Chinese Journal of Polymer Science Vol. 33, No. 3, (2015), 416–421

Chinese Journal of Polymer Science
© Chinese Chemical Society
Institute of Chemistry, CAS
Springer-Verlag Berlin Heidelberg 2015

Morphological and Dimensional Control *via* Assembly of Polyaniline Crystals

Yu-lun Tao*, Jin-hua Yao, Yuan-rui Wang, Guo-xing Ding, Guo-jun Cheng, Ji-nian Yang, Zhou-feng Wang, Yan-li Wang and Hong-yan Zhang
Department of Materials Science and Engineering, Anhui University of Science and Technology, Huainan 232001, China

Abstract A facile and general route to a new generation of polyaniline (PANI)-citric acid (CA) crystals such as 2D nanoplates, 2D nanosheets and 3D microrods self-assembled by the π-π stacking interaction is reported. Dramatic, 3D rectangular shaped microrods and 2D nanosheets are single crystals indicated by SAED patterns and HRTEM images. Moreover, the method does not depend on any specific equipment or heating, cooling and complex procedures. The novel polyaniline crystals will be useful for next generation organic electronics such as nano-transistors.

Keywords: Self-assembly; Polyaniline; Crystals; 2D nanosheets; 3D microrods.

Electronic Supplementary Material Supplementary material is available in the online version of this article at http://dx.doi.org/10.1007/s10118-015-1593-3.

INTRODUCTION

Circuits based on organic semiconductors are being actively explored for flexible, transparent and low-cost electronic applications[1–5]. One of important organic semiconductors-PANI currently dominates in many potential applications such as sensors[2], capacitors[3], organic electrodes[4] and electronic devices[5]. However, ordinary PANI has been described as disordered metals, which impeded metallic transport performance and stability of many devices[2]. Therefore, higher ordered arrangement of PANI is needed in both scientific and practical applications.

How to obtain high ordered PANI is a difficult problem. By using traditional approaches, including crystallization from a very dilute solution[4] or from the melt state by slow cooling process[5], single crystal can't be obtained, Therefore, great efforts have been made for the improvement of PANI crystallinity in recent years[6–12]. Deng *et al.*[13] observed PANI microspheres self-assembled by highly crystallized nanorods. Wu *et al.*[14] reported highly oriented polyaniline flake and fiber arrays self-assembled without any templates or surfactants. Wei *et al.*[1] prepared hexagonal 2D PANI nanoplates with anisotropic electrical transport. We[9, 15] have reported solution-induced crystallization methods for growing 3D hexagonal crystals of PANI for months.

Now, we explore a simple and fast method to create 3D single-crystal microrods of PANI. High-quality PANI crystals are easily obtained in aq/org mixtures, such as cyclohexane/water, at room temperature under normal pressure, which is especially suitable for scalable producing bulk quantities of high-quality and low-cost crystals. Moreover, a set of doping control experiments were carried out to find out the key factor to determine the morphology and crystallinity of PANI crystals. The idea of preparing crystals of PANI is very interesting and should potentially lead to significant advancements in organic electronics.

---

* Corresponding author: Yu-lun Tao (陶玉仑), E-mail: xxxxxx9067@163.com

Received May 23, 2014; Revised August 31, 2014; Accepted September 4, 2014
doi: 10.1007/s10118-015-1593-3

EXPERIMENTAL

Materials

All of the reagents such as aniline, ammonium persulfate, citric acid (CA) are of analytical grade and were used in experiments without further purification. All the aqueous solutions used throughout experiments were prepared using deionized water.

Preparation of PANI Crystals

A typical experimental procedure was as follows: The PANI- citric acid (CA) was synthesized by using 0.5 g aniline, 0.5 g ammonium persulfate (APS) and 0.1 g CA in cyclohexane/water mixture solution at room temperature. As-prepared poyaniline-CA was supersonic cleaned and washed with ethanol several times to remove the reaction byproducts and exceeding CA. To understand the influence of doping on crystallization of PANI, a set of doping control experiments were performed with different CA contents, while the other synthetic parameters were kept constant.

Characterization

For SEM studies, we drop-cast the sample solution on the silicon substrates followed by drying 12 h at 60 °C. Field emission scanning electron microscopy (FESEM) measurements were taken with a Hitachi S-4800 SEM. A Bruker X-Flash 5.0 detector was used to acquire EDS spectra. HRTEM measurements were taken by FEI Tecnai G2 S-TWIN F20 200 kV. XRD patterns were performed on a XD-6000 X-ray diffractometer using a Cu Kα radiation source (λ = 0.15418 nm). FTIR was measured with a Nicolet-380 FTIR spectrophotometer at fresh surfaces at room temperature (25 °C). Total C, N, O, S and H were determined with an automatic elemental analyser (Vario EL, Elementar Analysensysteme GmbH). UV-Vis absorption spectra of the samples dispersed in distilled water through ultrasonic irradiation were obtained with U-4100 UV spectrophotometer in the range of 200−850 nm.

RESULTS AND DISCUSSION

Figures 1(a) and 1(b) show 2D nanosheets doping with 0.1 g CA. 2D layered nanosheets can orderly self-assembled by π-π stacked (Fig. 1b). The thickness of the nanosheets is less than 100 nm. With the increase of CA to 0.5 g, 3D rectangular shaped microrods with the length about 5−10 μm appear in Figs. 1(c)−1(e). EDS spectrum of 3D microrods in Fig. 1(f) shows the peaks of C, N, O and S elements, where C and N elements originate from PANI molecules and oxygen element is contributed by the surface adsorbed oxygen or water on the PANI. S elements (2.1%) may come from ammonium persulfate.

Figure 2(a) shows layered nanosheets. The HRTEM image indicates crystal structures with several clear grain boundaries-white lines (Fig. 2b). Figure 2(c) shows a microrod with SAED pattern (inset in Fig. 2c), indicating that these PANI-CA microrods have a single crystal structure. The sharp reflections corresponding to a *d* spacing of ~0.35 nm possibly originate from the arrangement of CA molecules setting between neighboring PANI chains[13]. Figure 2(d) shows a clear HRTEM image, where the high order array of PANI molecules is along the *c*-axis as well. The polymer chains are very straight with a *d*-spacing of 0.35 nm fitting the results of SAED patterns well.

To further study doping effects on the crystallization of PANI, a set of doping control experiments is carried out with different doping contents of CA such as 1.0, 1.5, 2.0 and 2.5 g, respectively. With the increase of CA to 1.0 g, the morphology of PANI becomes irregular aggregation as shown in Figs. 3(a) and 3(b). Only a few layered structures exist in the aggregation. Figures 3(c) and 3(d) show prismatic nanoplates arranged disorderly. After heavy doping of CA (2.0 g and 2.5 g), nanospheres form with the diameter of less than 200 nm (Figs. 3e−3h). The inset in Fig. 3(h) shows TEM images of nanospheres, which are hollow spheres.

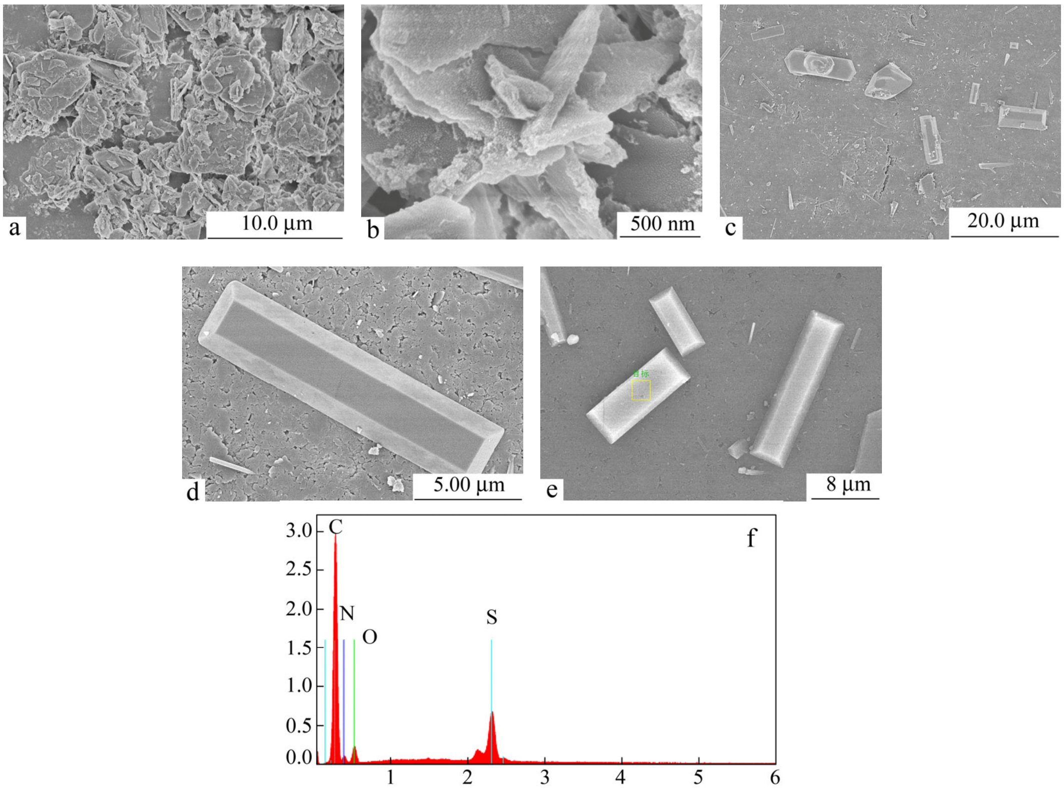

Fig. 1 SEM images of PANI crystals: (a, b) doped with 0.1 g CA and (c–e) doped with 0.5 g CA; (f) EDS spectrum of 3D microrods

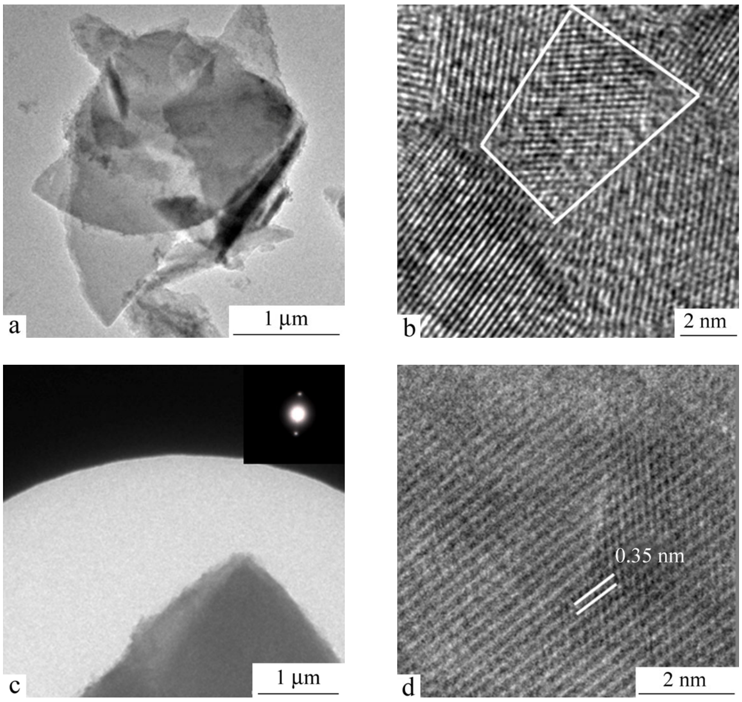

Fig. 2 TEM images and HRTEM of 2D nanosheets and 3D microrods: (a) TEM image of 2D nanosheets, (b) HRTEM image of the nanosheets, (c) TEM image and SAED pattern of 3D microrods and (d) HRTEM image of the microrods

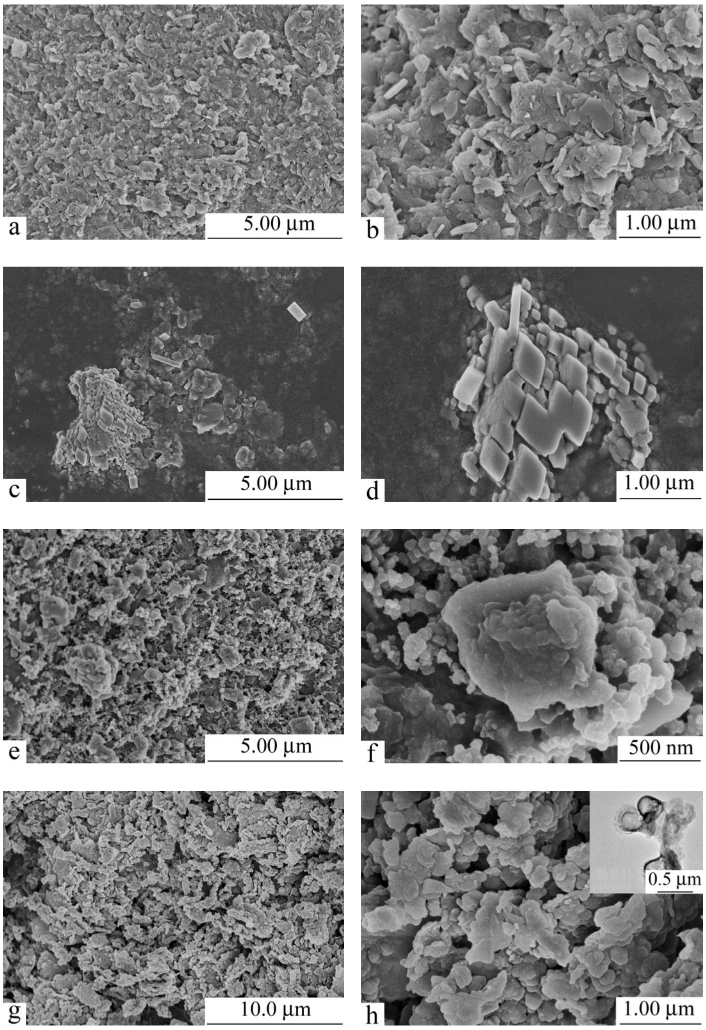

Fig. 3 SEM images of PANI crystals doped with: (a, b) 1.0 g CA, (c, d) 1.5 g CA, (e, f) 2.0 g CA and (g, h) 2.5 g CA

The great changes of the crystal structure are seen in wide-angle X-ray diffraction (XRD) studies. Figure 4(A) shows a series of XRD patterns for confirming doping effects on PANI crystallization. It is worthy to mention that high crystalline structures have a similar strong peak at $2\theta = 6.64°$, 19.23° and 25.86° when a small amount of doping acid such as 0.1 and 0.5 g CA is employed (Figs. 4A a–b). However, amorphous PANI appeared with increase of content of CA from 1.0 to 2.5 g CA (Figs. 4A c–f). Such observations are consistent with the physical appearances of the nanostructures.

Crystallinity of PANI samples with different doping contents of CA is presented in Fig. 4(B). It can be seen that nanosheets and microrods doped with low levels have higher crystallinity (above 80%) than that with high levels of more than 0.5 g CA. In fact, low doping level of CA induces PANI to crystallize. Interestingly, the highest doping level also increases the PANI crystallization but the crystallinty is relatively low.

From the above discussion, doping with CA is an effective way to induce crystallization of PANI. Especially in proper low doping level, PANI crystallized and then self-assembled to form 3D microrods. PANI microrods self-assemble by π-π stacking because π-π stacking predominates in many interactions between CA and PANI chains such as H-bonds. During the interesting stages, their irregular polymer chains could easily stretch, aggregate and crystallize into coded nanorods with highly ordered polymer chains, uniform shape and morphology by intermolecular noncovalent bonding, then these nanorods self-assembled into 3D microrods along the optimal dynamic path[15]. In a word, doping level has strong relationship to the crystallization and self-assembly of PANI.

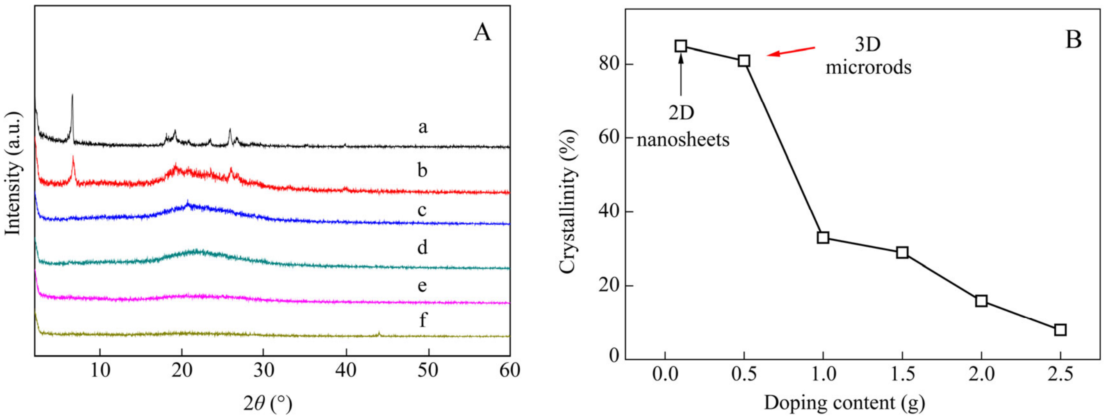

Fig. 4 (A) XRD patterns of PANI samples doped with (a) 0.1, (b) 0.5, (c) 1.0, (d) 1.5, (e) 2.0 and (f) 2.5 g CA, respectively; (B) Crystallinity of the above PANI samples, respectively
The crystallinity of above samples was calculated by using Jade + software (MDI, Livermore, CA)[10].

Table 1. Elemental analysis of 3D microrods

Element	C	N	H	S	O
Content (wt%)	64.0	11.3	5.9	1.5	17.3

Elemental analysis in Table 1 shows N, C, H, S and O elements. The mole ratio of C/N is about 6, which is close to the theoretical value[12]. It is proven that the crystals are composed of PANI. The S element (1.5%) is originated from ammonium persulfate. The results fit the analysis of EDS spectrum well.

The FTIR spectra of PANI nanosheets and microrods are shown in Fig. S1. The two samples of different doping levels have similar characteristic peaks at 1500 and 1635 cm^{-1} which can be assigned to the stretching vibration of benzenoid rings and quinoid rings[3], respectively. It is clear that microrods have the highest intensity rate of benzenoid ring/quinoid ring. The band observed at 1300 cm^{-1} corresponds to C—N stretch vibration of secondary aromatic amine. Combining with FTIR results, we concluded that the crystals are composed of PANI. Figure S2 shows UV-Vis spectra of PANI crystals including nanosheets and microrods, respectively. Interestingly, nanosheets and microrods have similar absorption peaks at 262 and 390 nm. The peak at 262 nm is due to the much shorter conjugation length of PANI crystals compared to that of tetraaniline crystals. A strong absorption at 390 nm is ascribed to the polaron-π^*.

CONCLUSIONS

The PANI crystals have been produced through a novel, simple one-step method in which bulk PANI self-crystallizes in a mixture solvent. PANI crystals including nanosheets and 3D microrods are obtained through the crystallization process without any specific equipment or heating, cooling and complex procedures. The variation of nanostructures could be useful for next generation organic electronics such as nano-transistors. The crystallization method will be readily scalable to produce bulk quantities of PANI crystals with high-quality and low-cost.

REFERENCES

1 Yan, Y., Wang, R., Qiu, X. and Wei, Z., J. Am. Chem. Soc., 2010, 132: 12006
2 Wang, Y., Tran, H.D., Liao, L., Duan, X. and Kaner, R.B., J. Am. Chem. Soc., 2010, 132: 10365

3 Murphy, A.R. and Fréchet, J.M., Chem. Rev., 2007, 107: 1066
4 Qiao, Y., Wei, Z., Risko, C., Li, H., Bredas, J.L., Xu, W. and Zhu, D., J. Mater. Chem., 2012, 22: 1313
5 Keller, A., Phys. Rev. Lett., 1957, 2: 1171
6 Tang, B.Z., Geng, Y., Li, B., Jing, X., Wang, X., Wang, F., Pakhomov, A.B. and Zhang, X.X., Chem. Mater., 1999, 11: 1581
7 Wessling, B., Hiesgen, R. and Meissner, D., Acta Polym., 1993, 44: 132
8 Huang, J. and Kaner, R.B., J. Am. Chem. Soc., 2003, 126: 851
9 Tao, Y., Shen, Y., Yang, L., Han, B., Huang, F. and Li, S., Nanoscale, 2012, 4: 3729
10 Huang, J. and Kaner, R.B., J. Am. Chem. Soc., 2003, 126: 851
11 Kohlman, R.S., Zibold, A., Tanner, D.B., Ihas, G.G., Ishiguro, T., Min, Y.G., MacDiarmid, A.G. and Epstein, A.J., Phys. Rev. Lett., 1997, 78: 3915
12 MacDiarmid, A.G. and Epstein, A., J. Synth. Met., 1995, 69: 85
13 Park, M., Sun, Q. and Deng, Y., Macromol. Rapid Commun., 2007, 28: 1237
14 Tang, Q., Wu, J., Sun, X., Li, Q., Lin, J. and Huang, M., Chem. Commun., 2009, 21: 66
15 Tao, Y. and Shen, Y., Chem. Commun., 2014, 50: 12757