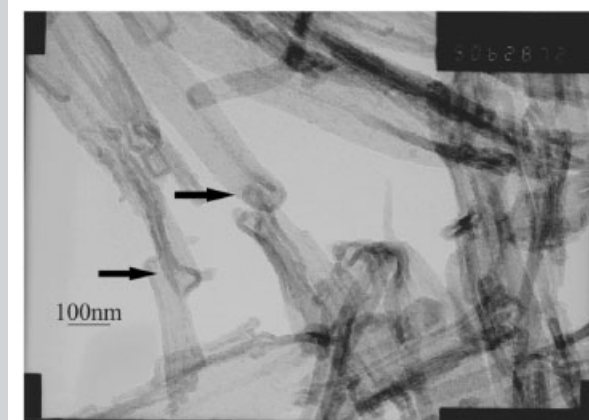


**Summary:** Polypyrrole nanotubes with high electric conductivity and azo function have been fabricated in high yield via an in-situ polymerization. During the process fibrillar complex of FeCl<sub>3</sub> and methyl orange (MO), acting as a reactive self-degraded template, directed the growth of polypyrrole on its surface and promoted the assembly into hollow nanotubular structures.

TEM image of uncompleted PPy nanotubes synthesized in MO solutions after reaction for 40 min.



# Facile Fabrication of Functional Polypyrrole Nanotubes via a Reactive Self-Degraded Template

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**Keywords:** conducting polymers; methyl orange; nanotube; polypyrroles; reactive template

## Introduction

Beginning with the discovery of carbon nanotubes,<sup>[1]</sup> materials with nanotubular structure have attracted considerable attention because of their unique properties and promising applications in molecular electronics, optics, and biomedical science.<sup>[2]</sup> For instance, nanotubes and fibers of conducting polymers have been widely investigated in recent years owing to the switchable conductivity between insulator and metal.<sup>[3]</sup> Among them, polypyrrole (PPy) stands out because of its high conductivity, good environmental stability, and hitherto a large variety of applications.<sup>[4]</sup> Besides the conventional template-synthesis method,<sup>[5]</sup> “soft templates” or “template-free” approaches such as liquid crystalline phases, reverse microemulsion, surfactant gel, and micelles have been reported and used to prepare polyaniline or PPy nanofibers or nanotubes.<sup>[6]</sup> However, the design and controllable fabrication of functional nanomaterials with particular shape and morphology are a challenge all the same. In this study we report a new approach, that is, the use of fibrillar complex as a reactive

seed template that instantaneously forms when adding the anions azo dye methyl orange (MO) and FeCl<sub>3</sub> together prior to the polymerization of pyrrole and automatically degrades during the subsequent polymerization due to the reduction of oxidizing cations. Along with the self-degradation of the fibrillar complex, growth of PPy on its surface and evolution to hollow nanotubular structures with capability of photoelectrochemical conversion of MO and electric conductivity of PPy are achieved. The morphology of the product exhibits almost exclusively nanotubes, without the need for additional template removal steps. This finding could inspire creative imagination to design new system and orchestrate particular shape and morphology of nanostructures.

## Experimental Part

In a typical procedure, 0.243 g (1.5 mmol) of FeCl<sub>3</sub> was dissolved in 30 mL of 5 mM MO (sodium 4-[4'-(dimethylamino)phenyldiazo]phenylsulfonate ((CH<sub>3</sub>)<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>-

$\text{N}=\text{NC}_6\text{H}_4\text{SO}_3\text{Na}$ ) deionized water solution (0.15 mmol). A flocculent precipitate appeared immediately. Then 105  $\mu\text{L}$  (1.5 mmol) of pyrrole monomer (Aldrich) was added into it and the mixture was stirred at room temperature for 24 h. The formed PPy precipitate was washed with deionized water/ethanol several times until filtrate was colorless and neutral, and finally dried under a vacuum atmosphere at 60 °C for 24 h.

The morphologies of PPy-MO nanotubes were observed by scanning electron microscopy (SEM) [JSM-6300 and energy dispersive spectrometer (EDS) accessory for elemental measurement, KeveX-Sigma] and transmission electron microscopy (JEM-200CX, JEOL Company, Japan). The conductivities of compressed pellets of PPy were measured by using the standard four-probe method at room temperature. The molecular structure of PPy-MO was characterized by Bruker Vector-22 FT-IR spectrometer. Wide-angle X-ray diffraction was taken with a Rigakud/Max-Ra diffractometer using Ni-filtered Cu K $\alpha$  radiation. UV-vis absorption spectra of PPy-MO in *m*-cresol solution were recorded on a UV-240 spectrometer (Shimadzu, Japan). A SDT 2960 thermogravimetric analyzer was used to investigate the thermal stability of the PPy-MO with air as pure gas at a flow rate of 50 mL  $\cdot$  min $^{-1}$ . The heating rate was 10 °C  $\cdot$  min $^{-1}$ .

## Results and Discussion

In the SEM images [Figure 1(a) and (b)], the tubular and granular morphology, which correspond to the case of presence or absence of the MO, are observed. The tubular structure of PPy-MO is further confirmed by TEM micrograph [Figure 1(a), inset, right] where outer and inner diameters of the hollow nanotubes are determined as about 70 and 50 nm, respectively.

It is important to note that by replacing the oxidant  $\text{FeCl}_3$  with ammonium peroxydisulfate (APS), no fibrillar precipitates are observed when it is mixed with MO. Also, no nanotubes of PPy are obtained during the subsequent polymerization. This suggests that there is a remarkable relation between precipitates of  $\text{FeCl}_3$  and MO and the formation of PPy nanotubes.

Based on the common knowledge, MO with a planar hydrophobic section and hydrophilic edge group ( $-\text{SO}_3^-$ ) is

water soluble and has anionic characteristic in aqueous solution. Unlike some large organic dopant anions such as naphthalenesulfonic acid, MO has no surfactant characteristic because of the absence of critical micelle concentration. In aqueous solution at 25 °C, MO could dimerize at a concentration of 1 mM and form higher oligomers between 5 and 10 mM.<sup>[7]</sup> On the other hand, it is known that complexation could be achieved between organic compounds like phenol or dye and flocculant like  $\text{Al}^{3+}$  or  $\text{Fe}^{3+}$ .<sup>[8]</sup> In our case,  $\text{FeCl}_3$  is considered to act as a flocculant which suppresses the electrostatic repulsions between MO aggregations and/or reacts with negatively charged aggregates of MO in solutions, then destabilize the charged particles and build an amorphous aggregate.<sup>[9]</sup>

Additional evidence for the concentration need for the MO aggregation was obtained experimentally. By varying the concentration of MO aqueous solution in a typical chemical polymerization from 5 to 1 mM, we found that only trace amount of flocculent precipitate were detected. Accordingly, a granular PPy containing a few tubules was formed. Furthermore, the precipitate became undetectable below 0.1 mM of MO concentration, and absolute granular morphology of PPy was observed. These results suggested that a concentration of MO higher than 1 mM was necessary for the formation of MO aggregation and predominately tubular PPy. This is consistent with the above-mentioned phenomenon. According to EDS analysis, the flocculent precipitate is composed of C (64.03%), N (10.90%), O (13.45%), S (5.53%), Cl (4.10%), and Fe (1.98%), indicating the formation of a complex of  $\text{FeCl}_3$  and MO.

To confirm that the polymerization reaction on the surface of the complex templates helps direct the assembly of PPy hollow nanotubular structures, a number of experiments were performed. First, the obtained  $\text{FeCl}_3$ -MO precipitates are examined by SEM and TEM observation as shown in Figure 2. The diameter of 60–70 nm of the  $\text{FeCl}_3$ -MO precipitates is a little larger than the inner diameter of PPy tubes (about 50 nm), which may be caused by the degradation of precipitates during polymerization. TEM images of the resulted PPy tubes without any treatment reveal absolute tubular structure (not shown

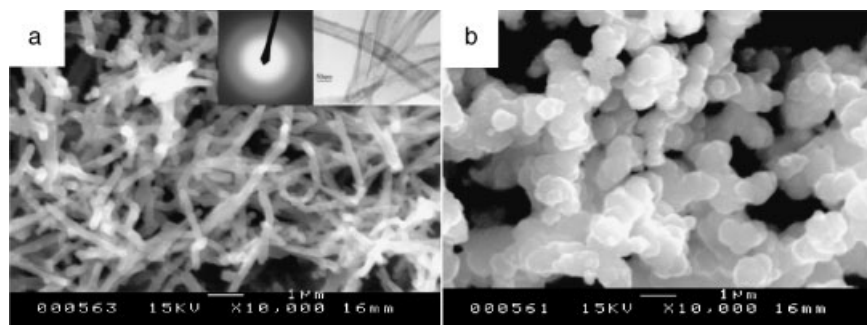


Figure 1. SEM images of PPy chemically synthesized (a) in the presence of MO (insets: TEM image and its electron diffraction pattern); (b) in the absence of MO as the dopant.

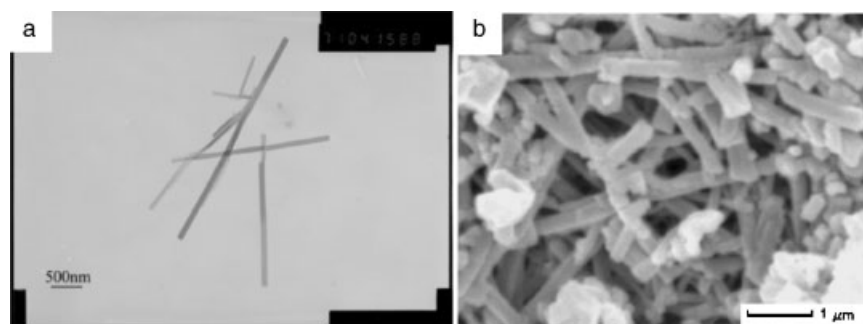


Figure 2. TEM (a) and SEM (b) image of complex of  $\text{FeCl}_3$ -MO.

here). It is concluded that the complex template itself degraded automatically during polymerization but not removed during the washing process. In addition, polymerization of pyrrole with complex of  $\text{FeCl}_3$ -MO as a reactive template is carried out in a duration of 40 min. Specifically, in situ sampling at regular intervals is made for TEM observation. As expected, pyrrole is polymerized just about on the surface of the fibrillar seed templates and undergoes a process from uncompleted [Figure 3(a) and (b)] to almost completed PPy tubes [Figure 3(c) and (d)]. During the process, the fibrillar reactive template directed the growth and formation of PPy nanotubular structures. At the same time, the template itself degraded automatically due to the reduction of oxidizing cations. Therefore, we believe that the formation of PPy nanotubes is significantly dependent on the concentration of MO and the presence of complex of  $\text{FeCl}_3$  and MO. Complex of  $\text{FeCl}_3$  and MO reveals its unique characteristics: (a) it itself possesses nano-ordered

morphology and (b) it is also capable of oxidatively reacting with the pyrrole monomer, although its structure is still not very clear.

Spectroscopically, IR spectrum of the resulted PPy tubes is in good agreement with its literature spectrum of granular PPy synthesized in a common method and confirms that this material is highly doped, as expected. A number of characteristic broad bands of PPy are observed, such as ring fundamental vibration at  $1544$  and  $1457\text{ cm}^{-1}$ , the  $=\text{C}-\text{H}$  in-plane vibration at  $1303$  and  $1040\text{ cm}^{-1}$ , the  $\text{C}-\text{N}$  stretching vibration at  $1175\text{ cm}^{-1}$ , and a  $\text{C}-\text{H}$  wagging vibrations at  $783\text{ cm}^{-1}$ .<sup>[10]</sup> For the IR spectrum of reduced PPy tubes, there is a rapid loss of intensity accompanied by frequency shifts in most bands. Among them the peak at  $1457\text{ cm}^{-1}$  almost disappears, implying benzoid structure of reduced PPy. EDS analysis provides the composition of PPy-MO nanotube, i.e., C (77.00%), N (11.76%), O (5.48%), S (3.86%), Cl (1.80%), and Fe (0.10%), indicating

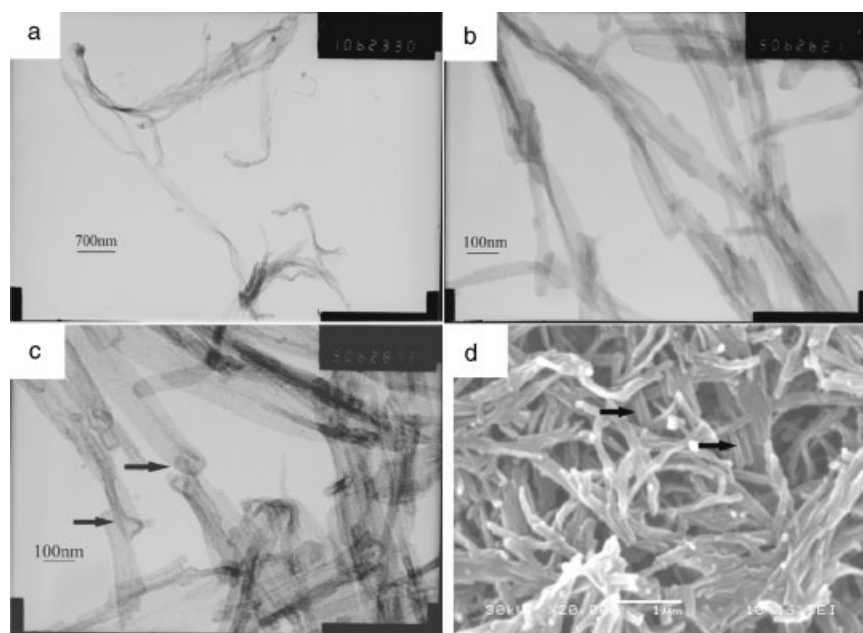


Figure 3. TEM images of PPy nanotubes synthesized in MO solutions after reaction for (a) 5 min; (b) 20 min; (c) 40 min. (d) SEM image of (c).

that PPy-MO is doped with MO,  $\text{Cl}^-$ , and a small amount of iron complex anion. From the EDS data, the degree of doping of the PPy-MO nanotube can be calculated by  $[\text{MO}]/[\text{Py}]$  ratio (denoted by the ratio  $[\text{S}]/([\text{N}]-3[\text{S}]) = 0.25$ ) and  $[\text{Cl}]/[\text{Py}]$  ratio (denoted by the ratio  $[\text{Cl}]/([\text{N}]-3[\text{S}]) = 0.11$ ). These results mean that for the PPy-MO nanotube, every four pyrrole rings there is one MO molecule doped and every ten pyrrole rings there is one  $\text{Cl}^-$  counterion doped. By comparison, the degree of doping of the granular PPy,  $[\text{Cl}]/[\text{Py}]$  ratio (0.25), is correspondingly low. Evidently, MO consisted in  $\text{MO}/\text{FeCl}_3$  complex plays a role of not only template but also a dopant after being self-degraded.

From the X-ray diffraction patterns (not shown here) of the PPy-MO nanotubes, it can be seen that the characteristic peaks of MO disappear after the tubes were dedoped in ammonia, indicating the amorphism of the PPy nanotubes. Furthermore, the amorphous structures of PPy-MO tubules may have an improved spatial order, which was confirmed by the narrowed shape of XRD pattern of dedoped PPy-MO tubules. The thermogravimetric results indicate that the decomposition temperature of the PPy-MO tubules is only a little higher (about  $10^\circ\text{C}$ ) than that of the granules ( $272^\circ\text{C}$ ) formed from PPy-Cl. This result could be interpreted to the amorphous structures but improved spatial order of these tubules demonstrated by both TEM electron diffraction pattern [Figure 1(a), inset, left] and XRD data. Accordingly, the electric conductivity of the tubules at room temperature is as high as  $96\text{ S}\cdot\text{cm}^{-1}$ , which is much higher than that of granular sample ( $8.2\text{ S}\cdot\text{cm}^{-1}$ ) doped only with  $\text{Cl}^-$  under the same polymerization conditions.

UV-vis absorption spectrum of PPy-MO tubules [Figure 4(b)] shows that, compared with that of PPy grains [Figure 4(a)], besides the  $\pi-\pi^*$  absorption band and bipolar broad absorption band of PPy at about 430 and 950 nm,<sup>[11]</sup> a

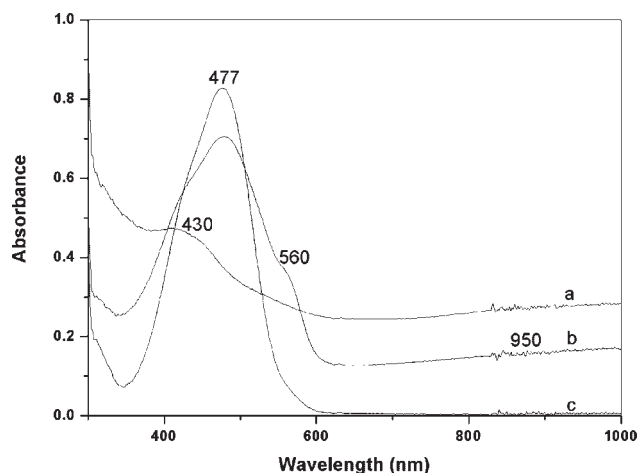


Figure 4. UV-vis spectra of PPy in *m*-cresol solution, synthesized (a) in the absence of MO; (b) in the presence of MO as the dopant; (c) UV-vis spectrum of MO.

strong peak at 477 nm [identical with the absorption band of MO, Figure 4(c)] and a shoulder peak at 560 nm appeared which are attributed to the  $n-\pi^*$  transition of the *trans*-azobenzene units<sup>[12]</sup> and polaron absorption of PPy,<sup>[11]</sup> respectively. This result suggests the presence of the MO in PPy tubules.

## Conclusion

In conclusion, this study describes for the first time: (1) a facile, one-step fabrication of azo functionalized conductive PPy nanotubes in high yield without consideration about elimination of conventional templates, surfactants, and so on; (2) the use of  $\text{FeCl}_3$ -MO reactive self-degraded template to direct the growth of PPy on its surface and promote the assembly into hollow nanotubular structures, and also increase the degree of doping of the PPy nanotubes. Further studies on the above system are underway and the results will be reported in near future.

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