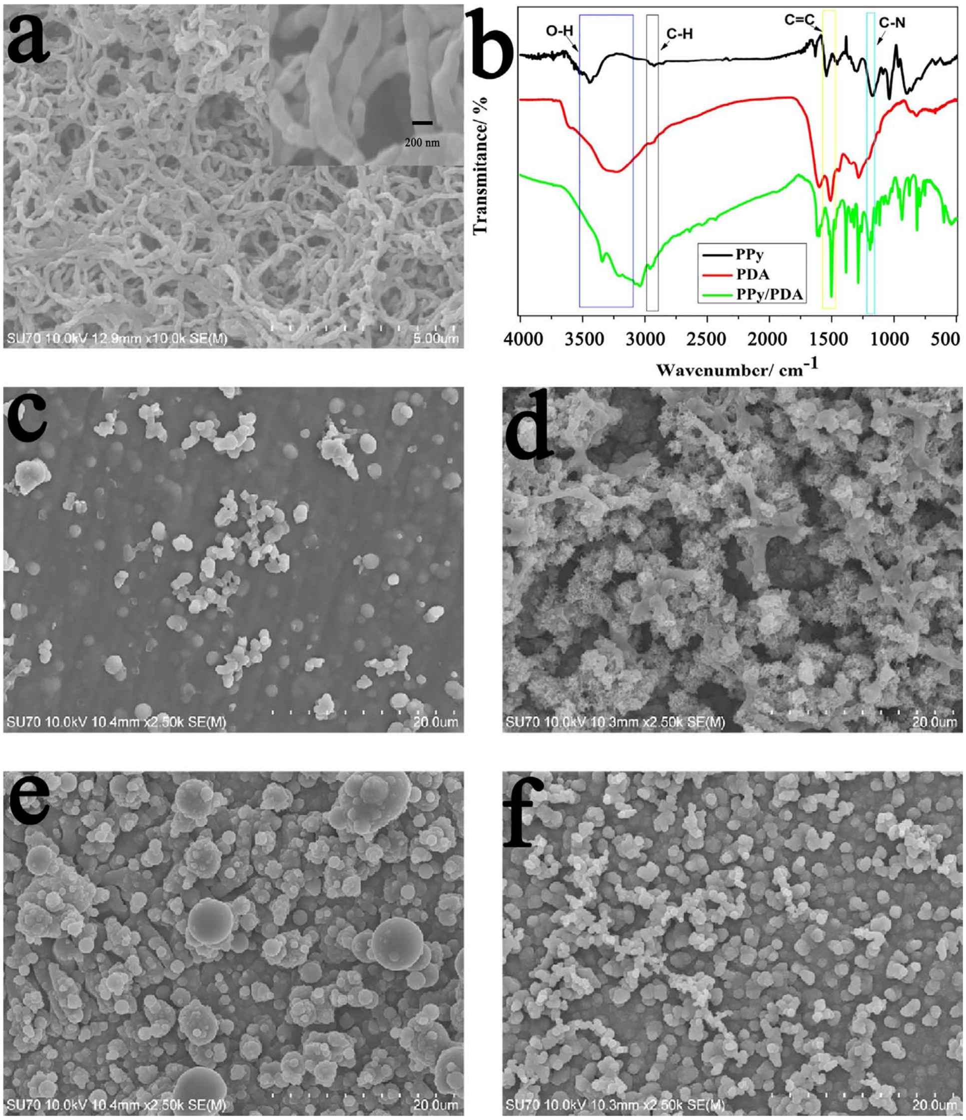

Fig. 1. SEM image of PPy-PDA films doped by **a**) SDBS, **c**) phosphate, **d**) $LiClO_4$, **e**) TosNa and **f**) NaCl. **b**) FT-IR spectra of PPy, PDA and PPy-PDA films. The insets of a) show the high-resolution SEM images of PPy-PDA film doped by SDBS.

exhibited sticky superhydrophobicity. Water drop could adhere to the film tightly even when the film was turned upside down. Currently, the conducting polymers with sticky superhydrophobicity were often prepared by using fluoride as dopant or polymerizing of fluorinated or alkyl chain-bearing monomer [18–22], which usually involved extensive synthesis. To the best of our knowledge, there is no report on the simple use of PDA to modify the conducting polymers to obtain sticky superhydrophobic surface. We hope that the SDBS-doped PPy-PDA nanowire film with enhanced adhesion and sticky superhydrophobicity, which was synthesized by a simple one-step electrochemical method, will find great potential applications in the fields of electrode surface modification, water harvesting, oil/water separation, energy systems, and biomedical science.

2. Experimental

2.1. Materials and reagents

Pyrrole (Py, 98%), Sodium dodecyl benzene sulfonate (SDBS, 95%) was purchased from J & K Chemical Technology. Py was distilled under the protection of nitrogen gas and stored frozen before use. DA was purchased from Sigma-Aldrich and used as received. Titanium foil (99.7%) was purchased from Alfa Aesar. All other chemicals were of analytical grade and were used as received. All solutions were prepared using deionized Milli-Q water (Millipore).

2.2. Electrochemical synthesis of PPy-PDA films

The PPy-PDA films were electrochemically deposited on titanium (1.5×2.5 cm) from an electrolyte solution containing 0.2 M SDBS, 0.28 M Py monomer and DA (1, 8, and 12 mg ml^{-1}). To investigate the effects of dopants on the morphologies of the PPy-PDA films, the electrolyte solution of the control group was containing 0.2 M NaCl, $LiClO_4$, TosNa or phosphate-buffered saline (PBS), 0.2 M Py monomer and 8 mg ml^{-1} DA. The electrolyte solution pH was adjusted to about 6 by hydrochloric acid before electrochemically deposited to prevent spontaneous DA oxidation to PDA. The obtained PPy-PDA films were denoted as PPy-PDA-1, PPy-PDA-8 and PPy-PDA-12. The electrochemical process was carried out using CHI 660E Electrochemical workstation in a one compartment cell with three-electrode configuration: a platinum counter electrode, a saturated calomel electrode as a reference electrode and a titanium working electrode. The constant potential of 0.75 V and 0.5 V were used for the synthesis of pure PPy and PPy-PDA films, respectively. The amount of material deposited on the electrode surface was controlled by the total charge passed during deposition (0.3C cm^{-2}). After electrodeposition, the samples were removed from the polymerization medium and rinsed with distilled water and dried in air.