High-Yield Synthesis of Superhydrophilic Polypyrrole Nanowire Networks

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ABSTRACT: Polypyrrole (PPy) nanowire networks have been synthesized in high yield (higher than 90%) by chemical oxidative polymerization of pyrrole in the presence of hexadecyltrimethylammonium bromide (HTAB) and organic diacids (oxalic acid, tartaric acid, or glutaric acid) and triacid (citric acid). The diameter of nanowire is 60−90 nm. The influence of reaction conditions, such as polymerization temperature, polymerization time, and the molar ratios of HTAB to organic acids and pyrrole, on the morphologies of the PPy nanowire networks has been systematically investigated. In addition, the interconnected PPy nanoparticles are prepared without using HTAB. The film of PPy nanowire networks and nanoparticles is superhydrophilic. A plausible formation mechanism of PPy nanowire networks is discussed.

Introduction

Micro/nanostructured conductive polymers have attracted growing attention due to their potential applications in sensor,[1] biomedicines,[2] actuators,[3] etc. In particular, polypyrrole (PPy) has been studied in great detail because of its good electrical conductivity, redox properties, and environmental stability. Up to now, nanostructured PPy with various morphologies have been synthesized, assembled, and characterized. For instances, PPy nanofibers have been prepared by using the solid template method and seeding approach.[4] PPy micro/nanotubes have been fabricated by template or template-free methods.[5] Submicroscopic tubes of PPy with junctions and dendrites have been prepared via self-assembly.[6] Core−shell particles with the shell of PPy have been reported.[7] PPy nanowires, microcontainers, and networks have been synthesized by electrochemical methods,[8] and individually addressable PPy nanowires were fabricated by electrochemical method.[9] In addition, nanostructured PPy have been fabricated on diverse substrates' surfaces by various approaches.[10] Recently, PPy nanowires have been reported to be prepared by using the cationic surfactant (cetyltrimethylammonium bromide (CTAB)) under neutral aqueous or 1.0 M hydrochloric acid (HCl) conditions.[11,12] Additionally, high yield of PPy has been prepared (nonfibrillar) by using anionic surfactant.[13] However, the method of synthesizing PPy nanowires with high yield and uniform diameter is still in need of exploration.

The surface wettability is a very important property to the solid materials and in general has a close relationship to both the surface free energy and the surface geometric structure. Materials with superhydrophobic surface (with water contact angle (CA) larger than 150°) or superhydrophilic surface (with water CA lower than 5°) have been extensively investigated due to both fundamental research and practical applications.[14] The wettability of PPy has similarly been studied. Mecerreyes et al. reported that CA of PPy doped with various amount of fluorinated counterion changed from 12° to 96°.[15] Recently, Xu et al. reported that the wettability of PPy film could switch from superhydrophobic to superhydrophilic by changing the electrical potential. They suggested that the porous structure with roughness on both coarse and fine scales played an important role in achieving superhydrophobicity or superhydrophilicity.[16] However, as far as we know, the study on the wettability of PPy with uniform nanostructures has seldom been reported. We have previously developed a general chemical route to prepare three-dimensional PANI nanowire networks with high yields, uniform diameters by using both organic diacids (oxalic acid) and cationic surfactant (hexadecyltrimethylammonium bromide (HTAB)).[17] Herein superhydrophilic PPy nanowire networks were successfully synthesized with high yields (higher than 90%) by employing a similar route with organic diacids (oxalic acid, tartaric acid, or glutaric acid) or triacid (citric acid) and HTAB.

Experimental Section

Materials. The pyrrole monomer was purified by distillation. HTAB, oxalic acid dehydrate (OX), tartaric acid (TA), citric acid hydrate (CI), glutaric acid (GL), ammonium persulfate ($(NH_4)_2S_2O_8$, APS), and methanol were of analytical grade and used as received.

Preparation of PPy Nanowire Networks. Under stirring, HTAB (1.82 g, 0.005 mol), one of the organic acids (OX, 0.63 g, 0.005 mol; TA, 1.10 g, 0.0075 mol; CI, 1.70 g, 0.008 mol; or GL, 1.45 g, 0.011 mol), and pyrrole (0.55 mL, 0.008 mol) were dissolved in 250 mL of deionized water at about 15 °C for 3 h. An aqueous solution of APS (20 mL, 0.008 mol; the molar ratio of APS to pyrrole, 1:1) was added into above solution in one portion. The reaction was allowed to proceed for 4 h at about 15 °C under stirring. The resulting product was washed with deionized water and methanol repeatedly and then centrifuged at 5000 rpm for 10 min. Finally, the product was dried in a vacuum oven at 40 °C for 24 h. The yields of PPy were 0.67, 0.72, 0.77, and 0.70 g, respectively.

Characterization. Samples of PPy for characterization of field-emission scanning electron microscopy (FESEM, JSM-6700 F) and transmission electron microscopy (TEM, JEM 3010, JEOL) were prepared by first redispersing the collected product with deionized water. The electrical conductivity was measured under laboratory conditions by a four-probe method with a 2400 digital source meter (Keithley) as a current source and a 6517 A high resistant meter

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(Keithley) as a dc voltage meter. Fourier transform infrared spectra (FT-IR) were obtained from Nicolet NEXUS 670. Water CAs was detected by contact angle system (OCA20, Dataphysics). The elemental analysis of O and N was measured by TC-436 (Leco), and C and S were measured by CS-4444 (Leco).

Results and Discussion

The morphologies of PPy prepared with different organic diacids and triacid are shown in Figure 1, which reveals that they are all nanowires and packed in rough porous structures. Additionally, it is difficult to find individual and/or monolayer nanowires in FESEM images. The low-magnification FESEM images (Figure 1a,c,e,g) show that these uniform nanowires can be fabricated in a large area for all resulting products obtained from different systems.

The TEM images of PPy synthesized with different organic diacids and triacid are shown in Figure 2. Here individual PPy nanowire is difficult to be found, but instead, numerous PPy nanowires are packed compactly. Moreover, they are linked together via some "cross-linking points" (pointed out in Figure 2 images) to form three-dimensional porous networks but not just packed structures. From Figures 1 and 2, it can be found that PPy nanowires are not formed in the same plane, so not all the "cross-linking points" of the nanowires can be clearly observed. Additionally, since the nanowires are packed densely, only those ones existing on the fringe can be clearly observed by TEM. The PPy nanowires prepared with different organic diacids and triacid are uniform and almost have the same diameter, 60−90 nm, which is smaller than that of polyaniline nanowires synthesized by employing a similar route[17] but a little higher than that of PPy nanofibers (20−40 nm) reported by Wu and co-workers.[12] The conductivity of the PPy nanowire networks prepared with OX (the molar ratio of HTAB to OX and pyrrole, 1:1:1.6), TA (the molar ratio of HTAB to TA and pyrrole, 1:1.5:1.6), CI (the molar ratio of HTAB to CI and pyrrole, 1:1.6:1.6), and GL (the molar ratio of HTAB to CI and pyrrole, 1:2.2:1.6) is about 0.27, 0.09, 0.07, and 0.01 S cm^{-1}, respectively. The difference of conductivity is probably assigned to the acidity of the organic acids.

The FT-IR spectra of PPy nanowire networks prepared with different organic diacids and triacids reveal that their characteristic peaks are almost the same. The characteristic peaks of PPy at the wavenumbers of about 1560 and 1480 cm^{-1} are due to the fundamental stretching vibration of pyrrole rings.[18] Bands at about 1200 and 920 cm^{-1} are assigned to the stretching vibration of doped PPy. Bands at about 1050 and 1319 cm^{-1} are attributed to the C−H deformation vibrations and C−N stretching vibrations,[19] respectively. The new peak at about 1690 cm^{-1} is assigned to the C═O stretching vibration of the carboxylic groups.[8b] The result shows that PPy may be doped by OX, TA, CI, and GL. To understand the chemical compositions of the PPy nanowires, the energy dispersion spectrometer (attachment to the transmission electron microscope) was used. It is found that Br$^-$ (belonging to HTAB) does not exist in those PPy nanowires prepared with OX, TA, CI, and GL. The result is similar to that reported by Zhang.[19] Whereafter, the elemental analysis is used to determine the elemental composition of the PPy nanowires. The result reveals a composition (mass percent, prepared with OX, TA, CI, and GL) [C] 59.01, 56.30, 56.45, 60.48; [O] 18.41, 22.30, 24.13, 17.07; [N] 15.85, 14.12, 12.93, 14.75; [S] 3.01, 3.26, 2.69, 3.21, respectively. Then the chemical composition of those PPy nanowires should be $(\text{pyrrole})_1(\text{SO}_4)_{0.083}(\text{OX})_{0.17}$, $(\text{pyrrole})_1(\text{SO}_4)_{0.101}(\text{TA})_{0.163}$, $(\text{pyrrole})_1(\text{SO}_4)_{0.091}(\text{CI})_{0.181}$, and $(\text{pyrrole})_1(\text{SO}_4)_{0.095}(\text{GL})_{0.157}$, respectively. In this way, the result further proves that PPy should have been doped by OX, TA, CI, or GL, respectively. And then it can calculate that the conversions of pyrrole monomers in these systems are about 96%, 92%, 90%, and 93%, respectively.

To further understand the system of forming PPy nanowire networks, the influences of the recipe, i.e., molar ratios of pyrrole to organic diacids (or triacid) and HTAB (the concentration of HTAB is 0.02 M), on the morphologies of PPy networks are systematically investigated. The results are briefly summarized as follows. (1) If HTAB is not used in the reaction solution, all products of PPy prepared with OX, TA, CI, or GL are all nanoparticles with diameter of 100−300 nm. From the images of FESEM and TEM (Figure 4), it can be found that these particles are linked and packed together. Furthermore, the images reveal that the surfaces of PPy samples also possess rough and extended porous structures. (2) When the molar ratio of HTAB to OX and pyrrole (HTAB to TA and pyrrole, HTAB to CI and pyrrole, or HTAB to GL and pyrrole) is between 1:1:0.5 and 1:1:3.8 (1:1.5:0.9 and 1:1.5:3.5; 1:1.6:1 and 1:1.6:3.5; or 1:2.2:1.2 and 1:2.2:2.5), PPy nanowire networks are obtained. (3) It can be found that the PPy prepared with organic diacids and triacid are particles when the molar ratio of pyrrole to HTAB is lower than 0.5 or higher than 5.0. (4) When the molar ratio of OX (TA, CI, and GL) to HTAB is higher than about 3.6 (3.4, 3.4, and 3.1), the morphology of PPy transforms into particles, too. From the above data, the conditions of fabricating PPy nanowire networks are similar to those of forming three-dimensional polyaniline nanowire networks.[17] Thus, it can be logically deduced that to synthesize PPy nanowire networks, the optimum molar ratio of HTAB to OX (TA, CI, and GL) and pyrrole should be around 1:1:1.6 (1:1.5:1.6, 1:1.6:1.6, and 1:2.2:1.6). In addition, the effect of temperature on the morphologies of PPy prepared with OX is examined. Figure 5a reveals that the PPy nanowires consist of nanoparticles when pyrrole is polymerized at 30 °C, while the PPy nanowires, as showed in Figure 5b, are short in length when the polymerization of pyrrole is carried out at 0 °C. This result suggests that it should be not appropriate to form well-defined PPy nanowire networks at 0 °C with the system. The above two results are probably assigned to the influence of temperature on the morphologies of the formed micelles, which consist of organic acid/HTAB/pyrrole. Moreover, the influence of polymerization time on the formed morphologies and yields of PPy nanowire networks are briefly evaluated. During the polymerization of pyrrole, APS solution is directly added into the mixture solution of HTAB, OX, and pyrrole (0.005, 0.005, and 0.008 mol, respectively) at about 15 °C. It can be found that the above mixture solution turns into black rapidly. The mixture solution is kept stirred and reacted for another 30 min and then centrifuged at 5000 rpm for 5 min. After that, black precipitates of PPy and colorless solutions are obtained. When the colorless solution is separated and added with APS, there is no obvious change in appearance. It suggests that pyrrole monomer should have been completely polymerized within 30 min. In other words, the polymerization yield of PPy should be high in this period. Additionally, the morphologies of PPy prepared for 30 min are almost the same as those for 4 h. These results indicate that the PPy nanowire networks could be prepared in a high yield in just a short period (30 min).

To examine the wettability of prepared PPy nanowire networks and nanoparticles, the film samples of PPy are prepared. The PPy was redispersed and deposited on glass wafers (used as substrate) first and then dried in a vacuum oven at 40 °C for 24 h. It can be found that the water droplets spread rapidly over the PPy films' surfaces as soon as they contact the

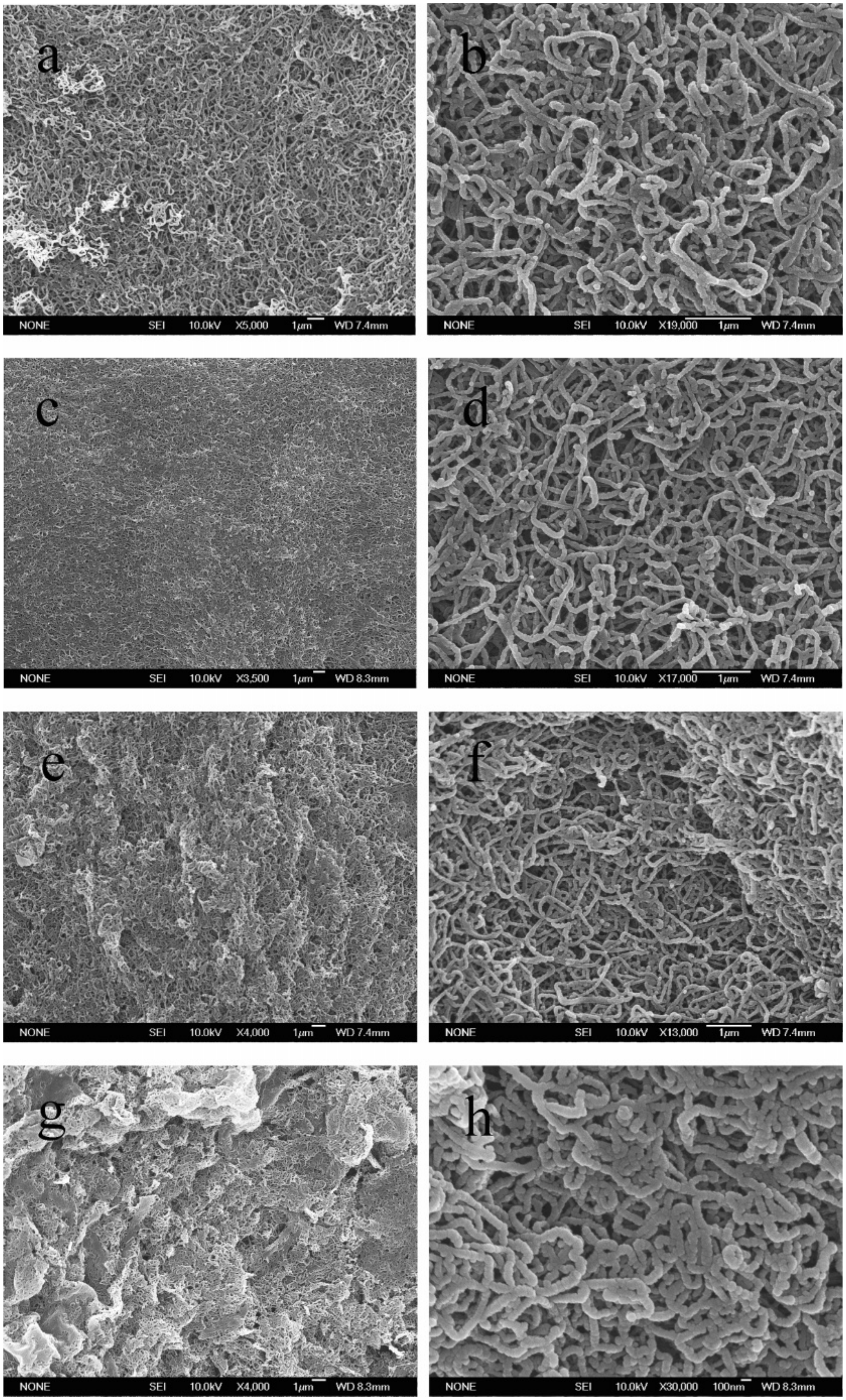

Figure 1. FESEM images of PPy nanowires prepared at 15 °C (low-magnification images a, c, e, g and high-magnification images b, d, f, h): (a, b) prepared with HTAB, OX, and pyrrole, 0.005, 0.005, and 0.008 mol, respectively; (c, d) prepared with HTAB, TA, and pyrrole, 0.005, 0.0075, and 0.008 mol, respectively; (e, f) prepared with HTAB, CI, and pyrrole, 0.005, 0.008, and 0.008 mol, respectively; (g, h) prepared with HTAB, GL, and pyrrole, 0.005, 0.011, and 0.008 mol, respectively.

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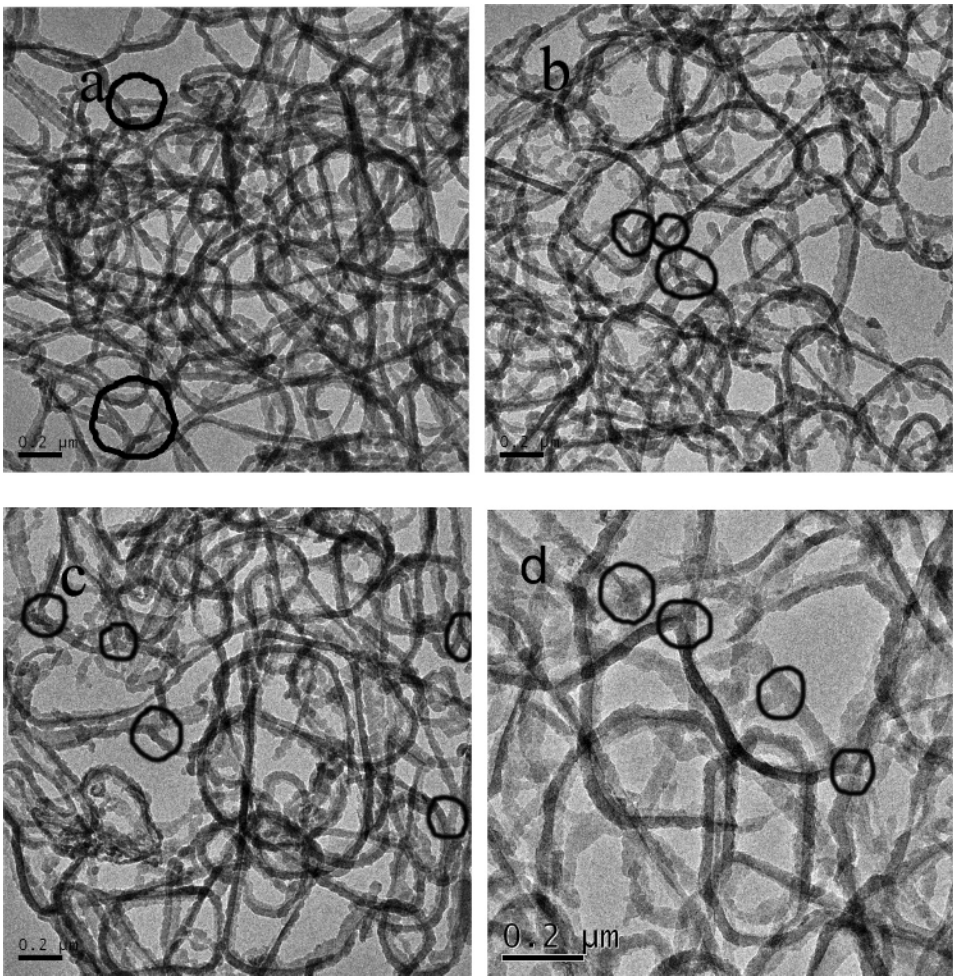

Figure 2. TEM images of PPy nanowires: (a) prepared with HTAB, OX, and pyrrole, 0.005, 0.005, and 0.008 mol, respectively; (b) prepared with HTAB, TA, and pyrrole, 0.005, 0.0075, and 0.008 mol, respectively; (c) prepared with HTAB, CI, and pyrrole, 0.005, 0.008, and 0.008 mol, respectively; (d) prepared with HTAB, GL, and pyrrole, 0.005, 0.011, and 0.008 mol, respectively.

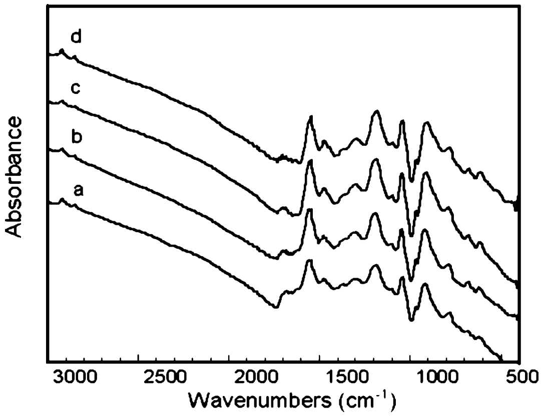

Figure 3. FT-IR spectra of PPy nanowire networks prepared with different organic diacids: (a) OX, (b) TA, (c) CI, and (d) GL.

films. All PPy films show superhydrophilicity with CA close to 0°. As we know, wettability of solid surface is governed by both the chemical composition and physical properties. The wettability of doped PPy also depends on the types of used dopants.[16,20] For instance, PPy doped with a fluorinated dopant is well hydrophobic.[15] In the present work, the neutral (dedoped) PPy is slightly hydrophilic for containing the pyrrole moiety. Besides, the dopants (organic diacids and triacid) of PPy may be hydrophilic. Moreover, the prepared PPy is nanowires or nanopaticles. As mentioned above, surface roughness enhances both hydrophilicity of hydrophilic materials and hydrophobicity of hydrophobic ones.[16,21] Therefore, here the film of PPy nanowire networks and nanoparticles can be obtained with superhydrophilicity. The resulting surfaces of the prepared PPy films, no matter made of nanowire networks or nanoparticles, are both rough with porous loose structures (Figures 1 and 4), in which there are numerous nanoscale reservoirs. With these structures, it is thought that the hydrophilic nanowires or nanoparticles absorb water into these reservoirs as soon as the water droplets contact the prepared PPy films. As the result, water droplets are pushed to spread over the surfaces rapidly, and the surfaces show the superhydrophilicity.

In our previous work, we have synthesized three-dimensional polyaniline nanowire networks via using organic diacids. It is found that a kind of white precipitate with a network-like structure is produced without APS. This structure used as “soft” templates can be elongated and form a three-dimensional polyaniline nanowire network.[17] Here the morphology of PPy nanowire networks is similar to that of three-dimensional polyaniline nanowire networks prepared with organic diacids. Moreover, when the PPy nanowire networks are prepared without APS, a kind of white precipitate is found, too. Therefore, the formation mechanism of PPy nanowire networks may resemble that of the three-dimensional polyaniline nanowire networks. It may have a bit of difference from the formation mechanism of PPy nanowires reported by some literature. Wu and co-workers have reported that the viscosity of reaction

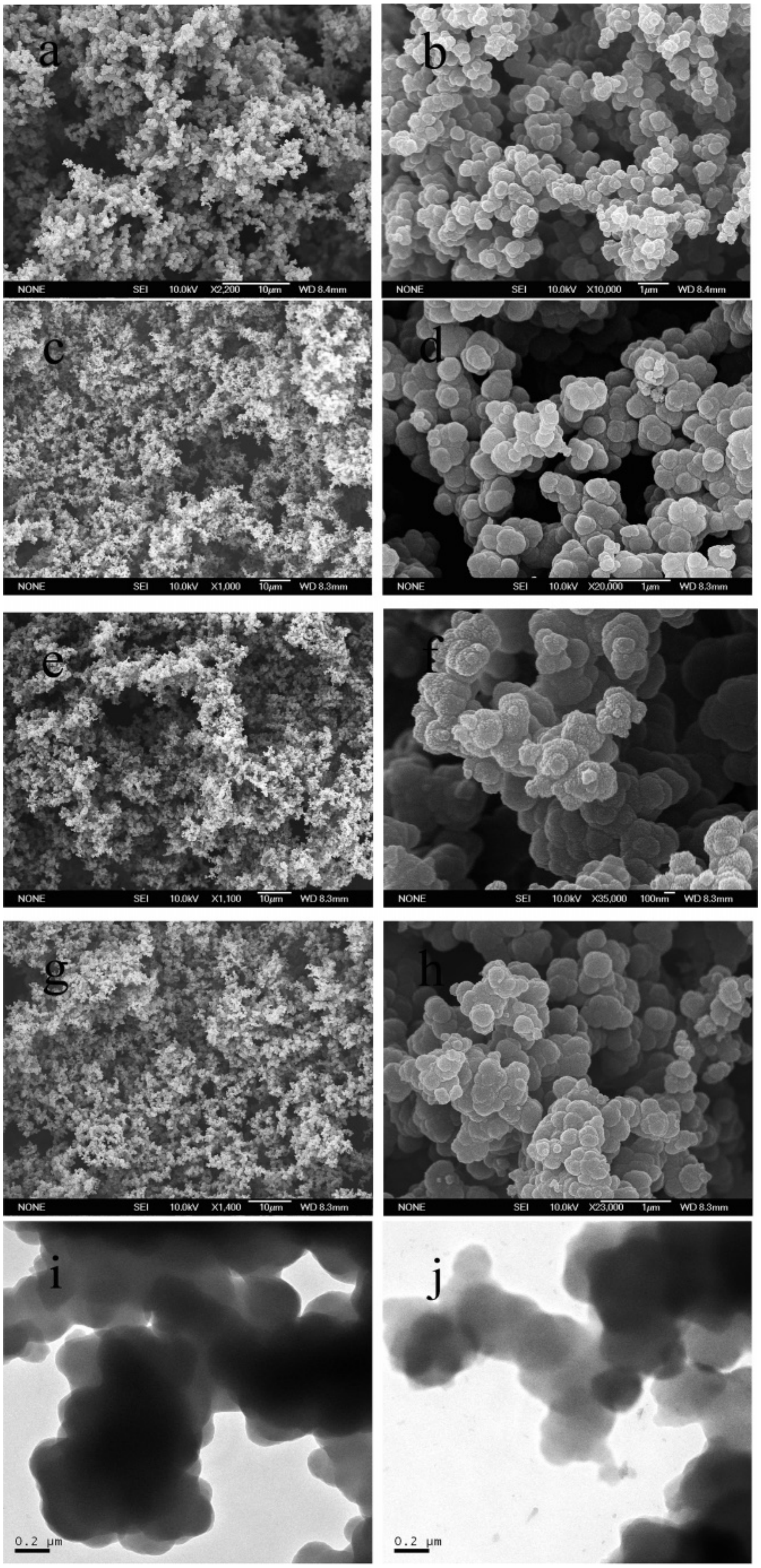

Figure 4. FESEM and TEM images of PPy nanoparticles (low-magnification FESEM images a, c, e, g; high-magnification FESEM images b, d, f, h; TEM images i, j): (a, b, i) prepared with OX and pyrrole, 0.005 and 0.008 mol, respectively; (c, d, j) prepared with TA and pyrrole, 0.0075 and 0.008 mol, respectively; (e, f) prepared with CI and pyrrole, 0.008 and 0.008 mol, respectively; (g, h) prepared with GL and pyrrole, 0.011 and 0.008 mol, respectively.

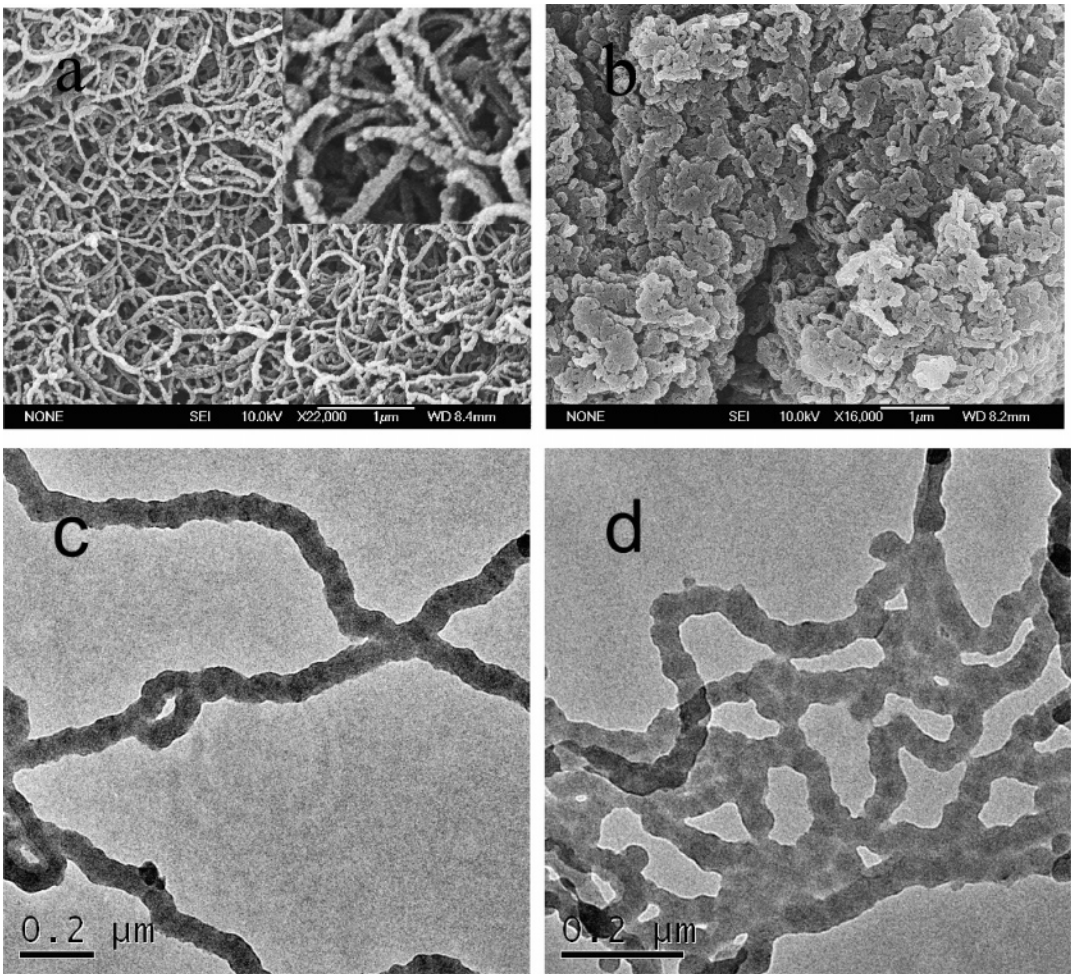

Figure 5. FESEM and TEM images of PPy nanostructures. PPy nanowires showed in FESEM images were prepared with HTAB, OX, and pyrrole, 0.005, 0.005, and 0.008 mol, respectively: (a) 30 °C; (b) 0 °C; (c) TEM images of PPy nanowires prepared with HTAB, ethanoic acid, and pyrrole, 0.005, 0.012, and 0.008 mol at 15 °C; (d) TEM images of PPy nanowires prepared with HTAB and pyrrole, 0.005 and 0.008 mol (without acid), at 15 °C.

mixture played a key role in the evolution of fibrillar morphology in the system of HCl, CTAB, and pyrrole. They found that the viscosity of a 1.0 M HCl aqueous solution with CTAB increased dramatically when pyrrole was added.[12] Zhang et al. have reported that a white flocculent precipitate appeared immediately when APS was added into the solution of CTAB and pyrrole. The yielding of white precipitate (lamellar mesostructural $(CTA)_2S_2O_8$ precipitate) was a key step for the formation of PPy one-dimensional nanostructure.[11] Fu and coworkers have reported the spherical micelles of CTAB molecules transformed into rodlike micelles when the molar ratios of 1,3-diphenyl-2-pyrazoline to CTAB were higher than 2.[22] In the present work, the experimental evidence reveals that PPy nanoparticles are interconnected without HTAB. The results suggest that organic diacids and triacid should have influence on the interconnection of PPy, too. To further understand the effect of organic diacids and triacid on forming the PPy nanowire networks, the organic diacids and triacid were replaced with ethanoic acid to prepare PPy under the same conditions (HTAB and pyrrole, 0.005 and 0.008 mol, respectively; at about 15 °C). The TEM images of PPy synthesized with ethanoic acid, HTAB, and pyrrole are shown in Figure 5c. It can be observed that PPy nanowires with the diameter of about 60−100 nm are linked, too. But it is easy to observe the monolayer PPy nanowires. Namely, the cross-linking structure of PPy nanowires prepared with ethanoic acid should be lower than that prepared with organic diacids and triacid. Additionally, when pyrrole is polymerized with HTAB but without any acid, it can be easily found that monolayer small-area PPy nanowires with the diameter of about 70−110 nm are linked (Figure 5d), too. The result is similar to those in the literature.[11,19] From the above results and literature,[11,12,19] it is suggested that PPy nanowires could be synthesized with HTAB and pyrrole with/without acid. Namely, the acid should not be a prerequisite for preparing PPy nanowires with the system. Since organic diacids and triacid have two or three carboxyl groups, they may improve micelles to link with each other. The micelles are made of cationic surfactant, HTAB and pyrrole. Therefore, organic diacids and triacid would drive HTAB micelles with pyrrole to aggregate with each other and form the networks of micelles by the interactions of hydrogen bonding and/or static charge (electrostatic force). Thus, when APS is added into the reaction mixture, the networks could be elongated and form PPy nanowire networks.[12,23]

Conclusion

PPy nanowire networks were synthesized in high yield (higher than 90%) by using HTAB as emulsifier, organic diacids (oxalic acid, tartaric acid, glutaric acid), or triacid (citric acid) as dopants and via the route of chemical polymerization of pyrrole. It is found that organic diacids and triacid may improve interconnections of nanostructured PPy. To synthesize well-defined PPy nanowire networks, the optimum molar ratio of HTAB to oxalic acid (tartaric acid, citric acid, glutaric acid) and pyrrole is around

1:1:1.6 (1:1.5:1.6, 1:1.6:1.6 and 1:2.2:1.6). Simultaneously, the film of PPy nanowire networks and nanoparticles is superhydrophilic. This simple, wide, rapid, and repeatable approach for preparing superhydrophilic PPy nanowire networks is thought of as a good application in the foreground.

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