

Supporting Information Available:

Vapor-phase synthesis of crystalline polyaniline with dendritic morphology

Yu Gao, Zhen-hui Kang, Xia Li, Xiu-jun Cui, and Jian Gong

Experimental Section

Materials All used chemicals were of analytical grade. Aniline (Beijing Chemical Co.) was distilled twice under vacuum before use. APS was purchased from Beijing chemical factory as the oxidant without further purification. HCl and $\text{NH}_3\cdot\text{H}_2\text{O}$ were purchased from Beijing chemical factory without further purification.

Characterization SEM images were obtained using a XL-30 ESEM FEG scanning electron microscope operated at 20 KV with gold sputtered on samples, with EDX attached to SEM. Samples dispersed in ethanol were transferred to copper grids for TEM (Philips JEM-2010). The FT-IR spectra were characterized using an Alpha-Centauri 560 Fourier Transform Infrared Spectrophotometer (frequency range 4000 to 400 cm^{-1}) with a KBr pellet. The UV-Vis absorption spectra of the PANI samples dispersed in distilled water through ultrasonic irradiation were obtained with Beckman-DU-8B UV spectrophotometer in the range of 350 - 850 nm. X-ray diffraction was performed on a D/Max III C X-ray diffractometer using a $\text{Cu K}\alpha$ radiation source. Scans were made from 3 to 45 ° (2 θ) at a speed of 2 ° min^{-1} . Indicator of the Diffraction pattern was completed using POWDER X procedure. Conductivity of the PANI was measured using a standard four-point probe method. Disk shape samples were prepared from powders using 20 MPa pressure at room temperature.

Synthesis of PANI by conventional solution method 0.2 g of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ was dissolved in 8 mL of deionized water at room temperature. 0.08 mL of aniline was added to the solution at 0-5 °C. Then, 0.32 mL of 1 mol/L HCl was added to the mixture. The final solution was immobilized for 48 h at 0-5 °C. The precipitate was washed several times with deionized water, ethanol, and ethyl ether, and then dried under vacuum for 24 h at 40 °C.

Synthesis of PANI by vapor-phase polymerization method In this experiment, 1 g of aniline was laid in a sealed glass container. The volume of the glass container was about 5000 cm^3 . When the glass container was full of aniline vapor, a beaker that was covered with ordinary plastic membrane having many needled holes with average diameter about 0.1 cm and contained the mixture solution of 2 mol/L of HCl and 0.2 g of APS was then put into the glass container.

The purpose of the plastic membrane with many needed holes is for decreasing the polymerization rate of aniline and keeping slow contact and reaction of the reactant vapors. Then, the polymerization system was kept at 0-5 °C for 5-15 days. Finally, great deal crystals of PANI were found on the surface around the holes. The dark-green crystals of PANI were washed several times with distilled water and ethanol, respectively. Major experiments carried out in this work are summarized in Table S1. The schematic drawing of the experimental setup was shown in Scheme S1.

Table S1. Summary of the reaction conditions and product morphologies.

An (g)	HCl (mol/L)	APS (g)	Temperature (°C)	Morphologies
1	1	0.2	0-5	Well-dendritic morphology
1	2	0.2	0-5	Incomplete dendritic morphology
1	4	0.2	0-5	Dendrite-like morphology
1	2	0.2	25	No PANI

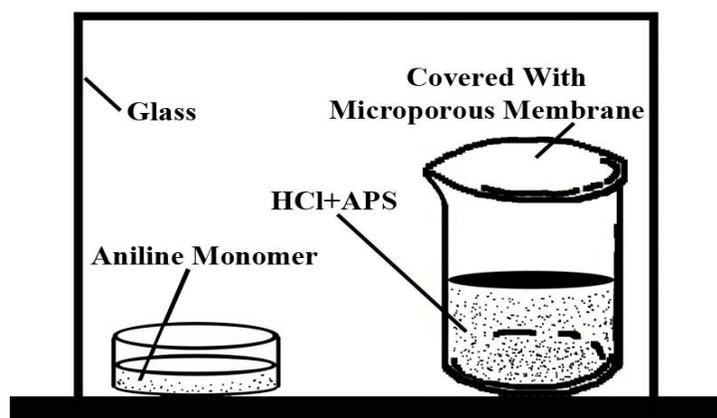


Fig. S1 Schematic drawing of the experimental installation for the synthesis of the crystalline PANI with dendritic morphology.

Table S2. Crystalline PANI with dendritic nano / micro structures: Angle, d Spacing, Intensity, and (hkl) Indexation

Angle (2 θ) (Experiment value)	Angle (2 θ) (Calculated values)	d, Å (Experiment value)	d, Å (Calculated values)	Intensity	(hkl)
9.960	9.970	8.8845	8.86500	W	(020)
10.575	10.448	8.3692	8.46036	W	(002)
15.180	15.211	5.8391	5.82024	W	(111)
15.660	15.699	5.66115	5.64024	W	(003)
18.305	18.297	4.8487	4.84496	VW	(032)
20.780	20.809	4.27645	4.26521	VS	(131)
21.764	21.764	4.0802	4.08029	S	(033)
23.060	22.938	3.85855	3.87403	W	(132)
24.110	24.335	3.69285	3.65464	VW	($\bar{1}$ 41)
25.175	25.093	3.53895	3.54600	VW	(050)
25.980	25.999	3.4311	3.42439	V	(133)
26.835	26.798	3.3237	3.32413	VW	(015)
27.565	27.571	3.2373	3.23267	V	(211)
28.615	28.635	3.12085	3.11491	VW	($\bar{1}$ 05)
31.780	31.703	2.81695	2.82012	S	(006)
32.700	32.755	2.73975	2.73193	VW	(232)
33.905	33.920	2.64505	2.64065	W	(241)
34.895	34.954	2.57225	2.56493	VW	(204)
35.520	35.455	2.5284	2.52979	VW	(242)

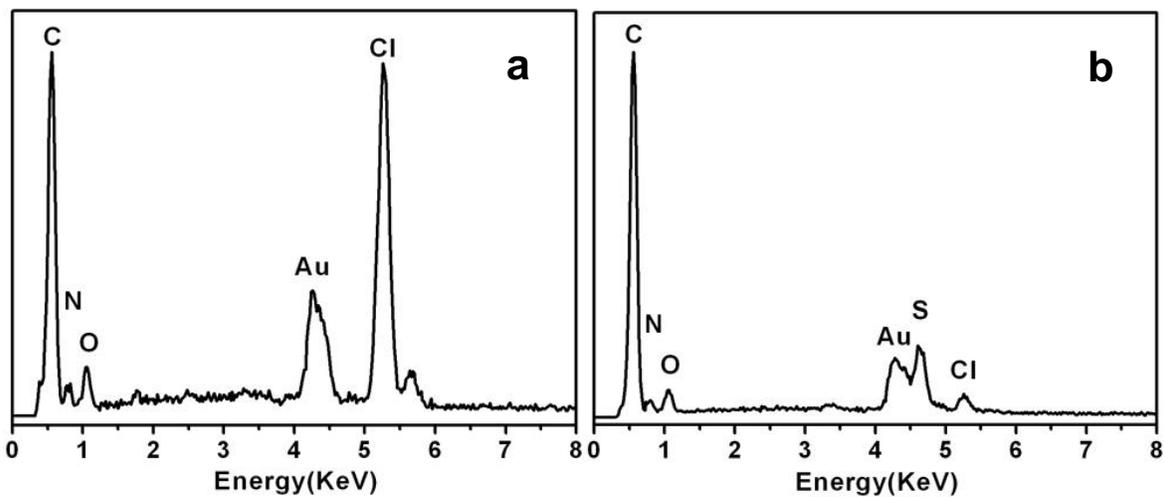


Fig. S2 EDX patterns of the PANI synthesized by the vapor-phase (a) and the conventional solution methods (b).

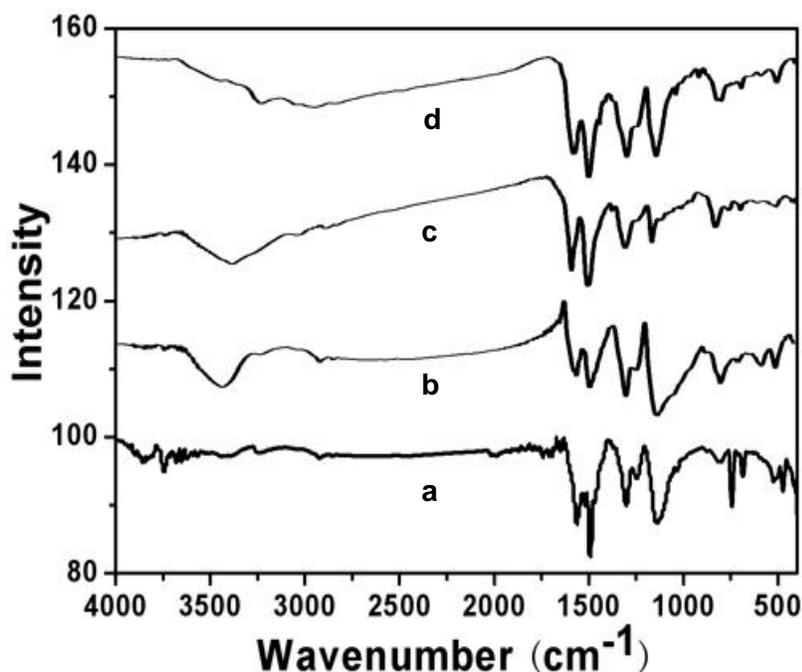


Fig. S3 FT-IR spectra of (a) the crystalline PANI synthesized by the vapor-phase polymerization method, (b) PANI synthesized by the conventional solution method, (c) dedoped crystalline PANI, and (d) redoped crystalline PANI.

The structure of crystalline PANI with dendritic morphology synthesized by the vapor-phase polymerization method is essentially identical to conventional emeraldine PANI. For the crystalline dendrite PANI, the C=C stretching vibration of the quinoid and benzenoid rings at 1562.59 and 1493.82 cm⁻¹, respectively, the C=N stretching mode at 1300 cm⁻¹, and the N=Q=N absorption peaks (Q represents the quinoid ring) at 1139.43 cm⁻¹, are all observed (curve a in Fig. S3), which is consistent with the PANI synthesized by the conventional solution method (curve b in Fig. S3).¹ When 1 mol/L of NH₃·H₂O is used to dedoped the crystalline PANI (pH = 10), the protonated states peak disappears and the peak at 1164.71 cm⁻¹ which is the PANI base characteristic peak appears (curve c in Fig. S3). As the pH of the solution is decreased from 10 to 4 (using 1 mol/L of HCl), because of the protonated effect, the PANI base is redoped and the peak at 1144.92 cm⁻¹ reappears again (curve d in Fig. S3).

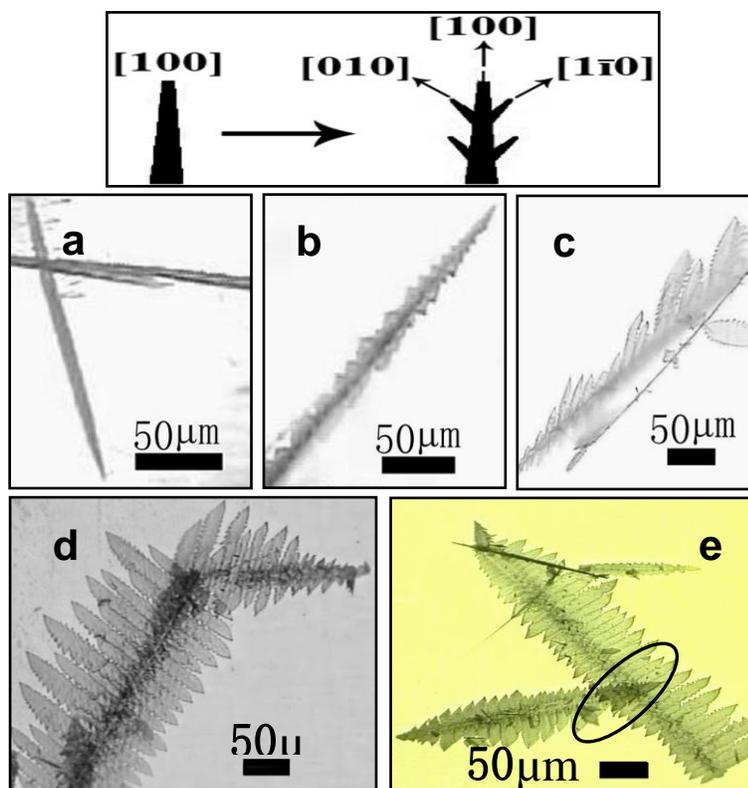


Fig. S4 Optical microscope images of the PANI crystal with dendritic morphology synthesized by the vapor-phase polymerization method for (a) 2 days, (b) 4 days, (c) 6 days, (d) and (e) 10 days. The top Figure is the schematic drawing of proposed growth process of the dendritic PANI crystal.

A possible formation process of the dendritic PANI crystal is proposed as following. One of the direction initiates faster growth along [100] than other directions. Subsequent growth along the other two equivalent directions leads to the formation of probably symmetric branches on both side. With further growth, the structure of dendrite is obtained. The growth process of the dendrites can be explained in top figure in Fig.S4. Meanwhile, optical microscope images which were taken under transillumination imaging mode of the PANI synthesized by the vapor-phase polymerization method for 2 days, 4 days, 6 days, 10 days are shown in Fig. S4 a-e, respectively. These images further support the formation process of the dendritic PANI crystal which proposed by us. Furthermore, we can see that the color of the polyaniline crystals is green and transparent, as shown in the ellipse (Fig. S4e).

Generally, the conductivity of the PANI strongly depends both on their degree of crystallinity and on the degree of order of the dopant anions.² In our experiment, four-probe pressed-pellet conductivity for the crystalline PANI is 0.2 S/cm, similar to that of PANI synthesized by the conventional solution method (0.05 S/cm). The conductivity of the crystalline PANI isn't much higher than that of the PANI synthesized by the conventional method, which indicates that well-crystallized PANI is possessed of lower conductivity because of the decrease of proton mobility caused by the presence of nonconjugated units.³

Ref.

1. Z. Zhang and M. X. Wan, *Adv. Mater.*, 2002, **14**, 1314.
2. W. Luzny and E. Banka, *Macromolecules*, 2000, **33**, 425.
3. H. Liu, X. B. Hu, J. Y. Wang and R. I. Boughton, *Macromolecules*, 2002, **35**, 9414.