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Molybdic acid doped polyaniline micro/nanostructures via a self-assembly process

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ABSTRACT

Molybdic acid (H_2MoO_4, MA) doped polyaniline (PANI) micro/nanostructures were prepared by a self-assembly process in the presence of ammonium persulfate ($(NH_4)_2S_2O_8$, APS) as the oxidant. The morphology of PANI-MA changed from nanofibers or nanotubes ($\sim$160 nm in diameter) to co-existence of nanofibers and microspheres ($\sim$3 μm in diameter) and that accompanied an enhancement of the conductivity from 5.42×10^{-3} S cm^{-1} to 2.8×10^{-1} S cm^{-1}as the molar ratio of MA to aniline varied from 0.01 to 1.5. With increasing the polymerization time, moreover, the pH value of the reaction solution not only decreased due to sulfuric acid produced during the course of the polymerization, but also accompanied a change in morphology from microspheres to nanofibers. All abovementioned observations could be interpreted by spherical and cylindrical micelle composed of MA as the "soft-template" in forming the micro/nanostructures.

1. Introduction

Design and synthesis of materials with novel functions and special micro/nanostructure (e.g. hollow spheres and nanotubes or nanofibers, even their oriented arrays) have received great attention in the nanoscience and nanotechnology [1,2]. The micro/nanostructured polyaniline (PANI) has recently attracted considerable attention due to its unique properties, such as high conductivity, easy of preparation, good environmental stability and potential application in nanoelectronic devices [3]. Up to now, template-synthesis method [4], electro-spinning technique [5,6], interfacial polymerization [7,8], emulsion or reversal-emulsion [9,10] and template-free method [11–20] have been used to prepare hollow spheres, nanotubes or nanofibers of PANI. Among those methods, template-free method, which sometimes is called as "soft-template" method, is simple and cheap because of omitting template and post-treatment of removal template. Up to date, micro/nanostructured PANI has been doped by inorganic acids (HCl, H_2SO_4, H_3PO_4, HBF_4) [21], organic functionalized acid with $-SO_3H$ [22] or –COOH group [23] and sulfated C_{60} [24] or carbon nanotubes [25]. It is found that the morphology of PANI micro/nanostructures is strongly affected by the nature and concentration of the dopant because of it acting as the doping and "soft-template" function at the same time [26]. Thus, searching for a new type of dopants to prepare the micro/nanostructured PANI by the "soft-template" method is still necessary.

The molybdic acid (H_2MoO_4, MA) is not only a kind of ramification of molybdenum, but also a typical metal acid. MA has resembled structure of carboxyl (–COOH) with

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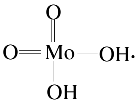
metal–oxide double bonds, whose molecular structure is shown as



$$O{=}\overset{\displaystyle O \atop \displaystyle \|}{\underset{\displaystyle | \atop \displaystyle OH}{Mo}}{-}OH$$

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As one can see, its –MoOOH group can be used to dope PANI because of proton doping being character of PANI [27], while the coordination chemistry of Mo(VI) has aroused considerable interest in bio-chemical and catalytic field [28–31]. To the best of our knowledge, there is no paper regarding MA doped PANI micro/nanostructures prepared by hard- or soft-template method [32].

Here MA doped PANI micro/nanostructures are reported, which are prepared by a “soft-template” method in the presence of ammonium persulfate ($(NH_4)_2S_2O_8$, APS) as the oxidant. It is found that the morphology of PANI-MA changes from nanofibers or nanotubes (~160 nm in diameter) to co-existence of nanofibers and microspheres (~3 μm in diameter) and the conductivity increases from 3.15×10^{-3} S cm^{-1} to 3.8×10^{-1} S cm^{-1} as the molar ratio of MA to aniline increases from 0 to 1.5. With the increase of polymerization time, not only the pH value of the reaction solution decreased due to production of sulfuric acid in the process of the polymerization, but also the morphology changed from microspheres to nanofibers. The observations are discussed based on the micelle composed of MA.

2. Experimental

Molybdic acid (H_2MoO_4, MA) doped PANI micro/nanostructures were prepared by a “soft-template” method in the presence of ammonium persulfate ($(NH)_4S_2O_8$, APS) as the oxidizing agent. Synthesis process of PANI-MA micro/nanostructures is similar to our previous report [23]. For instance 0.2 mL aniline monomer and quantitative amount of MA were dissolved in 20 mL of de-ionized water under ultrasonic stirring for 10 min to form an emulsion of aniline/MA complex at 0–5 °C. The mixture was cooled in an ice bath and 10 mL pre-cooled aqueous solution of APS (0.46 g) was added to the above mixture. The reaction was kept for 12 h in the ice bath. The resulting precipitate was washed with water, methanol and ether several times, respectively. Finally, the product was dried in vacuum at room temperature for 24 h. The effect of the molar ratio of MA to aniline (represented by MA/An ratio) on the morphology and conductivity of the micro/nanostructures was investigated. Moreover, the influence of the polymerization time on pH value of the reaction solution and morphology of the as-synthesized micro/nanostructures was also measured to understand the formation mechanism of the self-assembled micro/nanostructures. The morphologies of PANI-MA micro/nanostructures were investigated with a JEOL JSM-6700F field emission scanning electron microscope (SEM) and a JEOL JEM-2010 transmission electron microscopy (TEM), respectively. The electron and molecular structure was characterized by UV–visible and FTIR spectra as well as X-ray photoelectron spectra. The absorption spectra of the PANI-MA dissolved in *m*-cresol were recorded from 300 to 1200 nm on a UV–visible spectrophotometer (Hitachi UV3100). FTIR spectra were performed on a Bruker EQUINOX55. X-ray photoelectron spectroscopy (XPS) spectra were obtained at room temperature on an ESCA 300 spectrometer employing Mg Kα radiation. All the spectra were energy-referenced to the C(1s) photoionization peak, to which was assigned a binding energy of 285.0 eV. The conductivity of the compressed pellets at room temperature was measured by four-probe method using a Keithley 196 System DMM Digital Multimeter and an Advantest R1642 programmable dc voltage/current generator as the current source.

3. Results and discussion

3.1. Micro/nanostructured morphology and related formation mechanism

It is found that morphology of PANI-MA is strongly affected by the MA/An ratios. As shown in Fig. 1, the nanofibers (~160 nm in diameter) or nanotubes (~145 nm in diameter) are observed (Fig. 1a–d) when the MA/An ratio is 0.01 and 0.05, respectively. When the MA/An ratio increased to 0.3 and 1.5, on the other hand, hollow microspheres (~3 μm in diameter) (Fig. 1e and f) are observed except for nanotubes or nanofibers, resulting in co-existence of microspheres and nanofibers or nanotubes. Those results indicate variation of the MA/An ratios leads to change in morphology of the PANI-MA.

According to our previous report [26], the micelles composed of MA are formed in the reaction solution due to its hydrophilic –MoOOH group of MA that act as the “soft-templates” in the formation of PANI-MA micro/nanostructures. Our previous measurements on Freeze-fracture Electron Micrographs-TEM (FFEM-TEM) [33] also suggested that the spherical micelles are formed, and those spherical micelles can be aggregated to form cylindrical micelles, depending on the reaction conditions, especially the molar ratio of dopant to aniline. In addition, aniline can be diffused into the micelles to form aniline filled micelles. At a low MA/An ratio, the cylindrical micelle filled with or without aniline might be regarded as a “soft-template” in forming the PANI-MA nanotubes or nanofibers. This is consistent with our observations as shown in Fig. 1a–d. At a high MA/An ratio, on the other hand, hydrogen bonding of –OH group of MA with amine group of PANI may be a driving force to form hollow microspheres [23,34], resulting in co-existence of hollow spheres and nanotubes or nanofibers.

In order to further understand the self-assembly process of those micro/nanostructures, the effect of existence of MA and the polymerization time on pH value of the reaction solution and morphology of the as-synthesized micro/nanostructures was measured. In the absence of added MA, nanotubes or microspheres were not observed under the synthesis conditions used in this experiment, indicating MA plays an important role in the formation of the self-assembled micro/nanostructures. It is found that the pH value of the reaction solution decreases with the increase of the polymerization time due to sulfuric acid (H_2SO_4) produced during the polymerization of aniline monomer with APS as the oxidant [3,35] as shown in

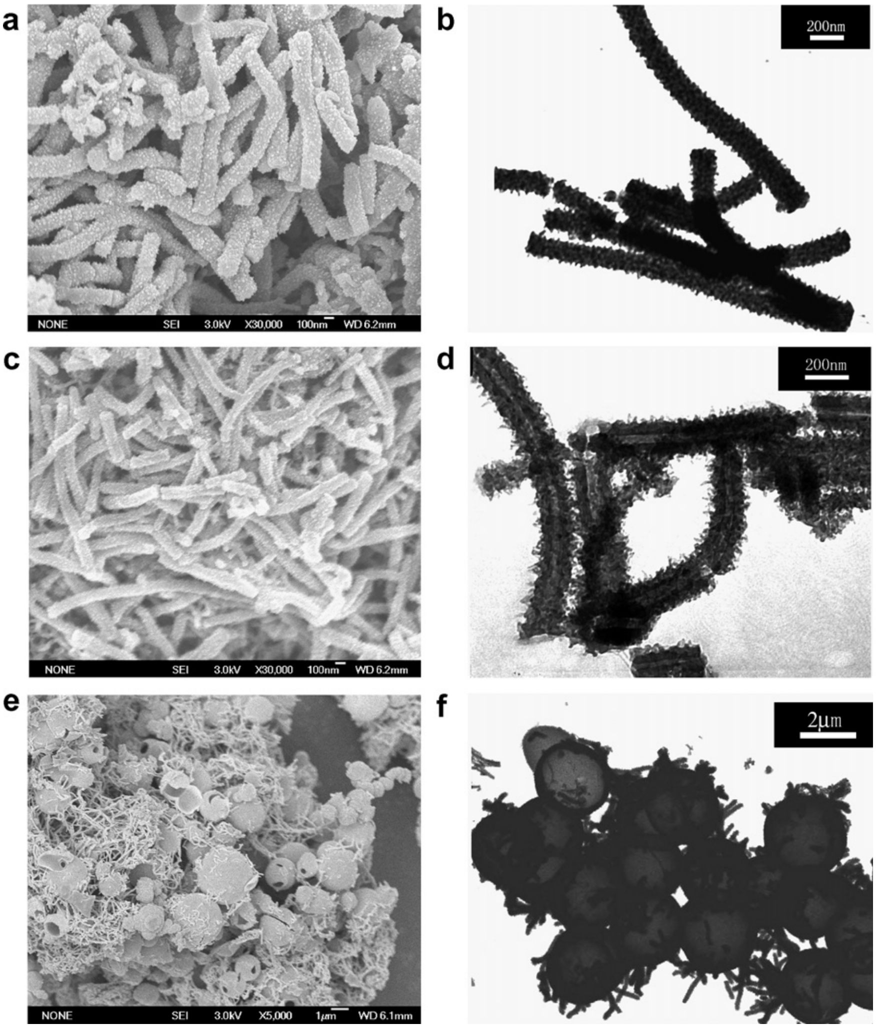


Fig. 1. SEM and TEM images of PANI-MA prepared at different MA/An ratio: (a) and (b) 0.01, (c) and (d) 0.05; (e) and (f) 0.3.

Fig. 2. However, drop down speed of the pH value with time is affected by with and without MA as the dopant. In the case of no MA, for instance, the pH value decreased very quickly with the polymerization time, which maybe unfavorable to form nanostructure. The initial pH value of the reaction solution with and without MA is measured to be 6.5 and 6.9, respectively. However, the final pH value is the same in all the experiments, indicating the pH value of the reaction solution is mainly controlled by the sulfuric acid produced from APS. It needs to be noted that the variation of pH value with polymerization time strongly depends on the MA/An ratio during the middle range of polymerization (e.g. 2–10 h). With the increase of polymerization time, the morphology of the PANI-MA changed from microspheres to co-existence of microspheres and nanofibers as shown in Fig. 3. Under the condition of co-existence of microspheres and nanofibers, it is found that the formation of the nanotubers or nanofibers are behind the microspheres, for instance, the microspheres were formed after polymerization for 2 h whereas the nanofibers were not appeared until seven hours reaction. This indicates that spherical micelles formed during the initial stage are dominated and served as the “soft-templates”

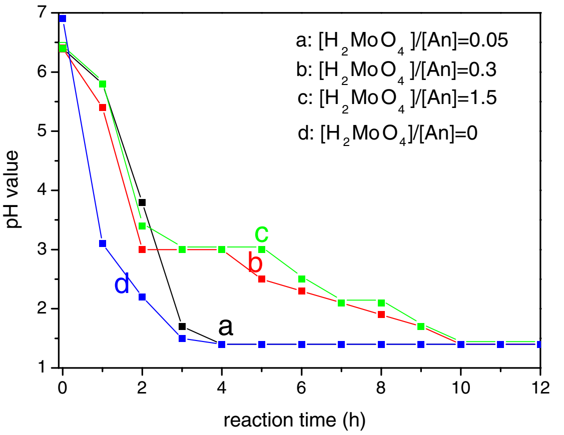
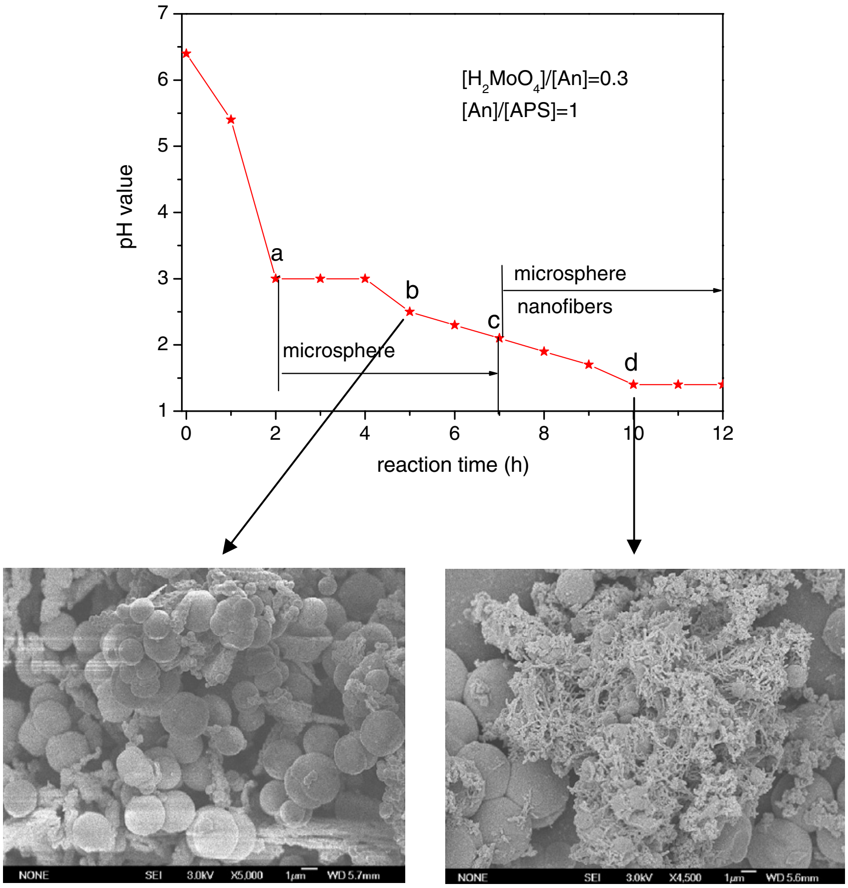


Fig. 2. Effect of polymerization time on the pH value of solution at different MA/An ratio: (a) 0.05, (b) 0.3, (c) 1.5 and (d) 0.



b : t=5h, pH=2.5

d: t=10h, pH=1.4

Fig. 3. SEM images of as-synthesized PANI-MA micro/nanostructures at the MA/An ratio of 0.3 for (a) pH 2.5 for 5 h, and (b) pH 1.4 for 10 h.

in the formation of microspheres during initial polymerization stage. With the increase of polymerization time, those spherical micelles aggregate to form cylindrical or junction micelles through an aggregation process that are served as the "soft-templates" in the formation of nanotubes or microspheres, depending on the MA/An ratios. Above-descriptions suggest that morphology of the "soft-templates" is different, depending on the MA/An ratios and polymerization time. Therefore, it is reasonable to understand why morphology of the PANI-MA micro/nanostructures is affected by the MA/An ratios and polymerization times.

3.2. Structural characterizations and electrical properties

The molecular structure of the micro/nanostructures was characterized by UV–visible absorption, FTIR and XPS spectra. Fig. 4 is UV–visible absorption spectra of the micro/nanostructures dissolved in *m*-cresol that showed the two bands at 400–430 nm and longer than 700 nm are observed. Both of peaks are identical to the emeraldine salt form of PANI, the first one is related to the partial protonation of PANI, while the second broad peak with a long tail is assigned as the polaron band [36]. However, the polaron band shifted to 700 nm from 825 nm as the MA/An ratio increasing from 0.05 to 1.5, as shown in Fig. 4.

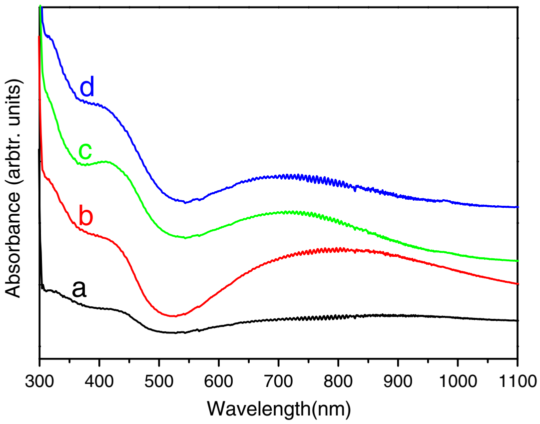


Fig. 4. UV–visible spectra of the PANI-MA dissolved in *m*-cresol at different MA/An ratio: (a) 0.05, (b) 0.3 (c) 1 and (d) 1.5.

The FTIR spectra of PANI micro/nanostructures obtained in the different molar ratio of MA to An were measured as

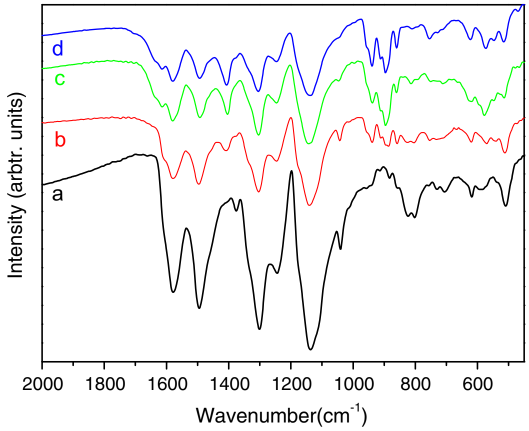


Fig. 5. FTIR spectra of the PANI-MA prepared at different MA/An ratio: (a) 0.05, (b) 0.3, (c) 1 and (d) 1.5.

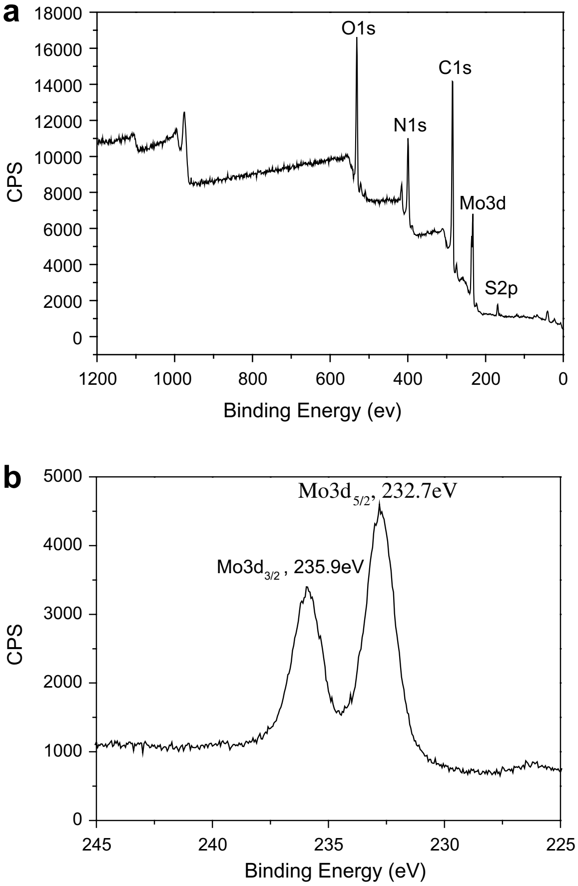


Fig. 7. XPS spectra of PANI-MA nanofibers: (a) wide scan and (b) narrow scan of Mo^{VI}.

shown in Fig. 5. The stretching vibration of the quinone ring at 1578 cm^{-1} and of the benzene ring at 1496 cm^{-1}, as well as the C–H stretching vibration of aromatic conjugation at 1303 cm^{-1} and 1140 cm^{-1} were observed. Especially, the bands at 804 and 423 cm^{-1} related to the C–H deformation, the band at 570 cm^{-1} attributed to the amine deformation as well as the band at 512 cm^{-1} ascribed to the C–N–C torsion were also observed. These results indicated that the polymer chains of the micro/nanostructures are identical to the conventional PANI [27,37]. Meanwhile, the bands at 938, 891, 865, 754, 620, and 570 cm^{-1} relating to the stretching vibrations and bendings of MA appeared [29], indicating PANI is doped by MA as the dopant. Moreover, the bands at 938 and 891 cm^{-1} corresponding to the stretching of Mo=O double bond become stronger with the increase of MA/An ratio, which means more and more MA doped into the main chain of PANI. The conductivity measured by four-probe-method increased from 3.15×10^{-3} S cm^{-1} to 2.8×10^{-1} S cm^{-1} when the MA/An ratio changed from 0 to 1.5 due to the increase of the doping level from 12.3% to 29.9% (XPS result) as increasing the MA/An ratio (Fig. 6), which is consistent with the result of FTIR (Fig. 5) and further confirm that the PANI is doped by MA. The results obtained on X-ray photoelectron spectroscopy (XPS) also suggested that the existence of Mo^{VI} with a binding energy of Mo3d$_{5/2}$ (232.7 eV) in the micro/nanostructures (Fig. 7) [38]. That means Mo did not take redox reaction and keep the original style in the PANI micro/nanostructures.

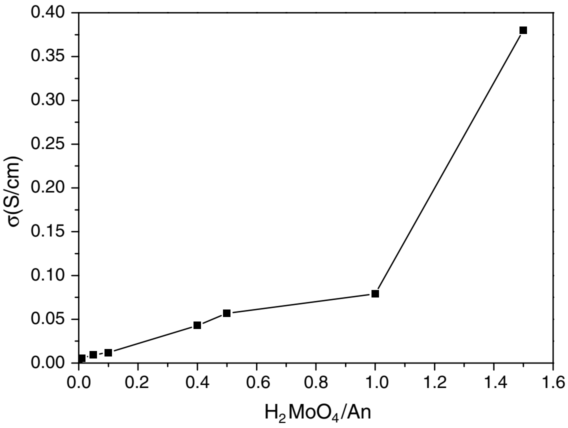


Fig. 6. Dependence of the conductivity of PANI-MA with the MA/An ratio.

4. Conclusions

This paper presented an excellent example that a change in morphology of PANI-MA from nanofibers or nanotubes to co-existence of hollow spheres and nanofibers or nanotubes could be realized by only changing the molar ratio of MA to aniline through a self-assembly process. With the increase of polymerization time, the pH value of the reaction solution not only decreased due to sulfuric acid produced from APS, but also accompanied a variation of the morphology from spheres to nanofibers because of the existence of MA. All above-described observations could be interpreted by spherical and cylindrical micelles made in MA acting as the “soft-templates” in the formation of the PANI-MA micro/nanostructures.

References

[1] Mann S. The chemistry of form. Angew Chem 2000;39(19):3392–406.

[2] Yang H, Coombs N, Ozin GA. Morphogenesis of shapes and surface patterns in mesoporous silica. Nature 1997;386(6626):692–5.

[3] MacDiarmid AG. "Synthetic metals": a novel role for organic polymers (Nobel Lecture). Angew Chem, Int Ed 2001;40(14):2581–90.

[4] Martin CR. Nanomaterials: a membrane-based synthetic approach. Science 1994;266(5193):1961–6.

[5] Norris ID, Shaker MM, Ko FK, MacDiarmid AG. Electrostatic fabrication of ultrafine conducting fibers: polyaniline/polyethylene oxide blends. Synth Met 2000;114(2):109–14.

[6] Reneker DH, Chun I. Nanometer diameter fibers of polymer, produced by electrospinning. Nanotechnology 1996;7(3):216–23.

[7] Wallace GG, Innis PC. Inherently conducting polymer nanostructures. J Nanosci Nanotechnol 2002;2(5):441–51.

[8] Huang J, Kaner RB. Nanostructures: nanofiber formation in the chemical polymerization of aniline: a mechanistic study. Angew Chem, Int Ed 2004;43(43):5817–21.

[9] Kosonen H, Ruokolainen J, Knaapila M, Torkkeli M, Jokela K, Serimaa R, et al. Nanoscale conducting cylinders based on self-organization of hydrogen-bonded polyaniline supramolecules. Macromolecules 2000;33(23):8671–5.

[10] Kim B-J, Oh S-G, Han M-G, Im S-S. Preparation of polyaniline nanoparticles in micellar solutions as polymerization medium. Langmuir 2000;16(14):5841–5.

[11] Wei Z, Wan M. Hollow microspheres of polyaniline synthesized with an aniline emulsion template. Adv Mater 2002;14(18):1314–7.

[12] Huang J, Wan M. Temperature and pressure dependence of conductivity of polyaniline synthesized by in-situ doping polymerization in the presence of organic function acid as dopants. Solid State Commun 1998;108(4):255–9.

[13] Chiou N-R, Lee LJ, Epstein AJ. Self-assembled polyaniline nanofibers/nanotubes. Chem Mater 2007;19(15):3589–91.

[14] Chiou N-R, Epstein AJ. Polyaniline nanofibers prepared by dilute polymerization. Adv Mater 2005;17(13):1679–83.

[15] Zhou C, Han J, Song G, Guo R. Polyaniline hierarchical structures synthesized in aqueous solution: micromats of nanofibers. Macromolecules 2007;40(20):7075–8.

[16] Trchova M, Sedenkova I, Konyushenko EN, Stejskal J, Holler P, Ciric-Marjanovic G. Evolution of polyaniline nanotubes: the oxidation of aniline in water. J Phys Chem B 2006;110(19):9461–8.

[17] Konyushenko EN, Stejskal J, Sedenkova I, Trchova M, Sapurina I, Cieslar M, et al. Polyaniline nanotubes: conditions of formation. Polym Int 2006;55(1):31–9.

[18] Zhang L, Peng H, Zujovic ZD, Kilmartin PA, Travas-Sejdic J. Characterization of polyaniline nanotubes formed in the presence of amino acids. Macromol Chem Phys 2007;208(11):1210–7.

[19] Zhang L, Peng H, Hsu CF, Kilmartin PA, Travas-Sejdic J. Self-assembled polyaniline nanotubes grown from a polymeric acid solution. Nanotechnology 2007;18(11):1156071115607/1–76115607/6.

[20] Zhang L, Peng H, Kilmartin PA, Soeller C, Travas-Sejdic J. Polymeric acid doped polyaniline nanotubes for oligonucleotide sensors. Electroanalysis 2007;19(7–8):870–5.

[21] Zhang Z, Wei Z, Wan M. Nanostructures of polyaniline doped with inorganic acids. Macromolecules 2002;35(15):5937–42.

[22] Zhang Z, Wei Z, Zhang L, Wan M. Polyaniline nanotubes and their dendrites doped with different naphthalene sulfonic acids. Acta Mater 2005;53(5):1373–9.

[23] Zhang L, Long Y, Chen Z, Wan M. The effect of hydrogen bonding on self-assembled polyaniline nanostructures. Adv Funct Mater 2004;14(7):693–8.

[24] Qiu H, Wan M, Matthews B, Dai L. Conducting polyaniline nanotubes by template-free polymerization. Macromolecules 2001;34(4):675–7.

[25] Wei Z, Wan M, Lin T, Dai L. Polyaniline nanotubes doped with sulfonated carbon nanotubes made via a self-assembly process. Adv Mater 2003;15(2):136–9.

[26] Wei Z, Zhang Z, Wan M. Formation mechanism of self-assembled polyaniline micro/nanotubes. Langmuir 2002;18(3):917–21.

[27] Chiang JC, MacDiarmid AG. 'Polyaniline': protonic acid doping of the emeraldine form to the metallic regime. Synth Met 1986;13(1–3):193–205.

[28] Moreno-Castilla C, Perez-Cadenas AF, Maldonado-Hodar FJ, Carrasco-Marin F, Fierro JLG. Influence of carbon–oxygen surface complexes on the surface acidity of tungsten oxide catalysts supported on activated carbons. Carbon 2003;41(6):1157–67.

[29] Haber J, Lalik E. Catalytic properties of MoO3 revisited. Catal Today 1997;33(1–3):119–37.

[30] Otaki JM. Color-pattern modifications of butterfly wings induced by transfusion and oxyanions. J Insect Physiol 1998;44(12):1181–90.

[31] Zhao S, Petrus L, Serianni AS. 1-Deoxy-D-xylulose: synthesis based on molybdate-catalyzed rearrangement of a branched-chain aldotetrose. Org Lett 2001;3(24):3819–22.

[32] Gong J, Su ZM, Dai ZM, Wang RS, Qu LY. Syntheses, characterization and conductivity of polyaniline doped with H5SiM11VO40(M = Mo,W). Synth Met 1999;101(1–3):751.

[33] Wei Z, Zhang L, Yu M, Yang Y, Wan M. Self-assembling sub-micrometer-sized tube junctions and dendrites of conducting polymers. Adv Mater 2003;15(16):1382–5.

[34] Zhang L, Wan M. Self-assembly of polyaniline-from nanotubes to hollow microspheres. Adv Funct Mater 2003;13(10):815–20.

[35] Mattoso LHC, MacDiarmid AG, Epstein AJ. Controlled synthesis of high molecular weight polyaniline and poly(*o*-methoxyaniline). Synth Met 1994;68(1):1–11.

[36] Zhang L, Wan M. Synthesis and characterization of self-assembled polyaniline nanotubes doped with D-10-camphorsulfonic acid. Nanotechnology 2002;13(6):750–5.

[37] MacDiarmid AG, Chiang JC, Richter AF, Epstein AJ. Polyaniline: a new concept in conducting polymers. Synth Met 1987;18(1–3):285–90.

[38] Guenther S, Marsi M, Kolmakov A, Kiskinova M, Noeske M, Taglauer E, et al. Photoelectron spectromicroscopic study of the spreading behavior of MoO3 on titania and alumina model supports. J Phys Chem B 1997;101(48):10004–11.