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Shape-controlled fabrication of polypyrrole microstructures by replicating organic crystals through electrostatic interactions

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ABSTRACT

Polypyrrole (PPy) microstructures with diverse shapes were synthesized in an aqueous inorganic salt medium including organic crystals and pyrrole (Py). A series of sulfobenzoic acid salt forms with various cations (K^+, Na^+, Li^+, NH_4^+) in different positions (*para*, *meta*, *ortho*) of the sulfonate group on the benzene ring were used to form organic crystals as sacrificial templates. Using these crystals, we produced five different shapes of PPy microstructures (hexagonal microplates, curled nanofibers, lozenge-shaped microplates, rigid rods, parallelogram microplates), which replicated the shapes of the organic crystal templates through electrostatic interaction between the anionic crystal surfaces and the cationic PPy chains. In contrast, PPy that was polymerized without crystals showed bulky agglomerates of 200–500 nm size. The electrical properties were dictated by the molecular structures of the organic salt molecules used. While the highest conductivity (200.3 Scm^{-1}) was observed in PPy using crystals of *para*-linked 4-sulfobenzoic acid monopotassium salt, the lowest conductivity (0.8 Scm^{-1}) was observed in PPy prepared in the presence of crystals of *ortho*-linked 2-sulfobenzoic acid monoammonium salt.

1. Introduction

Various synthetic routes for conducting polymers have been developed, both chemically and electrochemically, for fabricating the micro/nanostructures. Among these methods, hard [1–3] and soft template [4–12] methods have been used to prepare micro/nanostructured conducting polymers in a controlled manner. These methods have successfully provided morphologically well-defined micro/nanostructures from zero-dimensional nanoparticles and microspheres to one-dimensional nanofibers and nanotubes with small diameters (<100 nm) and micrometer lengths. Such well-defined conducting polymer micro/nanostructures with highly controlled properties could extend the application area of conducting polymers in plastic electronics.

Despite the many different synthetic routes to conducting polymer micro/nanostructures, however, preparing uniform-sized and -shaped micro/nanostructures from conducting polymers in a practical, cost-effective way still remains a challenge. Recently, it was reported that various complexes of organic dopant/oxidant, organic dopant/monomer, or organic dopant/fluorosurfactant could be used as templates for fabrication of conducting polymer nano/micro structures [13–15]. Dai et al. successfully fabricated the conducting polymer microtubes using methyl orange fibrils formed in HCl solution as templates [16]. In addition, Wang et al. reported the chemical synthesis of spiral nanostructures of polypyrrole (PPy) and polyaniline (PANI) using a hydrated crystallite of surfactant as a template [17,18]. More recently, for the first time, we developed an organic single-crystal surface-induced fabrication method capable of producing PPy micro-hexagonal plates with an improved structural order and high conductivity (~400 Scm^{-1}) [19]. This method relies on a shape-copying process based on electrostatic interactions between anionic organic crystal surfaces and cationic PPy chains.

Here, we report a general strategy for fabricating diverse types of conducting PPy microstructures using crystals of organic salt molecules, 4-sulfobenzoic acid monopotassium salt (4-SBAK), 4-sulfobenzoic acid monosodium salt (4-SBANa), 4-sulfobenzoic acid monolithium salt (4-SBALi), 3-sulfobenzoic acid monosodium salt (3-SBANa), and 2-sulfobenzoic acid monoammonium salt (2-$SBANH_4$), as sacrificial templates. Using these organic crystals, we produced five different shapes of PPy microstructures, dictated by the shapes of the template organic crystals. Different from the previous reports, in our method, only the crystals of organic salt molecules were used as sacrificial templates for inducing the shape-copying process. The organic crystals were formed at zero or sub-zero temperature by rapid injection of organic salt solution

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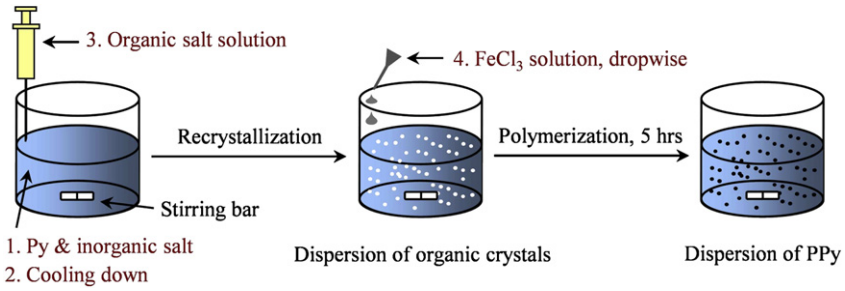

Fig. 1. Polymerization scheme of the PPy microstructues by replicating organic crystals.

into a nearly saturated solution of inorganic salt containing counter cations of the organic salt to prevent cation exchange between inorganic and organic salts. Inorganic salts, KCl, NaCl, LiCl, and NH_4Cl used in the experiment also lowered the freezing temperature of polymerization medium and decreased the solubility of organic salt molecules to facilitate the formation of the organic crystals. We systematically investigated the effect of different cations and different positions (*para*, *meta* and *ortho*) of the sulfonate group on the benzene ring on the morphologies of crystals and electrical properties of their replicated PPys. Wide-angle X-ray diffraction (WAXD), optical microscopy (OM), and scanning electron microscopy (SEM) analyses were conducted to confirm the morphology and formation mechanism of the PPy microstructures.

2. Experimental

2.1. Materials

Pyrrole (Py) (Sigma–Aldrich, 99%) was vacuum-distilled and stored at 2 °C. The oxidant, $FeCl_3$ (Riedel, 98%), was used without further purification. 4-SBAK (Sigma–Aldrich, 95%), 4-SBANa (Sigma–Aldrich, 95%), 4-SBALi (Sigma–Aldrich, 95%), 3-SBANa (Sigma–Aldrich, 97%), and 2-$SBANH_4$ (Tokyo Kasei) were purified by recrystallization in water and acetone. Inorganic salts, such as KCl (Sigma–Aldrich, 99%), NaCl (Sigma–Aldrich, >98%), LiCl (Sigma–Aldrich, 99%), and NH_4Cl (Sigma–Aldrich, 99.5%), were used as received.

2.2. Synthesis

A typical synthesis proceeded as follows. Py dissolved in 100 mL of aqueous inorganic salt solution, while the organic salt, 4-SBAK, 4-SBANa, 4-SBALi, 3-SBANa, or 2-$SBANH_4$, dissolved in 10 mL of water. The above monomeric solution was cooled to 0 or −10 °C, and then the organic salt solution was injected quickly with vigorous stirring. To prevent cation exchange between inorganic and organic salts, an inorganic salt containing the same cation as the organic salt was used in all reactions (*e.g.*, 4-SBAK solution in KCl solution and 4-SBANa solution in NaCl solution). A white organic crystal precipitates appeared immediately in the transparent mixture solution. $FeCl_3$ aqueous solution (20 mL) was added dropwise to the mixture. The white mixture gradually turned black. After 5 h, the PPys were filtered and washed with distilled water and acetone several times, and then dried in a vacuum oven at 60 °C for 24 h. The polymerization procedure of the PPy microstructures, by replicating organic crystals, is described in Fig. 1. Because the crystallization conditions of various organic salt molecules were different from each other, polymerization temperature and the concentrations of added organic salt and inorganic salt were set differently in each experiment. A conventional PPy sample was polymerized using the same procedure in the absence of organic salts. Details of the experimental recipes are presented in Table 1.

2.3. Characterization

The morphology of the organic crystals was observed by OM (Olympus BX-51) equipped with a charged coupled device (CCD) camera. The morphology of the synthesized PPys was observed by SEM (JEOL JSM6340). A zeta potential analyzer (Malvern model Zetasizer Nano-ZS) was used to measure the zeta potentials of the organic crystals and PPy dispersions at 20 °C. The dispersions were diluted with ethanol to 1.0 wt% before measurement. Fourier-transform infrared (FT-IR) spectra of the PPys in attenuated total reflection (ATR) mode were recorded on a PerkinElmer Spectrum 100 FT-IR spectrometer. The electrical conductivity (298 K) of a pressed pellet of the dried PPys was measured using the four-point probe method, with a Jandel contact-probe connected to a Keithley 238 high-current source-measuring unit. The conductivity data in Table 1 were measured from three independent samples of a single synthesis. WAXD measurements were carried out using a Rigaku Denki X-ray generator (D/MAX-2500) with CuKα radiation (λ = 1.5418 Å), operated at 40 kV and 100 mA. The bulk current–voltage (I–V) measurements were conducted using a conventional two-probe method. The probes were made of platinum and the distance between the two probes was maintained at 1.0 cm. The voltage was varied using a Keithley 2400 source-meter. X-ray photoelectron spectroscopy (XPS) measurements were performed using a Sigma Probe (Thermo VG, UK) system

Table 1
Polymerization recipe and yield of the PPy samples.

Sample	Pyrrole (mole)	Organic salt (mole)	Inorganic salt (mole)	Oxidant (mole)	Temperature (°C)	Yield[a] (%)
PPy-4SBAK	0.015	0.005	KCl (0.3)	0.03	0	47.3
PPy-4SBANa	0.015	0.005	NaCl (0.3)	0.03	0	49.1
PPy-4SBALi	0.015	0.008	LiCl (0.4)	0.03	0	45.7
PPy-3SBANa	0.015	0.005	NaCl (0.3)	0.03	−10	46.2
PPy-2$SBANH_4$	0.015	0.08	NH_4Cl (0.5)	0.03	−10	46.5
Conventional PPy	0.015		NaCl (0.3)	0.03	0	25.6

[a] Yield (%) = (weight of PPy/weight of Py monomer) ×100.