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Synthesis of novel hexagonal micro-sheet polypyrrole and micro-sheet polypyrrole with grooves in the presence of α-cyclodextrin/Acid Red G inclusion compounds

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ABSTRACT

Novel hexagonal micro-sheet polypyrrole (PPy) was synthesized via the self-assembly method in the aqueous solution containing α-cyclodextrin (α-CD)/5-acetamido-4-hydroxyl-3-(phenyliazenyl) naphthalene-2,7-disulfonic acid (Acid Red G) inclusion compounds (α-CD/ARG ICs) and ferrous cations. And micro-sheet polypyrrole with grooves was obtained by dipping the micro-sheet PPy into alkaline solution for 12 h. The existence of α-CD/ARG ICs in aqueous solution was testified by UV–vis spectra. Scanning electron microscopy (SEM) images revealed that the micro-sheet PPy was over 10 μm in average length, 0.6–10 μm in broadbrim and 100–200 nm in thickness. The conductivities of the micro-sheet PPy were in the range from 2.78 to 12.50 S cm^{-1} and the conductivities of the micro-sheet PPy with grooves were in the range from 3.70 to 7.69 S cm^{-1}. Cyclic voltammograms (CVs) were measured to examine the electrochemical behaviors of the prepared PPy, and the oxidation peak of micro-sheet PPy was increased to 1.34 V which was higher than those of other PPy samples. The experimental conditions were also optimized, and the optimization of experimental conditions was the quantities of pyrrole monomers, α-cyclodextrin and Acid Red G were 20, 4 and 4 mmol, respectively, and the perfect micro-sheet PPy was synthesized at 5 °C and no-stirring for over 12 h. It was found that the complex aggregations of α-CD/ARG ICs and ferrous cations might have the function as a "template" during the polymerization of pyrrole monomers, but this "template" was broken off from the prepared micro-sheet PPy in the alkaline condition.

1. Introduction

Polypyrrole (PPy) is a typical intrinsically conducting polymer and it has been extensively studied in recent decades for its high conductivity, long-term environmental stability and the ease of synthesis [1–5]. The structures and morphologies of macromolecules have a great influence on the properties of conductive polypyrrole and the perspectives of practical applications in various fields [6–8]. For instance, PPy microtubules were induced to assemble into mesoscale networks which have the swellability of the hydro-sponges with macroscopic features like polymer gels, and the electrical conductivity of this PPy hydro-sponges increased 7 orders of magnitude, as high as 126 S cm^{-1} [6].

PPy with novel macromolecular structures and morphologies have been synthesized by choosing appropriate dopants in the given polymerization conditions [3,9–11]. Recently, much attention was paid to azobenzene dyes as dopants when preparing conductive polymers for their special structure. Methyl orange (MO) is a regular azobenzene dye which can form a kind of bacilliform precipitate in aqueous solution when adding $FeCl_3$ or adjusting the pH value of the solution below 4.3 [12,13], this bacilliform precipitate was used as the "template" to synthesize PPy microtubules. 5-Acetamido-4-hydroxy-3-(phenyliazenyl) naphthalene-2,7-disulfonic acid (Acid Red G) is another azobenzene dye. Controlling compatible polymerization condition, PPy micro/nanotubules with rectangular sections were prepared while Acid Red G was employed as a dopant and template, the highest conductivity of the PPy doped with Acid Red G was 28.6 S cm^{-1} [14].

In recent years, there were more considerable interests in using cyclodextrins in the synthesis process of conductive polymers. Cyclodextrins (CD) are cyclic oligosaccharides consisting of six (α-cyclodextrin, α-CD), seven (β-cyclodextrin, β-CD), eight (γ-cyclodextrin, γ-CD) or more glucopyranose units linked by α-(1,4) bonds, which exhibit a torus-like molecular configuration, with a hydrophilic outsider and a hydrophobic cavity. So some molecules of appropriate dimensions and properties can be included into the

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cavities of CDs to form inclusion compounds [15]. And the inclusion compounds can form some specific aggregation structures for the molecular assembly and self-assembly in solutions [16]. In this way molecular architectures such as catenanes, rotaxanes, polyroxanes and tubes can be constructed, which cannot be prepared by other methods [15]. Especially in the presence of the transition metal ions, different nanoarchitectures (such as rod and squares) could be formed by the intermolecular self-assembly [17]. Therefore, some special microstructure polymers can be fabricated when these aggregations are used as the templates. However, preparing PPy with inclusion compounds (ICs) of CDs is few yet. As far as we know, there is only one report on synthesized PPy microtubes with actinomorphic morphology in the presence of inclusion compounds of [6-deoxy-6-(2-butenedinitrile-2,3-dimercapto sodium salt)]-β-cyclodextrin and methyl orange [18]. But PPy with the special morphology, prepared by using the aggregations of the ICs and the transition metal ions as the template, has never been reported.

In this paper, novel micro-sheet PPy and micro-sheet PPy with grooves were synthesized by a chemical oxidation method in the presence of the aggregations of the ICs with the ferrous ions by controlling synthetic conditions. The inclusion compounds of α-CD and 5-acetamido-4-hydroxyl-3-(phenyliazenyl) naphthalene-2,7-disulfonic acid (Aicd Red G) can form special polygonal aggregations with the ferrous ions (the products of the reduced ferric iron) as the template in the synthesis process. UV–vis and SEM were used to investigate the existence of α-CD/Acid Red G ICs in aqueous solution and the morphologies of PPy samples. The microstructures of the prepared PPy were characterized by FT-IR. The synthetic conditions were optimized and the electrochemical behaviors of the PPy samples were also measured. And the formation mechanism of micro-sheet PPy was also discussed.

2. Experiments

2.1. Materials

Pyrrole monomer was purchased from Sigma–Aldrich (98%) and distilled under vacuum. The treated pyrrole was refrigerated and stored in dark under the protection of nitrogen before it was used. Acid Red G (5-acetamido-4-hydroxyl-3-(phenyliazenyl) naphthalene-2,7-disulfonic acid) was obtained from Aldrich. The molecular structure of Acid Red G is shown in Fig. 1a. The sulfonate groups provide the hydrophilicity of Acid Red G, but the hydroxyl and azo groups adjacent to the naphthalene ring are strong ligands which could form complexes with transitional metal ions [19]. The Acid Red G was not pretreated in this experiment. α-Cyclodextrin was supplied by Li quan Chemical Industry Company (Shaanxi, China, biological grade) and its molecular structure is shown in Fig. 1b. Ferric chloride hexahydrate ($FeCl_3{\cdot}6H_2O$, 98%, Beijing Chemicals, China), methanol (anhydrous, 99.8%, Aldrich), sodium hydroxide (NaOH, 98.0%, Beijing Chemicals, China), graphite powder (chromatography pure, Sinopharm Chemical Reagent Co., Ltd., China), paraffin liquid (Chemical pure, Sinopharm Chemical Reagent Co., Ltd., China) and Na_2SO_4 (99.0%, AR, Sinopharm Chemical Reagent Co., Ltd., China) were used as received.

2.2. Synthesis of micro-sheet polypyrrole

Micro-sheet PPy was synthesized as follows: 1.0 mol L^{-1} $FeCl_3$ aqueous solution was prepared by dissolving ferric chloride hexahydrate ($FeCl_3{\cdot}6H_2O$) in the deionized water. The $FeCl_3$ solution was used as the oxidant. 6 mmol α-cyclodextrin and 4 mmol Acid Red G were dissolved in 30 mL deionized water with vigorous magnetic stirring for 60 min. Then 20 mmol (1.34 g) pyrrole monomers were added into the solution with vigorous magnetic stirring for

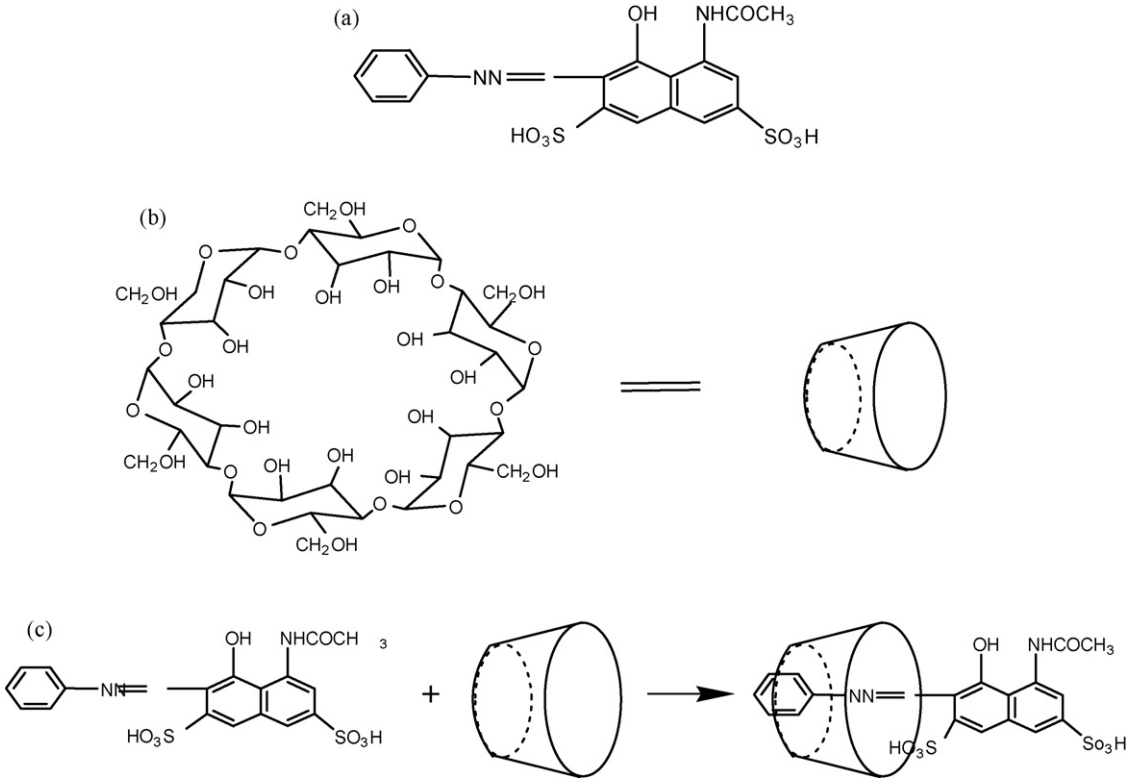

Fig. 1. Structure of (a) Acid Red G; (b) α-cyclodextrin; and (c) the inclusion complexes of α-CD/ARG in aqueous solution.