

Chemical synthesis and characterization of polypyrrole with novel morphology prepared via self-reactive MnO₂ microcube as sacrificial template and oxidizing agent

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Abstract

Intrinsically conducting polymers (ICPs) such as polyaniline and polypyrrole which have advantages such as high conductivity, high flexibility, ease synthesis routes, high stability and good mechanical properties, have aroused intense of many researches for various application such as electrolytic capacitors, electronic and electrochromic devices, sensors, light-weight batteries, membrane separation and radar absorbing materials (RAMs). In this research, polypyrrole (PPy) with novel morphology was synthesized successfully, using a microstructured MnO₂ microcube as a self-reactive template and oxidizing agent for the beginning of the polymerization reaction. MnCO₃ microcubes were synthesized by hydrothermal method at 150 °C. They were utilized as precursors for MnO₂ microcube synthesis. XRD patterns of MnO₂ and PPy revealed that the MnO₂ templates consumed almost completely as an initiator or an oxidizing agent in polymerization reaction. Also, FESEM images demonstrated that PPy structures are totally inherited their morphologies from MnO₂ templates.

Keywords: Self-reactive template, Conducting polymer, MnO₂, Polypyrrole.

1. Introduction

ICPs are termed organic polymers which possess the magnetic, electrical and optical properties of metals while maintaining their processability and mechanical properties. Since the synthesis of the first conducting polymer (polyacetylene) by Shirakawa *et al.*, ICPs have aroused intense of many researches [1].

Among the ICPs, polyaniline (Pani) and PPy and their composites have been studied extensively for military purposes such as camouflage and stealth technology due to their properties such as high electrical conductivity (compared with carbon), facile processability, low density (for example; polyaniline and polypyrrole densities compared with iron are 1.1,

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1.2 and 7.8 g/cm³, respectively), corrosion resistance (compared with metals), low cost and preference [2]. The main advantage of these polymers is ability to control their properties during the synthesis process. Also, by changing their morphology, their inherent properties become different completely. In continuation of our works toward the synthesis of different morphologies of PPy [3,4], in this work, we have successfully synthesized a novel morphology of PPy (the microcube morphology), for the first time. PPy with microcube morphology has different properties compared to PPy with other morphologies which has been synthesized yet and can be utilized in various applications. Herein, we have synthesized successfully MnCO₃ microcubes by hydrothermal method as precursor for preparation of MnO₂ template. Through controlling the MnCO₃ morphology as precursor, MnO₂ and PPy with cubic morphology were obtained.

2. Experimental

2.1 Materials

All the chemicals used here were of analytical grade. Pyrrole monomer (Py), potassium permanganate (KMnO₄, ≥ 99.0%), sucrose, hydrochloric acid (HCl, 37%) and methanol were obtained from sigma-Aldrich. Py was distilled before utilization and all other chemicals were used as received. All aqueous solutions were freshly prepared by using high-purity water.

2.2 Synthesis of MnCO₃ microcube

The synthesis of MnCO₃ microcubes were based on the previous work of Lu's group [5]. In brief, 7.5 mmol of KMnO₄ was dissolved into 40 ml deionized water. Then, the solution was added to 40 ml aqueous solution containing sucrose (2.7 mmol). The mixture was under stirring for 20 min to form a homogeneous mixture. Then, the mixture solution was transferred into a Teflon-lined (PTFE) stainless steel autoclave with a capacity of 100 ml, sealed and maintained in an oven at 150 °C for 24 h. After the autoclave was cooled down to room temperature, the resulting brown precipitates were collected by filtration and washed

with distilled water. The prepared MnCO₂ was dried at 60 °C overnight to obtain the as-prepared MnCO₃ sample.

2.3 Synthesis of MnO₂ microcube

The synthesis of MnO₂ microcubes were prepared almost similar to the previous work of Xu's groups [6]. The as-prepared MnCO₃, was calcined in a furnace at 350 °C for 2 h with a heating rate of 5 °C/min in air. The product was added to 0.1 M H₂SO₄ solution and stirred for 4 h. The resultant sample was filtered, washed with distilled water, and dried at 60 °C overnight to obtain the MnO₂ microcubes.

2.4 Synthesis of PPy microcubes

PPy microcubes were synthesized by MnO₂ as oxidant agent and rigid backbones for growth of PPy microstructures. In a typical procedure, 100 mg synthesized MnO₂ powders were dispersed in 20 mL HCl 0.1 M solution, using an ultrasonic bath. Then the pyrrole monomers were added dropwise into the above suspension under vigorous magnetic stirring at 0-5 °C. After few minutes, the reaction rapidly initiated as the small black seeds of MnO₂ suspension changed to larger black precipitates of PPy. After stirring for 2 h, the mixture was rest for 1 h. Finally, the resultant black PPy products were filtered and washed with deionized water and ethanol for several times, respectively until excess reagents were removed.

2.5 Characterization

Structural characterizations of MnO₂ and PPy microcubes were done by X-ray powder diffractometer (XRD, Bruker, D8 Advance), using Cu K α radiation at 45 kV and 20 mA ($k = 0.154056$ nm). The Chemical structure of PPy microstructures were characterized by FTIR technique (Bruker, Tensor 27). The morphology of the MnO₂ and PPy microcubes were observed by a Field-Emission Scanning Electron Microscope (FESEM; MIRA3-XMU TESCAN). A Thermo-Gravimetric Analysis (TGA) was carried out on about 15 mg PPy with a LINSEIS model STS PT 16000 thermal analyzer under air atmosphere at a heating rate of 5 °C.min⁻¹.

3. Results and discussions

Structural properties of MnO₂ and PPy microcubes were investigated by X-ray Diffraction. Figure 1 presents the XRD pattern of these samples. According to the Figure 1a, all of the diffraction peaks can be match well with the layered birnessite-type MnO₂ [7]. The sharp and narrow diffraction peaks indicate that the sample is well crystallized. The main XRD peak of PPy is a weak and broad peak at about $2\theta = 25$. The broad peak in the XRD pattern (Figure 1b) at about $2\theta = 25$, represents that the PPy is formed successfully and also it indicates that the sample has amorphous nature. With comparison to MnO₂ and PPy patterns (Figure 1), it is clear that only some peaks of MnO₂ pattern are present in PPy sample XRD. But the XRD peaks have much less intensity which represents that

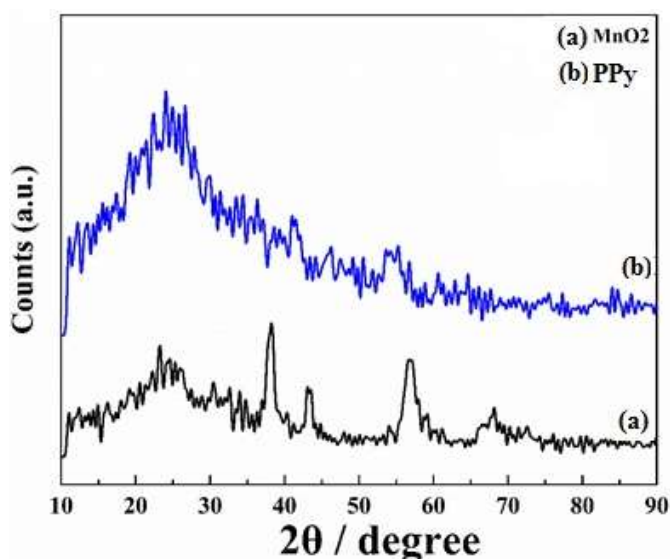


Figure 1. XRD patterns of the (a) MnO₂ microcubes and (b) PPy microcubes

the MnO₂ templates consumed as an initiator or an oxidizing agent in polymerization reaction, almost completely.

Fourier transform infrared spectroscopy of PPy microcubes synthesized with self-reactive template of MnO₂ is shown in Figure 2. The FT-IR spectrum (Figure 2) shows a broad peak at about 3100 cm⁻¹ which is attributed to the N-H stretching vibration of polypyrrole. A peak at about 1580 cm⁻¹ can be assigned to C-C stretching band. The peaks at about 1420 cm⁻¹, 1200 cm⁻¹, and 1058 cm⁻¹ represent a

conjugated C-N stretching band, C-H in-plane deformation band and N-H in-plane deformation band, respectively. The characteristic peak at about 937 cm⁻¹ corresponds to C-H out-of-plane vibration [8].

In order to investigate of the thermal stability of PPyMC, TGA measurement was carried out in air atmosphere. Figure 3 represents the TGA plot of PPy microcubes. Figure 3 makes it clear that the PPy mass decreased slightly by increasing the temperature. According to the Figure 3, one considerable weight loss

occurs in the present sample at temperatures between 30 and 120 °C, which can be attributed to the evaporation of the residual water. Also, the main degradation of PPy

microcubes backbone starts at about 270 °C according

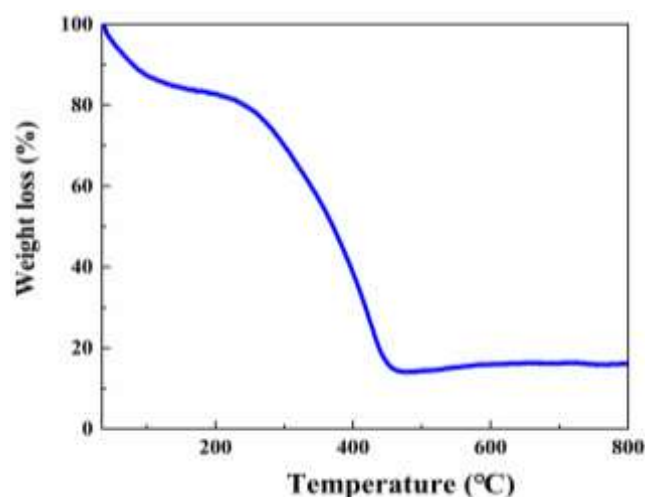


Figure 2. FTIR Spectra for PPy microcube synthesized with self-reactive template of MnO₂

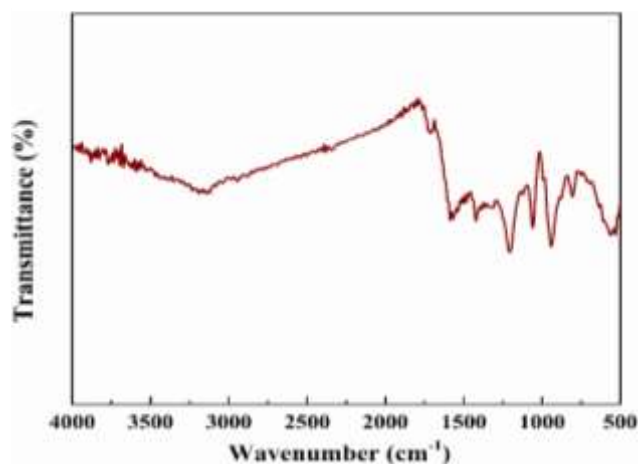


Figure 3. TGA curves of PPy microcube

to TGA measurements [9].

The morphology and size distribution of the MnO_2 and PPy microcubes were examined, using FESEM.

The produced MnO_2 crystals have uniform 3D

structure of microcubes as shown in Figs. 4(a)–(c).

Figs. 4(d)–(f) show the PPy microcubes synthesized in the present study. The present PPy structures are totally inherited

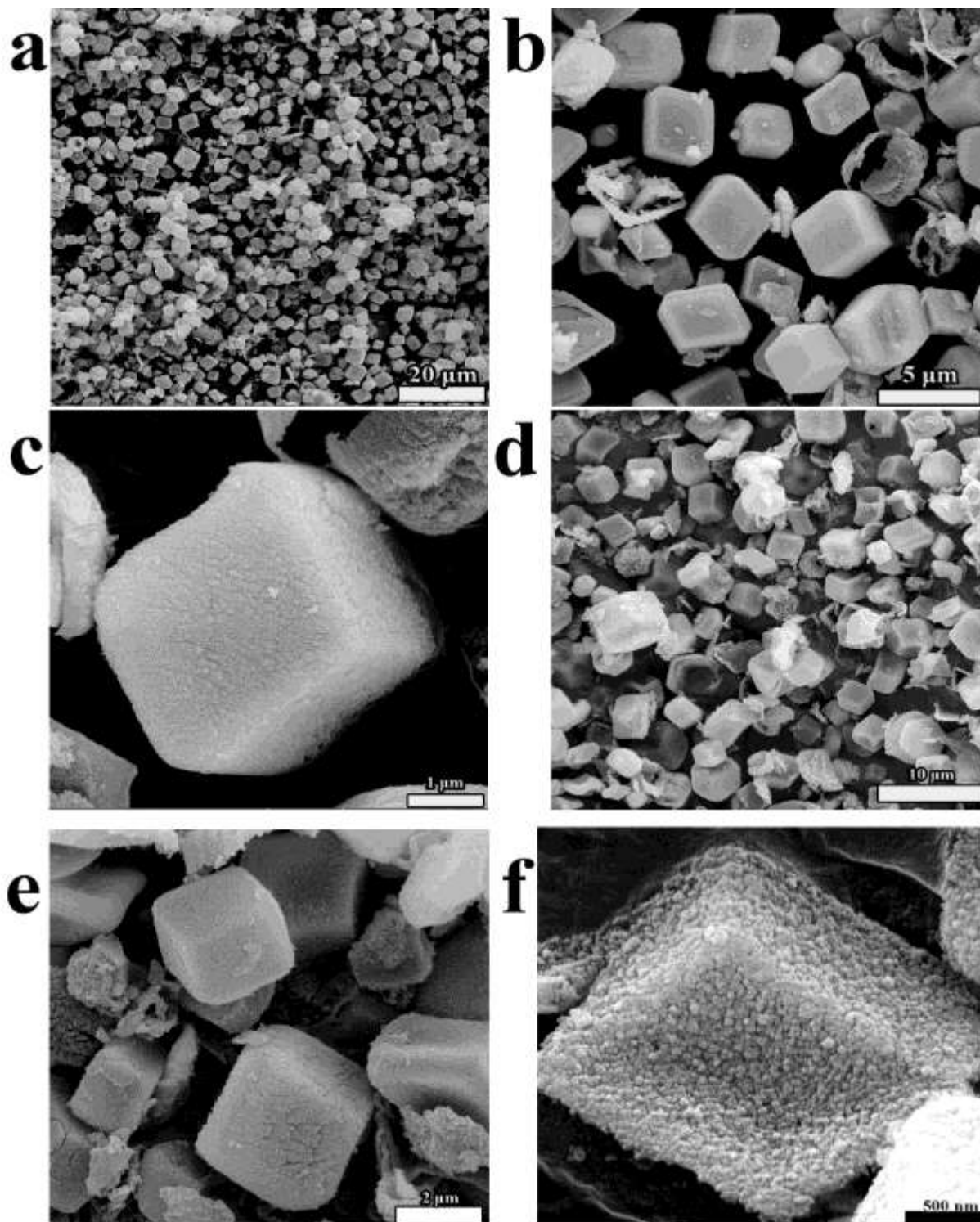


Figure 4. FESEM images of the MnO_2 microcubs (a-c), and PPy microcubes (d-f)

their morphologies from the MnO_2 templates, indicating that the reactive template synthesis is an

effective method for PPy 3D architecture fabrication. As matter of fact, MnO_2 templates act as rigid

backbones for PPy microcube formation. From the magnified image of the larger cube shown in Figure 4(f), the porous structure of PPy can be clearly observed.

4. Conclusions

In conclusion, the PPy microcubes were synthesized with MnO_2 as an oxidizing agent and self-reactive template. The oxidation potential of MnO_2 was sufficient to initiate the polymerization reaction of pyrrole, and polypyrrole microcubes formed on the surface of the MnO_2 microcubes. According to the XRD pattern of the PPy microcubes, it was clear that the main peaks of MnO_2 were absent, or if present, they have very low intensity. This showed that the MnO_2 template consumed almost completely as the oxidizing agent for initiation of the PPy polymerization reaction. Also, the FESEM images demonstrated that the external size and shape of formed PPy microcubes were similar to the MnO_2 microcube templates.

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