

Supramolecular Self-Assembly of Three Dimensional Polyaniline and Polypyrrole Crystals

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Experimental Section

1 Preparation of polyaniline nanofibers and nanospheres

All of the reagents including aniline, D-camphorsulfonic acid (CSA), ammonium persulfate (APS), ethanol and cyclohexane are of analytical grade. They were used in experiments without further purification. Double distilled water was used throughout the experiment to prepare the solutions. The polyaniline-CSA nanofibers were synthesized according to the method reported before.[1] As-prepared polyaniline-CSA nanofibers were supersonic cleaned and washed with ethanol several times to remove the reaction byproducts and exceeding CSA. Finally, the products were added to 20 mL ethanol in a 50 mL beaker at room temperature. The mixture was shaken for a few seconds and then left undisturbed for 30 days. The green polyaniline (ES form) dispersion became blue one (EB form) because CSA is gradually removed owing to a stronger hydrogen bond interaction existing between CSA and ethanol.[2] Then, nanospheres formed. The blue precipitate was filtered and washed with ethanol for six times, then dried at air.

2 Preparation of 3D polyaniline crystals

The above dried precipitate was placed into a beaker containing cyclohexane at room temperature. To deep understand the morphology and crystallization transition of polyaniline after aged in cyclohexane for 30 d. The 3D crystals were prepared.

3 Preparation of polypyrrole nanofibers and nanoellipsoids

Preparation of polypyrrole nanofibers and nanospheres polypyrrole fibers polymerization process was as follows: we began with an AAO membrane with 60 to 70-nm-wide pores, onto one side of which we evaporated 1 μm of gold using an electron-beam (e-beam) evaporator. Ten minutes electropolymerization for preparing nanofibers was carried out by using constant current voltage supply at 1.0 V in pyrrol buffer solution (0.55 M aniline, 1.1 M LiClO_4). The polypyrrole nanofibers on an AAO template was immersed in 10 wt% HF solution for 10 min to remove the AAO template. The as-prepared nanofibers of polypyrrole was ultracentrifuged at 12,000 rpm for 6 min in a 5-mL plastic centrifuge tube and separated as sediment by remove the upper solution. After washed with water two times, sediment was then purified by using 4 mL of ethanol one time to eliminate organic and inorganic impurities. The nanofibers of polypyrrole were immersed in 5-mL plastic centrifuge tube with 3 mL of ethanol for 30 days. Then the first transition from nanofibers to nanospheres was accomplished.

4 Preparation of 3D polypyrrole crystals

Above dried precipitate was placed into a beaker containing cyclohexane at room temperature, and then left undisturbed for 30 days. The 3D crystals were prepared.

5 Material characterization

For SEM studies, we drop-cast the sample solution on the silicon substrates followed by drying 12 h at 60°C. Field 55 emission scanning electron microscopy (FESEM) measurements were taken with a Hitachi S4800 Scanning SEM. High resolution transmission electron microscopy (HRTEM) measurements were performed on JEM model 2100 electron microscopes (Japan Electron Co.) operated at an accelerating voltage at 200 kV. Digital Camera Canon PowerShot A1100 IS (Fuji Instruments Co., Ltd., Jap) was used. Scanning tunneling microscopy (STM) was taken with a Veeco multimode 8. XRD patterns were performed on a XD-3 X-ray diffractometer using a Cu Kr radiation source ($\lambda=1.5418 \text{ \AA}$).

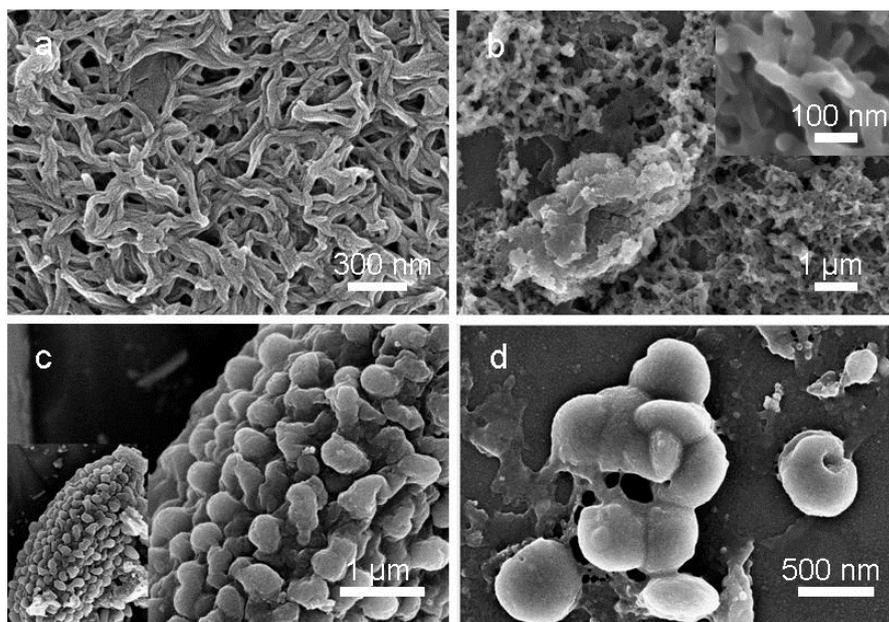


Fig. S1. SEM images for real-time polyaniline morphology transition after aging nanofibers in ethanol for (a) 0 days, (b) 3 days, (c) 7 days, and (d) 15 days, respectively.

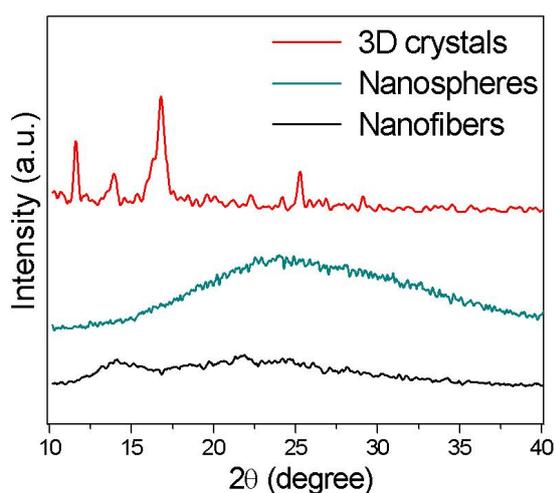


Fig. S2 XRD patterns of nanofibers, nanospheres and 3D crystals of polyaniline.

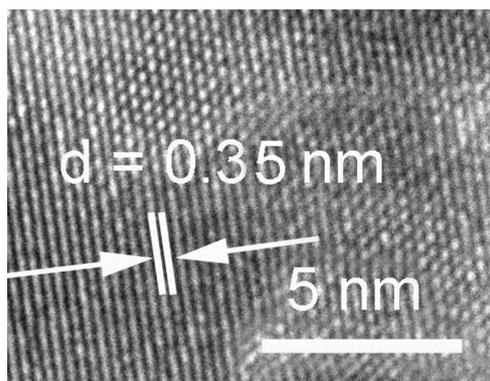


Fig. S3 HRTEM images of 2D nanosheets of polyaniline.

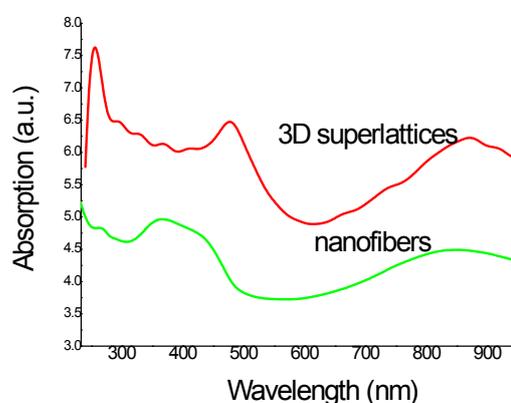


Fig. S4. UV-Vis spectrum of 3D crystals and nanofibers.

Fig. S4 shows UV-Vis spectrum of nanofibers and 3D crystals of polyaniline. Nanofibers doped with CSA have peaks at 350 and 850 nm indicating emeraldine salt form.

Interestingly, 3D crystals have peak at 260 nm corresponds to the $\pi \rightarrow \pi^*$ transition, which is a blue shift comparing to similar peaks at 260 nm in UV-Vis spectrum of polyaniline crystals reported by Kaner.[3] Absorptions at 450 nm and around 860 nm are ascribed to the polaron $\rightarrow \pi^*$ and $\pi \rightarrow$ polaron band transitions, respectively, indicating that the crystals are in their conductive emeraldine salt form.

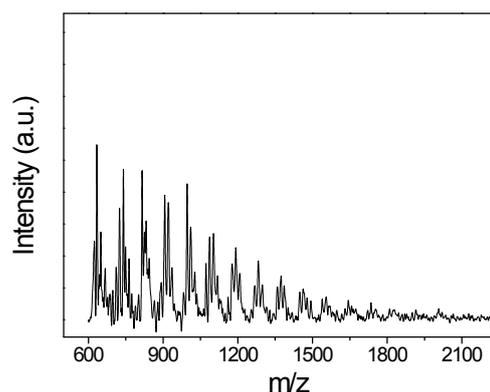


Fig. S5. MALDI-TOF mass spectra of polyaniline crystals.

Fig. S4 shows multiplet peaks indicating a nearly identical mixture, where the peak-to-peak distance is $m/z = 90$ (equivalent of a repeat unit $-C_6H_4=N-$). The m/z values at which peaks occur in the spectrum of polyaniline crystals are: 634, 725, 812, 908, 999, 1092, 1190, 1281, 1372, 1462, 1554, 1639, 1730, 1820, 1912, 2003. Most peaks [4] are easily assigned to the ions: $m/z=634 \rightarrow$ ion $2+$, $M=1268$, $m/z=725 \rightarrow$ ion $2+$, $M=1450$, $m/z=2003 \rightarrow$ ion $2+$, $M=4006$. The ion charge and the m/z value being known, the molecular mass of the polymer is easily calculated. It is about 1,200-4,000 Da, hence the longest chain will contain 40-50 repeat units and the shortest chain will contain 13 repeat units."

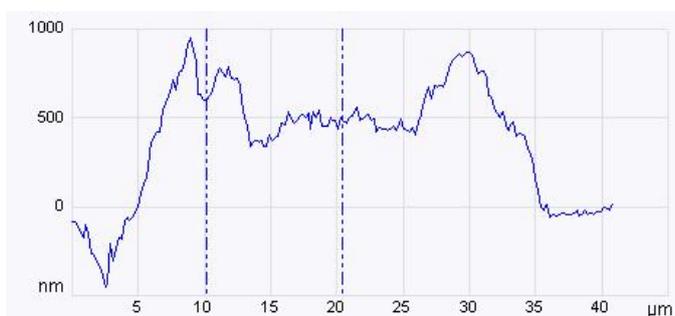


Fig. S6 Height profile of 3D crystals of polyaniline.



Fig. S7 Height profile of 3D crystals of polypyrrole.

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- [2]. Laslau C. Zujovic Z. [J]. *Prog. Polym. Sci.* 2010, 35, 1403-1419.
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- [4]. Laska J, Widlarz J. [J]. *Polymer*, 2005, 46, 1485-1495.