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Synthesis of micromulti-prisms polypyrrole boxes in the presence of α-cyclodextrin

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ABSTRACT

Polypyrrole (PPy) boxes with micromulti-prisms have been synthesized in aqueous solution via a self-assembled method using α-cyclodextrin (α-CD) as a dopant and $FeCl_3$ as an oxidant. The morphology and the micro-structure of the as-synthesized PPy boxes were characterized by scanning electron microscope (SEM), transmission electron microscope (TEM), and Fourier-transform infrared (FTIR) spectrum. The formation mechanism of the PPy boxes structure was also discussed. And the congregated structure of dissociative pyrrole monomers with the inclusion complexes (between α-CD and pyrrole monomer) was proposed to play a significant role in forming the multi-prisms sectional PPy-CD boxes.

1. Introduction

Conducting polymers have attracted wide attentions for their unique conductive properties and potential applications [1–5]. Particularly, conducting polymer nanotubes were successfully used to release individual drugs and bioactive molecules at desired points in time [6]. So conducting polymers with special micro-structures are of great interests for their outstanding properties. Recently, micro/nano-wires and microtubules of conducting polymers have been fabricated [7–9]. Polypyrrole hollow Y-junction and capsule were also synthesized by the rod junctions or particles of benzyl orange (BO) precipitates used as reactive templates [10]. It was reported that hollow spheres polyaniline was prepared via self-assembled method [11]. In addition, 3D-boxlike polyaniline with super-hydrophobic and high-crystalline properties was also prepared by a template-free method in the presence of perfluorosebacic acid (PFSEA) [12]. However, β-cyclodextrin was employed to prepare polymeric micelles and hollow spheres [13]. The conducting polymers with special micro-structure maybe have been widely used in biosensors and controllable drug release.

Among the conductive polymers, polypyrrole (PPy) is one of the most extensively studied conducting polymers due to its high conductivity and long-term environmental stability [14,15], and it is a biological compatible polymer matrix wherein number of drugs and enzymes can be incorporated [5]. But the application of the traditional PPy is limited for their poor properties. To improve some properties of PPy, Cyclodextrins are used in the synthesis of PPy recently. For instance, PPy has been synthesized in aqueous medium by using an inclusion complex of cyclodextrin with pyrrole as the monomer in 2000 [16]. Cyclodextrins are cyclic oligosaccharides consisting of six (α-cyclodextrin), seven (β-cyclodextrin), eight (γ-cyclodextrin) or more glucopyranose units linked by α-(1,4) bonds, which exhibits a torus-like molecules, with a hydrophilic outsider and a hydrophobic cavity. As a result of this cavity, cyclodextrins are able to form inclusion complexes with a variety of hydrophobic guest molecules [17]. It has been reported that ordered conducting PPy doped with sulfopropyl ether β-cyclodextrin had been synthesized by chemical and electrochemical methods [18]. And PPy microtubes with actinomorphic morphology in the presence of a β-cyclodextrin derivative-methyl orange inclusion complex have also been prepared [19]. But to the best of our knowledge, there are no PPy boxes synthesized with α-CD as a dopant by chemical polymerization.

2. Experiments

2.1. Materials

Pyrrole monomers (98%, Sigma–Aldrich) were distilled at reduced pressure and then was refrigerated and stored under the protection of nitrogen. α-Cyclodextrin (α-CD, 99%) was supplied by Liquan Chemical Co. Ltd., Shaanxi, China. Ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$, ≥98%, Beijing Chemicals, China) and methanol (anhydrous, 99.8%, Aldrich) were used as received.

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2.2. Synthesis

The synthesis process of the PPy boxes with multi-prisms microstructure was as follows: 4.87 g (5 mmol) α-CD was dissolved in 30 mL deionized water and then mixed with 1.34 g (20 mmol) pyrrole by magnetic stirring for 2.5 h at room temperature, and the white precipitate appeared. Subsequently, 33.4 mL of 1.0 mol L^{-1} $FeCl_3$ aqueous solution was added dropwise into above mixture in about 2.0 h with stirring synchronously. Stirring was stopped after $FeCl_3$ aqueous solution dropped completely. The whole polymerization maintained for 12 h without any stirring at 15 °C. Precipitated PPy was filtered and washed with deionized water and methanol several times until there is scarcely any colour. The product was then dried in a vacuum oven at 60 °C for 24 h and named as PPy-CD.

2.3. Characterization

The SEM images were gained from field emission scanning electron microscope (JEOL JSM-6700F and JEOL JSE-5800). The Fourier-transform infrared (FTIR, Nicolet, FT-IR 6000) spectra data were used to characterize the molecular structure of the obtained products. The crystalline phase of the sample was identified by an X-ray diffraction (XRD, Rigaku, D/MAX-2400X) using graphite monochromatized Cu Kα radiation (45 kV, 15 mA). The conductivity of these PPy-CD materials at room temperature was measured by a four-probe conductivity meter (SX1944).

3. Results and discussion

The morphology of the prepared PPy-CD boxes was shown in Fig. 1. Fig. 1a presented a cluster of PPy-CD boxes. The arrangement of these multi-prisms boxes was irregular. Fig. 1b showed that these multi-prisms boxes had obviously more than four arises. The average length of these PPy boxes was 20–30 μm, and the side length of these boxes section was estimated to be 2–6 μm (Fig. 1c). The TEM image of the PPy-CD boxes revealed that these boxes were hollow (Fig. 1d).

The FTIR spectra of the PPy synthesized without α-CD, α-CD, physical mixture of PPy and α-CD, PPy-CD boxes were presented in Fig. 2. Excepting one new absorption, the PPy-CD spectrum is similar with PPy synthesized without α-CD. For example, the bands due to the C=C and C=N stretching vibrations were occurred at 1541 and 1452 cm^{-1}, the C–C breathing fabrication at 1167 cm^{-1}, and the =C–H in-plane deformation at 1299, 1091 and 1040 cm^{-1}, the C–C out-of-plane bending vibration and out-of-plane ring deformation at 964 and 673 cm^{-1}, respectively, while other bands at 893 and 783 cm^{-1} are C–H out-of-plane deformation [9,20]. The existence of α-CD in the PPy-CD is indicated by the new broad peak at 3421 cm^{-1}, which is observed at 3400 cm^{-1} in the physical mixture system. The reason may be that the O–H bonds of α-CD are affected by PPy molecule chain, and this result strongly suggests that α-CD have threaded through PPy backbone [21]. There was not any other differential peak between spectra of PPy-CD boxes and PPy synthesized without α-CD, which indicates PPy polymer backbone is not changed when α-CD is employed as a dopant.

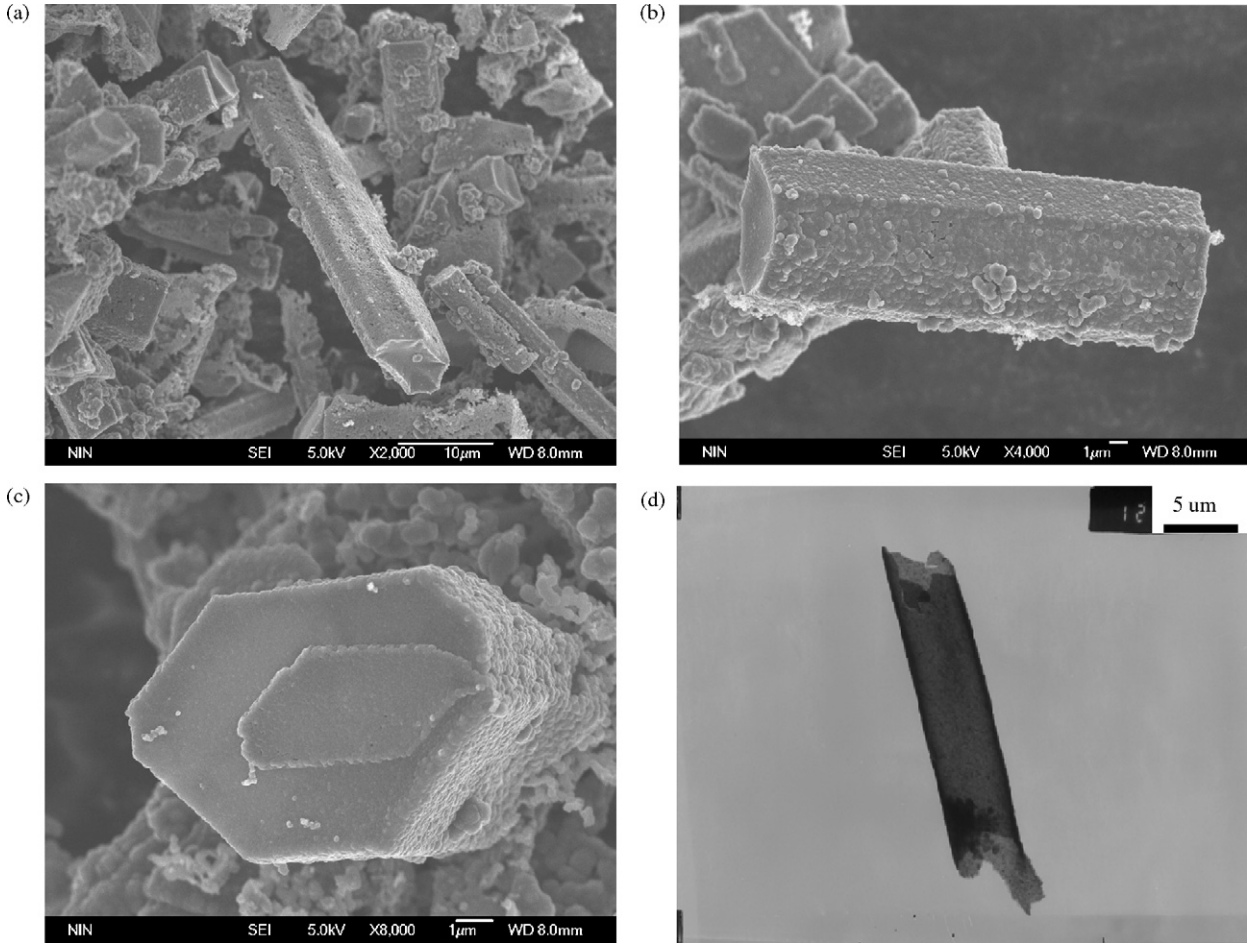

Fig. 1. (a), (b), (c) SEM and (d) TEM images of PPy-CD boxes with multi-prisms.