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PHYSICAL CHEMISTRY OF NANOCLUSTERS AND NANOMATERIALS

A General Route to 2D Nanoleaves and Nanoplates of Polyaniline[1]

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Abstract—Novel 2D nanoleaves and nanoplates are synthesized by a facile and general method. A set of doping control experiments are carried out to show how PANI self-assemble to nanoleaves and nanoplates. Interestingly, the nanoleaves and nanorods have high crystallinity, according to their XRD patterns. The novel method will be readily scalable to produce polyaniline crystals with different morphologies with high quality and low cost. The polymer semiconductor crystals could be useful for next generation organic electronics such as nanotransistors.

Keywords: self-assembly, polyaniline, nanoleaves, nanoplates.

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INTRODUCTION

In the family of conducting polymers [1–5], PANI are expected to play an important role in practical applications such as sensors, capacitors, organic electrodes and electronic devices due to their low density, conductivity and chemical properties. The metallic transport performance and stability of many devices are governed by how molecules or polymer chains assemble in the solid state [1, 2]. However, general conducting polymers have been described as disordered semiconductor [6–14]. Therefore, the improvement of PANI crystallinity [15–18] is needed for its applications in electronic devices.

Here, we report a general route to create a series of PANI crystals including nanoleaves and nanoplates which are extremely hard to prepare by traditional methods. The method does not depend on any specific equipment or heating, cooling and complex procedures. High-quality PANI crystals are easily obtained in non-polar solvent/polar solvent, such as cyclohexane/water at room temperature under normal pressure, which is especially suitable for producing bulk quantities of high-quality and low-cost crystals. The idea of preparing crystals of PANI is very interesting and should potentially lead to significant advancements in polymer crystallization.

EXPERIMENTAL SECTION

All of the reagents including aniline, acetic acid and ammonium persulfate are of analytical grade. They were used in experiments without further purification. Double distilled water was used throughout the experiments to prepare the solutions.

A typical experimental procedure was as follows: The PANI-acetic acid was synthesized from 0.5 g of aniline and 0.1 g of acetic acid in cyclohexane/water mixture at room temperature. To understand the influence of doping on crystallization of PANI, a set of doping control experiments were performed with different acetic acid content, while the other synthetic parameters were kept constant.

For SEM studies, we drop-cast the sample solution on the silicon substrates followed by drying for 12 h at 60°C. Field emission scanning electron microscopy (FESEM) measurements were taken with a Hitachi S-3000N Scanning SEM and a FEI-Sirion200 Scanning SEM. XRD patterns were performed on a XD-6000 X-ray diffractometer using a CuK_α radiation source (λ = 1.5418 Å). The conductivity measurements were performed using JD-ST2253 four-line probe instrument at room temperature. FTIR spectra were measured with a Nicolet-380 FTIR spectra were 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 Analysen-systeme GmbH).

RESULTS AND DISCUSSION

Figures 1a, 1b, and 1d show that nanoleaves have the size about several micrometers after doping of 2.5 g acetic acid. The thickness of nanoleaves is about 600 nm (Fig. 1c). SAED patterns (inset in Fig. 1d) indicate that these PANI nanoleaves have a crystal structure. The sharp reflections in the SAED pattern

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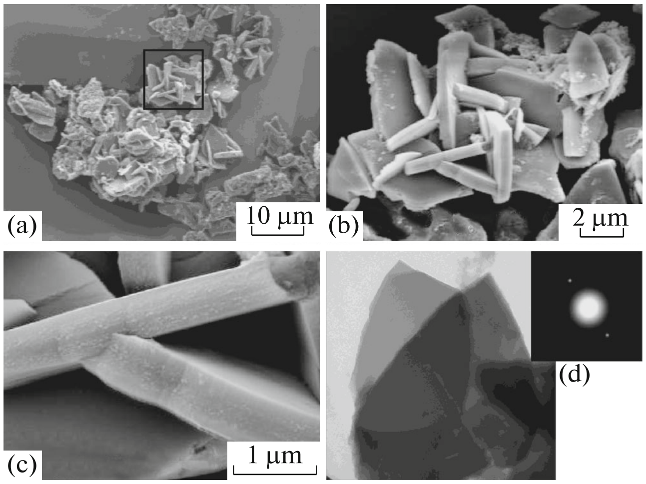


Fig. 1. (a–c) SEM images of PANI nanoleaves prepared in presence of 2.5 g acetic acid. (d) TEM images and SAED patterns of the PANI nanoleaves.

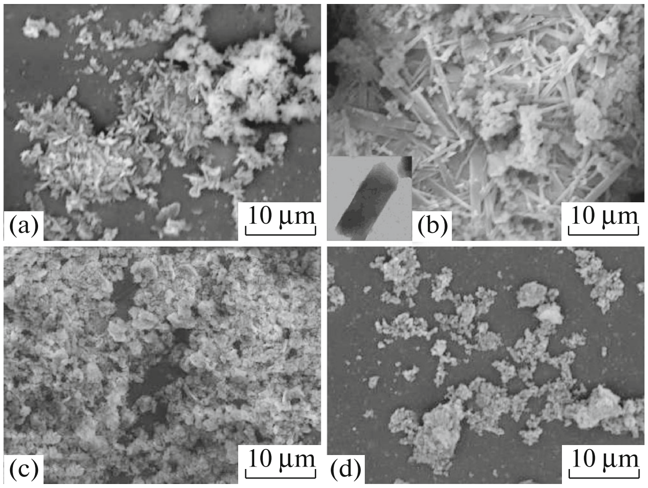


Fig. 2. SEM images of PANI crystals (a–d): prepared in presence of 0.025, 0.1, 1.5, and 5.0 g acetic acid, respectively.

corresponding to a *d* spacing of 13.7 Å could be assigned to the high-ordered reflections corresponding to the distance between PANI chains. Rather sharp reflections corresponding to a *d* spacing of ca. 3.5 Å may result from the π–π stacking of planar PANI molecules along the long axis of the nanoleaves.

To further study the preparation conditions on the crystallization of polyaniline, a set of experiments are carried out with different content of acetic acid such as 0.025, 0.1, 1.5, 2.5, and 5.0, respectively. When acetic acid quantity was 0.025 g, fractal morphology appears (Fig. 2a). With the increase of the content of acetic acid from 0.1 and 1.5 g, nanoplates and nanosheets form (Figs. 2b, 2c). Eventually, PANI prepared in presence of 5 g of acetic acid has disordered morphology (Fig. 2d).

Figure 3 shows a series of XRD patterns for confirming doping effects to PANI crystallization. It is worthy to mention that high crystalline structures have a similar strong peak at 2θ = 6.4°, 19.1°, and 25.8° when a amount of acid such as 0.025, 0.05, 0.1, and 1.5 g acetic acid is employed (Figs. 3a–3d). The three peaks (2θ = 6.4°, 19.1°, and 25.8°) correspond to *d* spacings of 13.7, 4.6, and 3.5 Å in the SAED patterns (inset in Fig. 1d), respectively. Note that, PANI prepared in presence of 2.5 g acetic acid is crystallized well as shown in Fig. 3e. Such observations are consistent with the physical appearances of the nanostructures. However, amorphous PANI appeared with increase of content of acetic acid to 5.0 g acetic acid (Fig. 3f).

From the above discussion, doping of acetic acid is an effective way to induce crystal of PANI. Especially in proper doping level, PANI crystallized and then self-assembled to form interesting leaf-like and plate-like nanostructure. However, high quantities of acetic acid (5.0 g) prevent PANI from crystallization and self-assembly because the hydrogen-bond interactions between acetic acid and PANI chains are stronger than that of π–π stacking in PANI. In a word, doping level has strong relationship to PANI crystallization.

Based on the evolution of the crystal morphologies, a hierarchical assembly mechanism is proposed (Scheme 1). First, small crystals with low stacking order are often the kinetic products of crystallization form disordered polyaniline chains. Then, crystal growth from the nucleation centers to form larger and more rigid 2D nanoplates around the nucleation centers. Subsequently, the 2D nanoplates can further self-assemble to well defined 2D nanoleaves under the guidance of high content of acetic acid (2.5 g). Alternatively, an apparently random stacking organization, possibly due to twin crystallization [16], can result in an as-grown flower-like morphology.

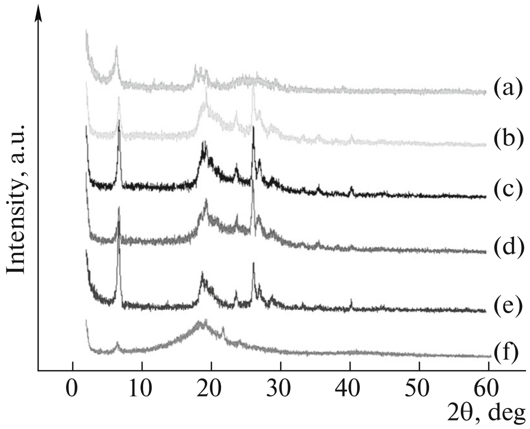


Fig. 3. XRD patterns of PANI crystals (a–f): prepared in presence of 0.025, 0.05, 0.1, 1.5, 2.5, and 5.0 g acetic acid, respectively.

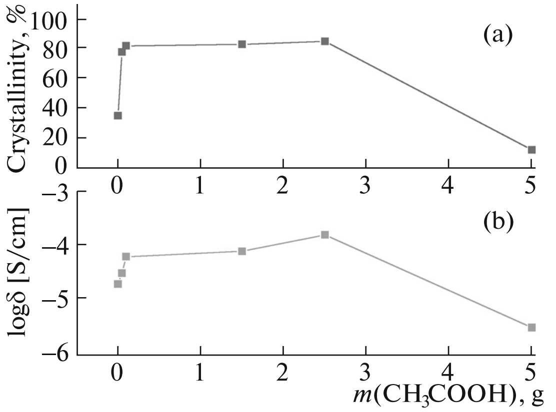


Fig. 4. (a) Crystallinity (b) conductivity of PANI crystals prepared in presence of 0.025, 0.05, 0.1, 1.5, 2.5, and 5.0 g acetic acid, respectively. The crystallinity of above samples was calculated by using Jade+ software (MDI, Livermore, CA) [14].

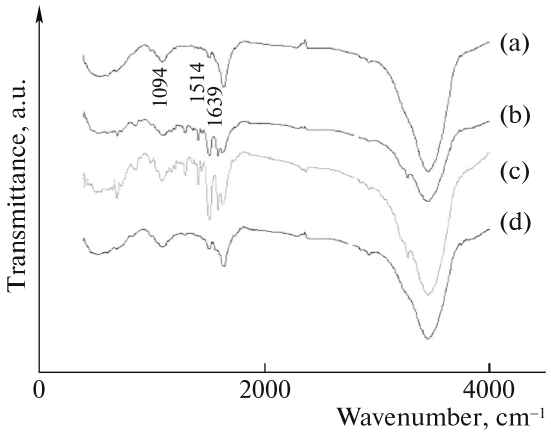
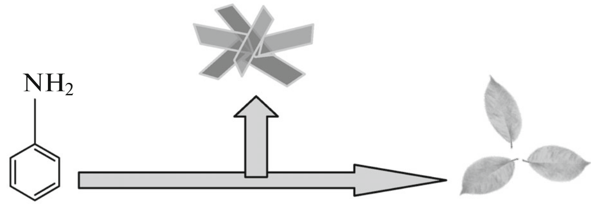


Fig. 5. FTIR of PANI crystals (a–d) prepared in presence of 0.025, 0.1, 2.5, and 5.0 g acetic acid, respectively.



Scheme 1. Illustration of the self-assembly mechanism believed responsible for the formation of 2D nanoleaves and nanoplates.

For deep understanding of the structure/conductivity relationship, crystallinity and conductivity of PANI crystals prepared in presence of different acetic acid quantities in Fig. 4, respectively. It can be seen in Fig. 4a that PANI crystals prepared in presence of relatively high quantities of acid have higher crystallinity (about 80%) than that in low level of less than 0.025 g acetic acid. In fact, proper doping level of acetic acid induces PANI crystallization and self-assembly. Interestingly, the highest acetic acid quantity (5 g) prevents the PANI from crystallization. Therefore, we can draw a conclusion that there is a strong correlation between higher crystallinity and doping effect of acetic acid.

Elemental analysis of nanoleaves

Element	N	C	H	S	O
Content, wt %	10.3	62.6	5.8	3.88	16.5

Dramatic, a similar trend shows in Figs. 4a and 4b. The material of high crystallinity with high doping level have the highest conductivity (about $10^{-3.5}$ S/cm) while amorphous PANI have the lowest conductivity ($10^{-5.5}$ S/cm). The phenomena agree well with previous work [14] that the higher conductivity is closely related to the higher crystallinity and doping level.

Elemental analysis in table shows N, C, H, S, and O content. The C/N mole ratio is about 7, which is close to the theoretical value [13]. It is proven that the crystals are composed of PANI. The sulfur originates from ammonium persulfate.

The FTIR spectrum of PANI crystals is shown in Fig. 5. The PANI crystals prepared in presence of different amounts of acetic acid have similar characteristic peaks at 1630 and 1500 cm^{-1}, which can be assigned to the stretching vibration of quinoid ring and benzenoid ring [3], respectively. It is clear that the peaks corresponding to quinoid ring is stronger than that of benzenoid ring when PANI crystals are doped with the lowest and the highest amounts of acetic acid (Figs. 5a, 5d). However, in the samples prepared with 2.5 g of acetic acid, benzenoid ring is dominant.

CONCLUSIONS

The PANI crystals have been produced through a novel, simple one-step method in which bulk PANI self-crystallize in mixture solvent. Single crystal nanoleaves are obtained without any specific equipment or heating, cooling and complex procedures. The variation of nanostructures could be useful for next generation organic electronics such as nanotransistors. This increase in conductivity of PANI is due to the better crystallinity and high doping level. The crystallization method will be readily scalable to produce bulk quantities of PANI crystals with high-quality and low-cost.

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