

Facile Route to Hierarchical Conducting Polymer Nanostructure: Synthesis of Layered Polypyrrole Network Plates

Taoqing Wang,¹ Wenbin Zhong,¹ Xutao Ning,¹ Yongxin Wang,² Wantai Yang²

¹College of Materials Science and Engineering, Hunan University, Changsha 410082, People's Republic of China

²Department of Polymer Science, Beijing University of Chemical Technology, Beijing 100029, People's Republic of China

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ABSTRACT: Polypyrrole (PPy) nanowire network plates with both average length and width in tens of micrometers were prepared in an aqueous solution containing cetyltrimethylammonium bromide (CTAB) and nitric acid (HNO₃) by chemical oxidative polymerization methods. It is found that PPy plates are constructed with double layers of nanowire networks. The influences of recipe such as the concentration of CTAB, HNO₃, and pyrrole, as well as the reaction temperature on the morphologies of pro-

duced PPy were systematically investigated. By control experiment employing H₂SO₄ or HCl in place of HNO₃, it is disclosed that HNO₃ probably plays a key role in forming PPy plates. A plausible forming mechanism of PPy plate structures is offered. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 3855–3862, 2009

Key words: polypyrrole; nanowire networks; hierarchical structures

INTRODUCTION

The synthesis of conducting polymer micro/nanostructures is being extensively studied due to their potential applications in many areas, such as sensors,¹ actuators,^{2,3} field effect transistors,⁴ devices,⁵ separation membranes,⁶ etc. Polypyrrole (PPy), one of the most important conducting polymers, has been fabricated into diverse micro/nanostructures.^{7–14} In general, template methods with “solid template” and “soft-template,” and self-assembly methods are widely used to prepare one-dimensional (1D) PPy nanostructures.^{15–32} As for “soft-template” method, cationic surfactant is often used to synthesize 1D conducting polymers (polyaniline (PANI) and PPy).³³ For example, PPy nanofiber, nanowires, and nanoribbons were attained in the presence of cationic surfactant by chemical oxidative polymerization.^{34–36}

In our previous study, PANI 3D nanowire networks and PPy nanowire networks have been successfully prepared with the help of cationic surfactant and organic diacids (or triacid).^{37,38} However, it is still a challenge to prepare higher level PPy hierarchical structure with those nanowire networks, especially in a convenient route.

It is well known that the properties and applications of materials depend greatly on the morphologies of nanostructures. Using 1D nanostructures as building blocks to construct superstructures is expected to offer great opportunities for exploring their outstanding properties and developing next generation of nanoscale electronic and optoelectronic devices.^{39,40} Thus, materials with superstructures based on 1D nanostructures have been widely developed by various strategies.^{41–45} As for PPy, monolayer dendritic networks have been fabricated on the surface of gold by microcontact printing technique and a template formed by octadecanethiol self-assembled monolayers.⁴⁶ Although lamellar crystalline PPy supramolecular structure has been synthesized by using cationic surfactant,⁴⁷ a convenient strategy to synthesize PPy plates with sub-level structure of layered nanowires networks, to the best of our knowledge, has rarely been reported so far. The PPy plate structures may be conveniently used as thin microstructure device. In this work, we report a facile approach to prepare PPy plates with sub-structure of layered nanowire networks by polymerization of pyrrole in the presence of

Correspondence to: W. Zhong (wbzhong@hnu.cn).

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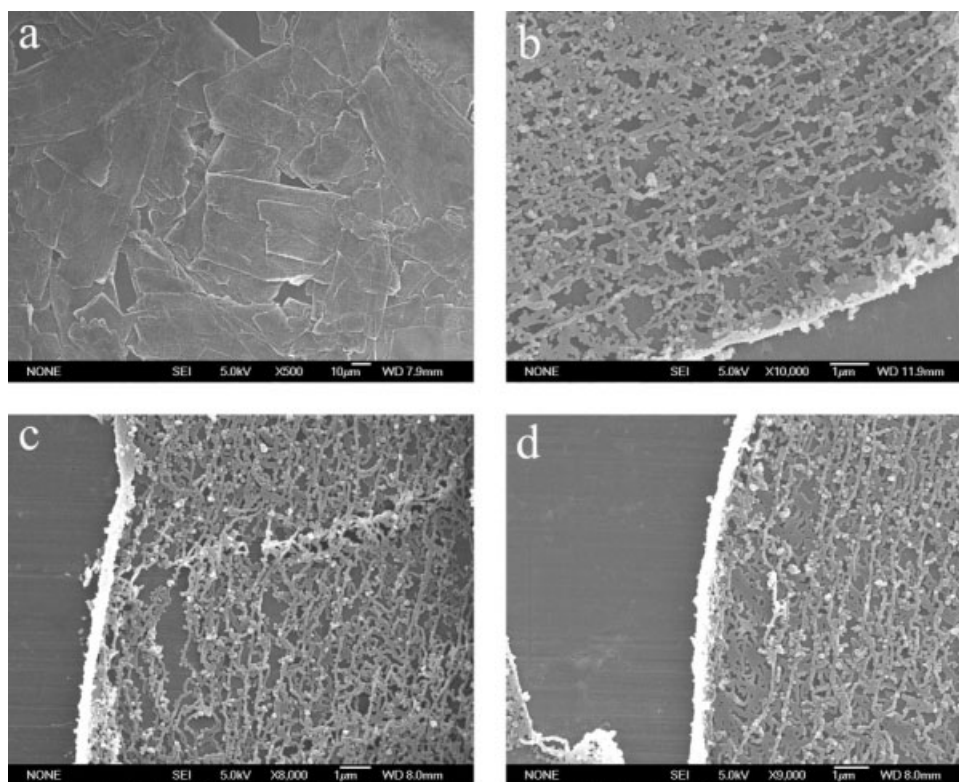


Figure 1 FESEM images of PPy nanowire network plates prepared in an aqueous solution containing CTAB (0.017M), pyrrole (0.019M), and 1M HNO₃ at about 10°C: (a) low-magnification image, (b–d) high-magnification images.

cetyltrimethylammonium bromide (CTAB) and nitric acid (HNO₃).

EXPERIMENTAL

Materials

The monomer pyrrole was purified by distillation under a reduced pressure. CTAB, HNO₃, ammonium persulfate ((NH₄)₂S₂O₈, APS), and ethanol were all of analytical grade and used as received.

Synthesis of layer PPy nanowire networks

In a typical synthesis, CTAB (1.82 g, 0.005 mol) and pyrrole (0.4 mL, 0.0058 mol) were dispersed in 300 mL HNO₃(1M) aqueous solutions under stirring and kept at about 10°C for 3 h. 20 mL APS (with a molar ratio to pyrrole of 1 : 1) aqueous solution was added to the above mixture in one portion. The reaction was allowed to proceed for 10 h at about 10°C under stirring. Finally, the products were washed by deionized water and ethanol repeatedly and then dried in vacuum at 40°C for 24 h.

Characterization

Field-emission scanning electron microscopy (FESEM, JSM-6700F) and transmission electron

microscopy (TEM, JEM 3010) were used to observe the morphologies and measure the size of the products. The molecular structures of the products were characterized by Fourier transform infrared (FTIR, TENSOR27). X-ray diffraction (XRD, SIEMENS Diffractometer, D5000) measurements were performed to characterize the structure of prepared PPy.

RESULTS AND DISCUSSION

Morphology

The morphologies of PPy prepared in an aqueous solution containing 1M HNO₃, 0.017M CTAB, and 0.019M pyrrole are shown in Figure 1. Low-magnification FESEM images of PPy reveal that almost all product of PPy have an average length in tens of micrometers, and PPy plates have flat surfaces [Fig. 1(a)]. From high-magnification FESEM images of PPy plates [Fig. 1(b–d)], it can easily be seen that the plates have clear rims and are comprised of double layers of nanowire networks, where the diameter of nanowire is about 70 nm. The thickness of the plate is about 150 nm. The morphology of present PPy is obviously different from those of PANI or PPy nanowire networks prepared with CTAB and organic diacids (or triacids) in our previous reports,^{37,38} and the diameter of PPy nanowires are a little bit larger than those of PPy nanofibers prepared in either 1M

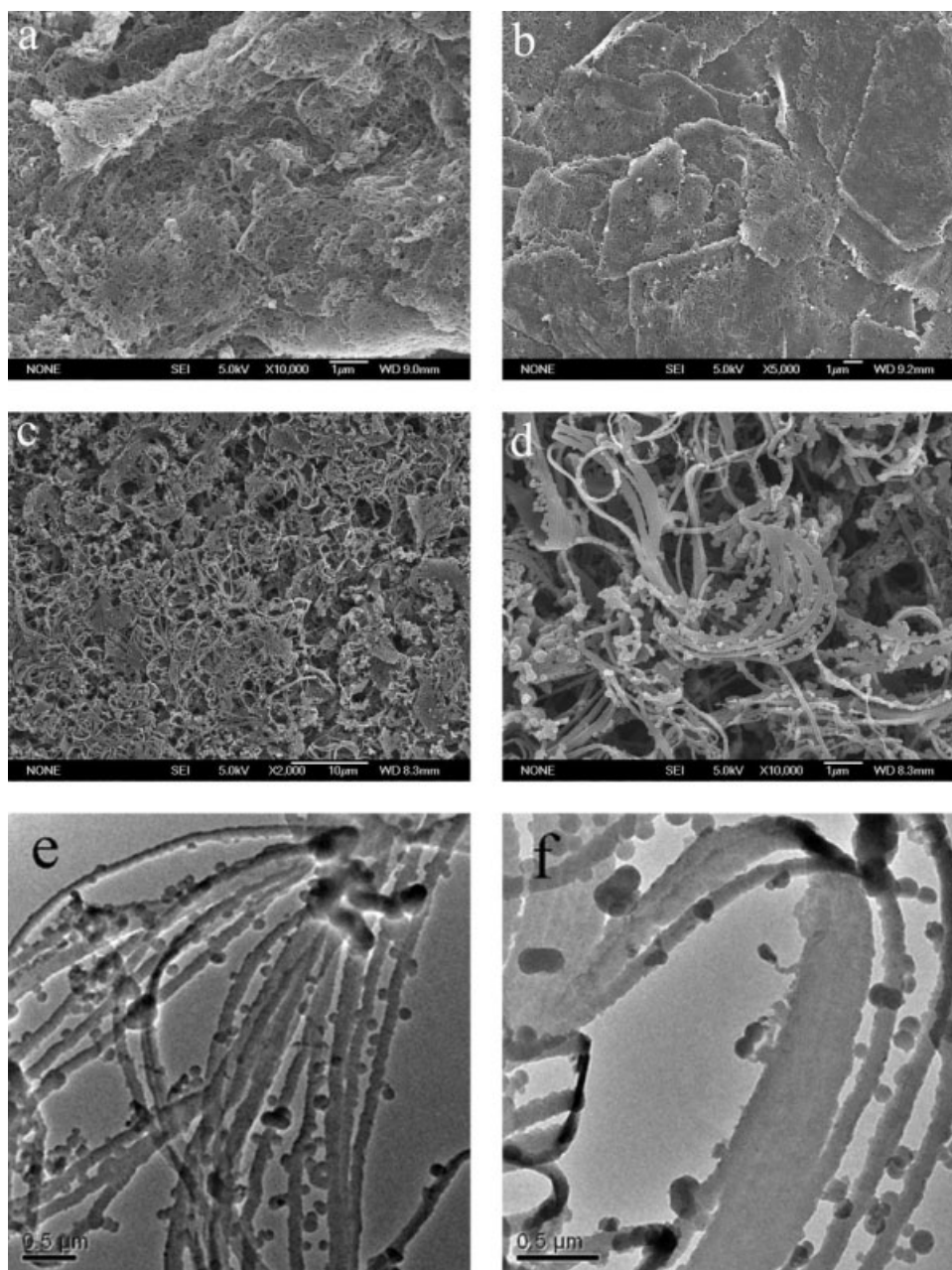


Figure 2 FESEM TEM images of PPy products prepared in an aqueous solution containing CTAB (0.017M), pyrrole (0.019M), and different concentrations of HNO₃ (a) 3M, (b) 0.5M, (c and d) 0.25M, reaction temperature at about 10°C. (e and f) TEM images of PPy prepared in the same conditions as those of c and d.

HCl (20–40 nm) or neutral aqueous solution (20–65 nm).^{34,35}

As we know, the concentration of inorganic acid is an important factor to control the morphologies of prepared conducting polymers.^{34,48} A series of concentrations of HNO₃ was tried in our experiments. It was found that large-area PPy nanowires were obtained as the concentration of HNO₃ was high (3M) in the solution, and each nanowire had a diameter of 60–70 nm [Fig. 2(a)]. This structure is similar to that of PPy nanofiber prepared in the presence of 2M HCl and CTAB,¹⁴ but it is markedly different

from the plates structure formed in 1M HNO₃ (Fig. 1). When the concentration of HNO₃ was lower (0.5M), plate-like structures comprised by compactly packed PPy nanowires appeared, and the surface of the “plate” was relatively flat [Fig. 2(b)], which is very different from the nanowire structures of PPy prepared in an organic acid solution.³⁸ When the concentration of HNO₃ decreased further to 0.25M, it was interesting to find that just clusters of PPy nanowires were formed: the intersectional diameter of PPy nanowires was about 100 nm and the length was about several micrometers [Fig. 2(c,d)]. This

structure was further confirmed by TEM images [Fig. 2(e,f)]. When the concentration of HNO_3 was much low between 0.05 and 0M, there were just PPy nanowires could be collected, which was common when PPy was synthesized in a neutral aqueous solution.^{35,36} The above results probably suggest that the concentration of HNO_3 controls the organization or assembly of PPy nanowires into special structures.

The concentration of monomer will no doubt influence the morphology of prepared conducting polymer nanostructures.^{35,36,49} In our experiment, it was studied under a given concentration of CTAB (0.017M) and HNO_3 (1M). When pyrrole was polymerized with a high-initial concentration of 0.043M, PPy “plates” with flat surfaces were prepared, but they were apparently made of nanoparticles, which had an average diameter of 90 nm [Fig. 3(a)]. As the initial concentration of pyrrole was 0.029M, obtained in the polymerization was still PPy “plates” with clear borders, but it was obviously constructed by nanowire networks [Fig. 3(b)]. However, when the initial concentration of pyrrole was decreased to 0.005M, only irregular PPy nanowires could be formed [Fig. 3(c)]. These results show that the initial concentration of pyrrole also controls the final structures of PPy. Moreover, it is found in our experiments that 0.01 to 0.023M is an optional concentration range to prepare PPy “plates” formed by nanowire networks.

As mentioned earlier, cationic surfactant CTAB is a good “soft-template” in synthesizing PPy 1D nanostructures.^{34–36,38} It has also been reported that the morphologies of PPy could be transformed from wires to ribbons by tuning the concentration of CTAB while fixing the concentration of pyrrole. Moreover, it was also observed that the morphology of 1,3-diphenyl-2-pyrazoline/CTAB could be transformed from nanoparticles to nanofibers by tuning the concentration of CTAB in the range of 5.4 to 0.9 mM.⁵⁰ In our study, CTAB plays important role on the morphologies of prepared PPy again (Fig. 4). When the concentration of CTAB was high like 0.034M, highly ordered PPy nanowires were obtained with average intersectional diameter of about 50 nm and length of several micrometers [Fig. 4(a,b)]. There were just little cross points could be seen among these nanowires. This structure has been double checked by TEM images [Fig. 4(f)]. However, when the concentration of CTAB was low, e.g., 0.0048M in the system, PPy plates could also be prepared but they were composed of both nanowires and nanoparticles [Fig. 4(c)]. This structure is obviously different from that of PPy synthesized with 0.017M CTAB (Fig. 1). As the concentration of CTAB further decreased to 0.002M, porous PPy films made of densely packed particles and wires were obtained

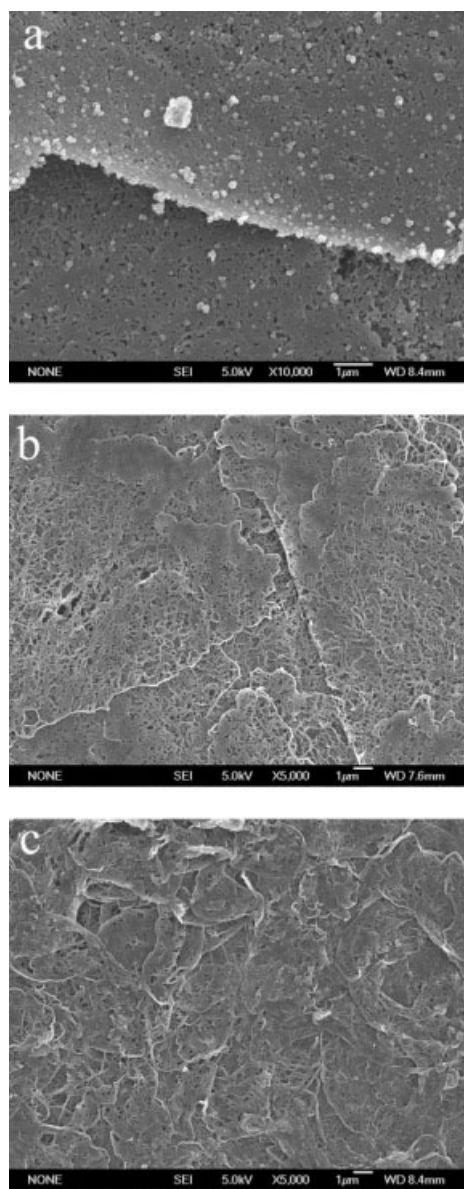


Figure 3 FESEM images of the PPy prepared with CTAB (0.017M), HNO_3 (1M), and different concentration of pyrrole, (a) 0.043M, (b) 0.029M, (c) 0.005M at about 10°C.

[Fig. 4(d)]. Furthermore, when pyrrole was polymerized totally free of CTAB, it was only PPy particles that could be produced [Fig. 4(e)]. The above results prove that the concentration of CTAB does influence the morphologies of prepared PPy in the system, and PPy prefers to form nanowire network plates when the concentration of CTAB is between 0.01 and 0.021M under the given concentration of pyrrole (0.019M) and HNO_3 (1M).

In general, the synthesis of 1D PPy nanostructures is performed at 0–5°C in the presence of CTAB.^{34–36} In the present system, PPy nanowires consisted of particles and nanoparticles can be obtained when the reaction was carried out at 30°C [Fig. 5(a)]. However, when pyrrole was polymerized at 0°C,

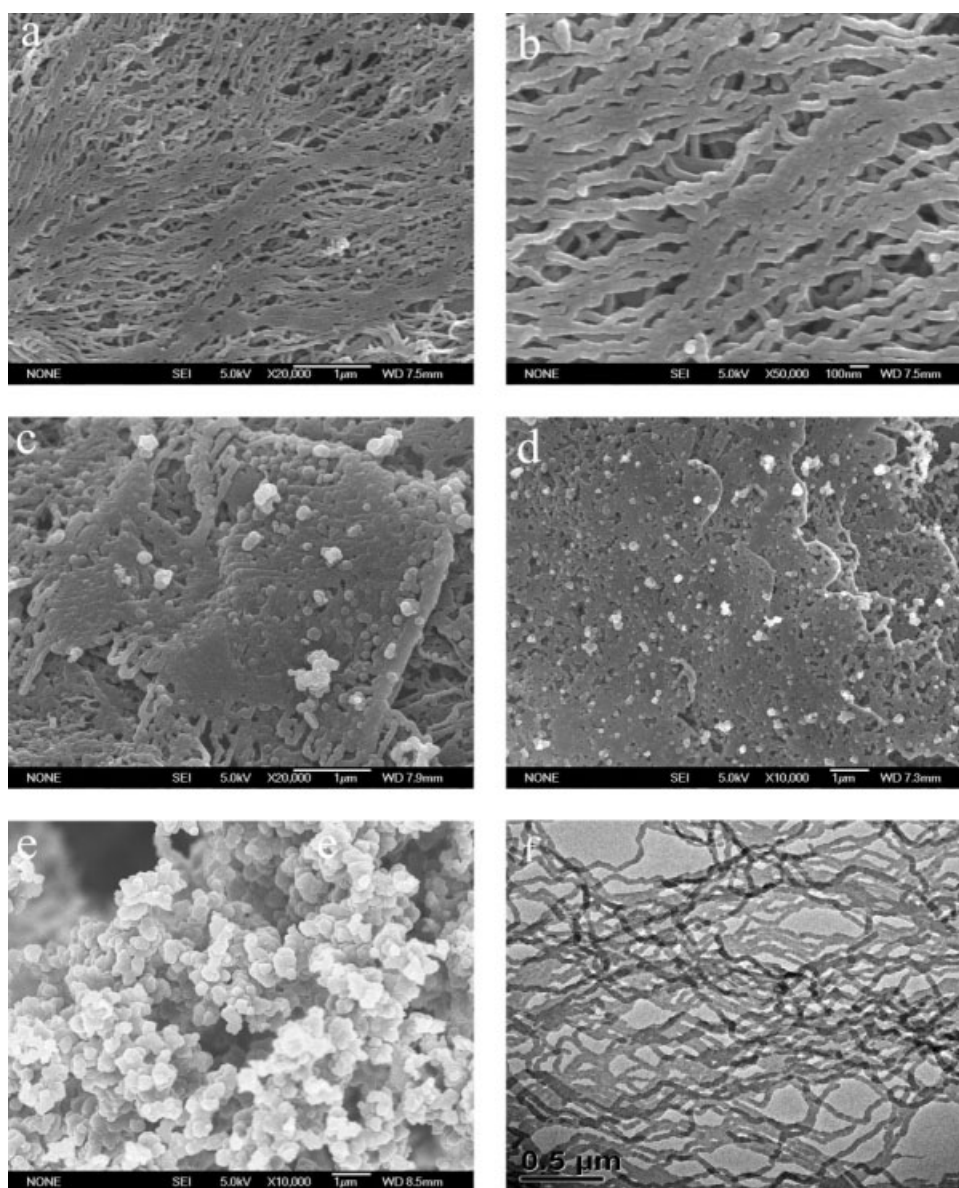


Figure 4 FESEM images of PPy products prepared in aqueous solution containing pyrrole (0.017M), HNO_3 (1M), and different concentrations of CTAB: (a and b) 0.034M, (c) 0.0048M, (d) 0.002M, and (e) 0M at about 10°C . (f) TEM image of PPy prepared in the same conditions as those of a and b.

PPy nanowire networks were formed with an irregular diameter [Fig. 5(b)]. These results show that either high (30°C) or low (0°C) temperature is not appropriate to synthesize PPy nanowire network plates. It is probably due to the influence of temperature on the morphology of micelles formed in the mixture.

In another control experiment, HCl and H_2SO_4 were used in place of HNO_3 . It was found that "plate" could not be formed. The PPy nanowires obtained just showed the difference of diameter, 50 nm and 40 nm, corresponding to 1M HCl [Fig. 5(c)] and 1M H_2SO_4 [Fig. 5(d)] was used.³⁴ This result indicates that charges of anions (such as SO_4^{2-}) have

little influence on the form of PPy nanowires in our system.

Structure characterizations

In our experiment, FTIR was employed to elucidate the chemical structure of produced nanowire network plates (Fig. 6). The bands shown at about 1556 cm^{-1} and 1475 cm^{-1} belong to the fundamental vibration of pyrrole-ring,^{28,29,38,51} and the strong absorptions at about 1190 cm^{-1} and 927 cm^{-1} indicate that the produced PPy has been doped. The bands of C–H deformation vibration and C–N stretching vibration clearly showed at about 1044

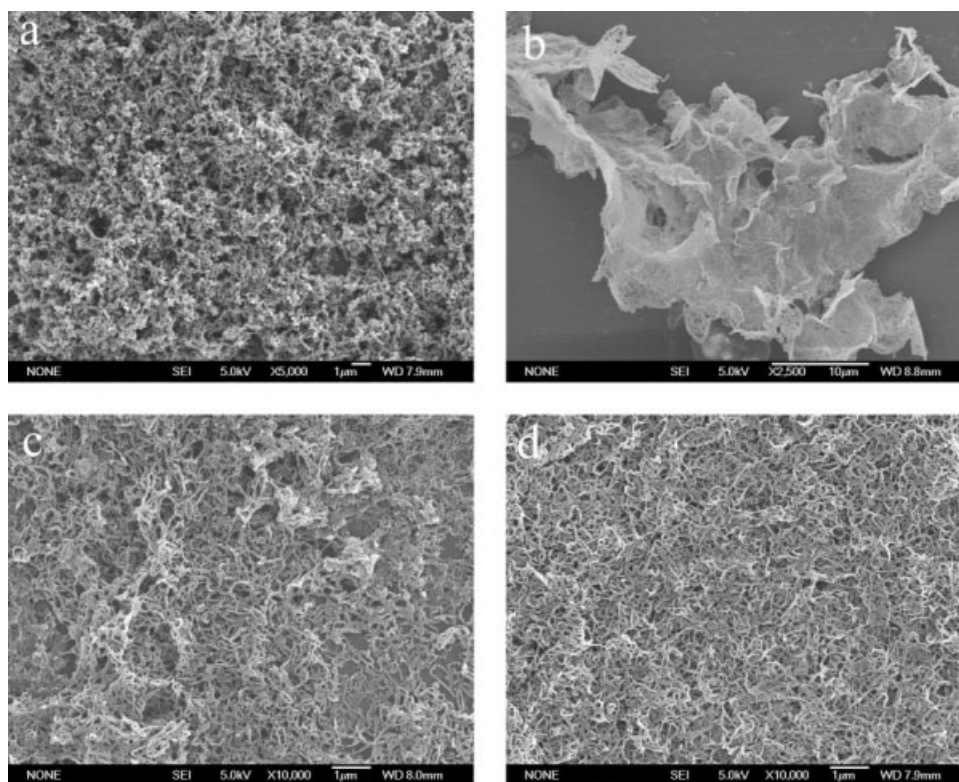


Figure 5 FESEM images of PPy products prepared in aqueous solution containing CTAB (0.017M), pyrrole (0.019M): (a) 1M HNO₃ at about 30°C, (b) 1M HNO₃ at about 0°C, (c) 1M HCl at about 10°C, and (d) 1M HSO₄ at about 10°C.

cm⁻¹ and 1313 cm⁻¹, respectively. The weak bands at about 2848 cm⁻¹ and 2929 cm⁻¹ are assigned to the stretching vibration of methylene, which may indicate that only small amount of surfactant; CTAB existed in PPy nanowire networks.^{36,38}

Mechanism on the formation of PPy plate structures

As a good “soft-template” to synthesize 1D conducting polymer nanostructures,^{35–40} CTAB can also cowork with other organic molecules to form fiber-like micelles in appropriate conditions.⁵⁰ Moreover, inorganic acid anions, in particular NO₃⁻ can also increase the packing parameter of cationic surfactant,⁵² which will then help the orderly growth of molecules.^{53–55} In this study, it was confirmed that the crystalline character of PPy nanowire network plates [Fig. 7(b)] was higher than that of PPy prepared without HNO₃ [Fig. 7(a)]. In addition, it was found that the color of CTAB/HNO₃/pyrrole mixture turned red when pyrrole was added; and a russet precipitation could be clearly observed when CTAB/HNO₃/pyrrole has been kept for 3 days at room temperature. However, this phenomenon cannot be observed in the system of CTAB/pyrrole or CTAB/NaNO₃/pyrrole. This result probably suggests that PPy oligomers are formed in the system of

CTAB/HNO₃/pyrrole. The redox potential of NO₃⁻ in acid medium is about 0.9 V (vs. SCE),⁵³ while the needed redox potential of pyrrole monomer is about 0.5 V (vs. SCE).²⁰ A composite with a higher redox potential than 0.5 V, such as copper (II) can initiate the oxidation of pyrrole.^{10,56–58} In this work, HNO₃

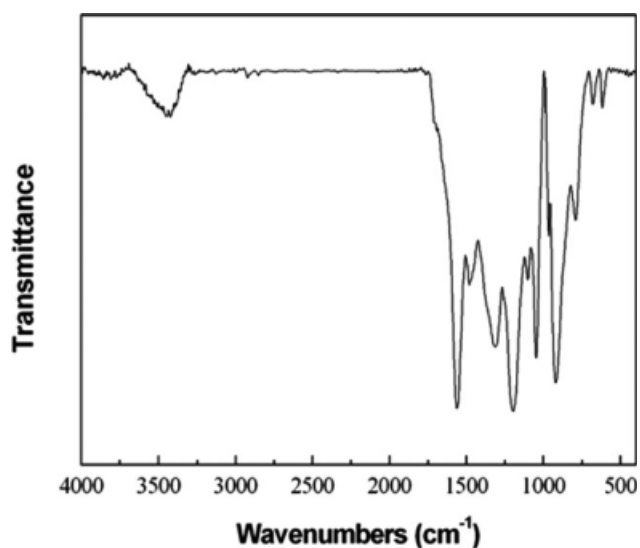


Figure 6 FTIR spectra of PPy nanowire network plates prepared with under CTAB (0.017M), pyrrole (0.019M) in 1M HNO₃ aqueous solution at about 10°C.

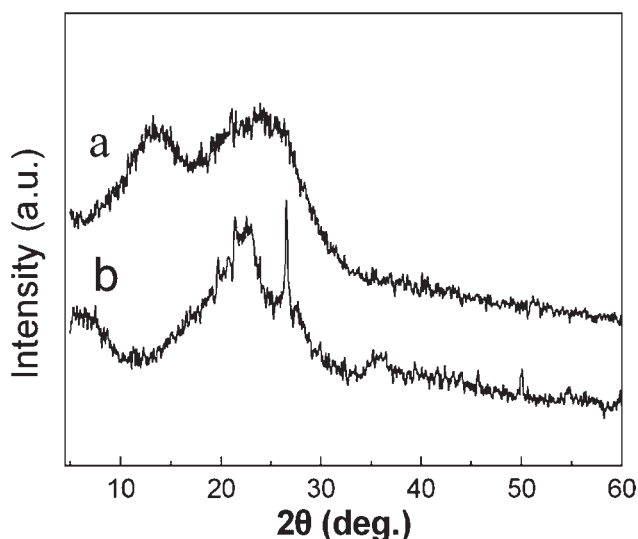


Figure 7 X-ray diffraction pattern of PPy spectra of PPy prepared with under CTAB (0.017M), pyrrole (0.019M) in (a) 0M HNO₃ and (b) 1M HNO₃ aqueous solution at about 10°C.

can be used as oxidant to prepolymerize pyrrole into PPy oligomers when pyrrole is added at room temperature. After that, the velocity of redox reaction decreases at about 10°C, PPy oligomers synthesized by HNO₃ further help the form of PPy 1D nanostructure.^{51,59,60} Besides, the form of PPy nanowire network plates is probably a cooperating result of three factors: HNO₃ served as oxidant to polymerize pyrrole into oligomers, CTAB used as soft-template to prepare nanowires, and NO₃⁻ increasing the packing parameter of cationic surfactants to guide the form of "plate."

CONCLUSIONS

In summary, PPy nanowire network plates were synthesized in a solution containing CTAB, HNO₃, and pyrrole, where APS served as oxidant. SEM and TEM images showed that PPy nanowires, nanowire networks, and plates could be formed in different conditions. It was also demonstrated that HNO₃ played a key role in forming PPy nanowire network plates. We expect the developed strategy could be a help for the synthesis of other polymer hierarchical micro/nanostructures.

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