Supplementary Information

Conductive Polyaniline Helixes Self-Assembled in Absence of Chiral Dopant

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(a) Experiment Section

Materials. Aniline (99.5%) was purchased from Tianjin Jinke Fine Chemical Institute, and was distilled under reduced pressure before use. Dodecylbenzenesulfonic acid (DBSA, 99.5%) was obtained from Chongqing Golute Chemical Co.,Ltd. Ammonium peroxydisulfate (APS, 98%) was purchased from Xilong Chemical Co.,Ltd.

Synthesis of the PANI helixes. PANI helixes were synthesized by emulsion polymerization using DBSA and APS as dopant and oxidant, respectively.¹⁻² 0.03 mol of DBSA was dispersed into 75 mL of deionized water and stirred for 1 h. Then aniline (AN) dissolved in methylbenzene and n-butanol was added to the DBSA solution in sequence with stirring for 1 h. The polymerization was then initiated by adding APS dissolved in 30 mL deionized water. The whole reaction is kept in 15°C with stirring clockwise. The molar ratio of DBSA, APS and AN was 1:1:1, while the molar ratio of methylbenzene, n-butanol, deionized water was 1:1:70. During stirring, it suddenly became viscous with color change to dark green, when liquid crystal is formed. The as-product was washed with deionized water and ethanol for several times by centrifuge, and then was dried at 40°C. The as-prepared PANI was dispersed in chloroform for CD measurements with the concentration of 0.001 g/mL and was compressed into pellets for conductivity measurement by four-probe method.

Characterization. The morphology of the product was examined using scanning electron microscope (SEM) (Hitachi, S-4300, Japan) and transmission electron microscope (TEM) (JEM-2100). The molecular structures were characterized by Fourier Transform Infrared Spectroscopy (FTIR) (Varian Excalibur 3100) and Ultraviolet-visible spectrophotometry (UV-vis) (Varian Cary 5000). The polymer conformation was examimed by Circular Dichroism (CD) (Jasco J810). The formation of liquid crystal was comfirmed by the polarizing optical microscopy (POM) (Leica, DM4000M, Germany) and small-angle X-ray diffraction (XRD) (X'Pert PRO MPD) at room temperature. The emulsion microstructure was characterized on a Cryo-electron microscope (Cryo-EM) (Tecnai 20). The conductivity of PANI was measured by a four-probe method with a digital multimeter (Keithley 2750).

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(b) Structural characterization of the PANI helixes



Figure S1. Structural characterization of the PANI helixes: a) FTIR spectrum, b) UV-Vis spectrum.

The FTIR spectrum (Figure S1a) indicates that PANI helix is identical to the emeraldine salt form of PANI. For instance the bands at 1561 cm⁻¹ and 1479 cm⁻¹ are assigned to the C=C stretching deformation of quinoid and benzenoid ring. In addition, the bands at 1296 cm⁻¹ and 1243 cm⁻¹ represent the C-N stretching of aromatic amine, as well as the peak at 1119 cm⁻¹ representing the C-H aromatic in-plane bending is related to the doped structure. As shown in the UV-Vis spectrum (Figure S1b), three peaks at 363 nm, 439 nm and 838 nm are observed. The peak at 363 nm is corresponded to the π - π ^{*} transition of the benzenoid ring while both peaks at 439 nm and 838 nm are due to the polaron band transition, indicating that molecular structure of the PANI helix is identical to the emeraldine salt form.

(c) Morphological characterization of the PANI helixes



Figure S2. (a) right handed PANI helix and (b) left handed PANI helix.

It is noticed that the peak in 460 nm of CD spectrum is weak (Fig. 1c). As shown in Figure S2, there are both right and left handed PANI helixes in our system stirring clockwise, one would expect that optical activity could be balanced out the same as racemization, which leads to the peaks becoming weak.

Based on the previous research,³⁻⁵ the positive peak at ~460 nm can be ascribed to left handed chirality and it might indicate that there are more left handed helixes with clockwise stirring.

(d) The effect of liquid crystal and reactants on formation of PANI helixes

(1) Liquid crystal



Figure S3. SEM images of PANI after adding oxidant. a) before and b) after polymer liquid crystal appears.

During the synthesis of PANI helixes, the reaction mixture became very viscous suddenly once the product presented color of dark-green. The cream-like mixture is confirmed to be liquid crystal by means of the polarizing optical microscope (POM) and small-angle X-ray diffraction (XRD), respectively. This liquid crystal is considered to be lyotropic liquid crystal because its formation is effected by the concentration of PANI. Liquid crystal could be formed probably because reactants are very concentrated in this reaction system, compared with previous reports.^{1-2, 6} When the contents of AN and APS are 0.03 mol, 0.036 mol, 0.045 mol with no exchange of other conditions, liquid crystal is formed. However, when the content of AN and APS are 0.015 mol, liquid crystal cannot be formed due to the low concentration of PANI synthesized.

The products before and after liquid crystal appears are shown in Figure S3. There are large amount of nanoparticls are produced in the reaction system before liquid crystal appears. When the reaction mixture appears to be viscous, polymer liquid crystal appears and at the same time the PANI helixes are induced plentifully. Therefore, liquid crystal plays an important role in the formation of PANI helical nanostructure, and this viewpoint will be demonstrated in the following sections in which the effects of each reactants are studied.

(2) Surfactant



Figure S4. SEM images of PANI of different surfactants and doped acids with the same content of 0.03 mol. a) p-toluenesulfonic acid, b) dinonyl naphthalene sulfonate.

Under the premise of no change of other conditions, we choose p-toluenesulfonic acid for shorter alkyl chain surfactant and dinonylnaphthalenesulfonate for double long alkyl chain surfactant instead of DBSA (Fig. S4). There were no liquid crystal formed during polymerization. As a result, no helixes were found in products, neither. The micro-reactors formed under other surfactants for polymerization may be different from vesicles using DBSA as surfactant. Moreover, the different length of surfactants would affect the molecular arrangment, which will impede the formaiton of liquid crystalline polymer. Therefore, the change of surfactants caused the difference of the morphology for products and PANI helixes were hard to be produced.

(3) Oxidant



Figure S5. SEM images of PANI of different oxidants with the same content of 0.03mol. a) potassium dichromate, b) ferric sulfate.

Under the premise of no change of other conditions, we choose potassium dichromate and ferric sulfate instead of APS as oxidant (Fig. S5). From the experimental phenomenology, there is no liquid crystal formed during polymerization and only large particles or short nanorods as products. As previous researche reports, higher redox potential leads to higher polymerization or elongation rate, and different

oxidation capacities result in different morphologies.⁷ In this paper, potassium dichromate (Eox = 1.33 V) and ferric sulfate (Eox = 0.77 V) have lower oxidation reduction potential than APS (Eox = 2.05 V) and it is noticed that polymerization rate is APS > potassium dichromate > ferric sulfate. There are less PANI chains synthesised due to lower polymerization rate so that the concentration of polymer chains could not reach the level to form liquid crystalline polymer. As a result, helixes can not be obtained.

(4) Solvent



Figure S6. SEM images of PANI of different solvents with the same content of 0.08 mol. a) chlorobenzene, b) benzene.

Under the premise of no change of other conditions, we choose chlorobenzene and benzene instead of methylbenzene as solvent, which have a electron withdrawing group and no substituent, respectively. There is no liquid crystal formed during polymerization. The result confirms that the liquid crystal is lyotropic liquid crystal which is strongly dependent on solvent. The products were shown in Figure S6. From the products, there are only nanofibers and few helixes obtained. The use of chlorobenzene and benzene will cause various features of micro-reactor which is different from vesicles formed by methylbenzene (Fig. S7).



Figure S7. Cryo-EM images of micro-reactor structure via different solvents. a) chlorobenzene, b) benzene, c) no solvent. The micro-reactors formed before adding oxidant was mounted onto holey carbon grids, followed by

plunging into liquid ethane for a quick cooling. The grids were examined at the temperature of liquid nitrogen using a cryo-holder and a Tecnai microscope. In this way, samples are kept in their original structures. In order to find out the effect of solvents on the formation of vesicles, we choose different solvents or no solvent for AN in the polymerization (Fig. S7). When the solvent is chlorobenzene or benzene, or no solvent used, there are some other structures instead of vesicles in the reaction system before adding oxidant. Therefore, multi-lamellar vesicle plays an important role in forming PANI helixes.

(5) Stirring



Figure S8. SEM images of PANI by sonicating.

For comparing with different ways of mixing, the products by sonicating is shown in Figure S8. There are no liquid crystal during polymerizaiton, and nearly all nanoparticles mixed with some short nanorods produced by sonicating. Sonication will impede the self-assembly of PANI helixes and could not play as a driving force for the formation of helix-like structure with a sense of rotation.

Based on the results above, it is concluded that surfactant, oxidant, solvent and way of stirring can all affact the formation of liquid crystal. Moreover, surfactant and solvent have effects on the formation of vesicles. Mechanical stirring is the driving force for PANI helixes. However, further work is needed to investigate why these polymerization conditions have effects on the formation of vesicle and liquid crystal.

(e) The effect of mechanical stirring direction on formation of PANI helixes



Figure S9. CD spectrum for PANI helixes with stirring clockwise and anticlockwise.

In the formation mechanism, mechanical stirring works as a driving force which is the only condition with direction. When we changed stirring direction into anticlockwise, the peak at ~460nm disappears (the red line in Fig. S9) and it might indicate that there are equally left and right handed chirality produced with the anticlockwise stirring. Therefore, the mechanical stirring is not only the driving force for the self-assembly of PANI helixes, but also could affect the chirality for PANI polymer chains. The further research relevant is still under studying.

References

- 1 J. E. Österholm, Y. Cao, F. Klavetter and P. Smith, Polymer, 1994, 35, 2902.
- 2 J. E. Österholm, Y. Cao, F. Klavetter and P. Smith, Synth. Met., 1993, 55, 1034.
- 3 Y. Yan, Z. Yu, Y. W. Huang, W. X. Yuan and Z. X. Wei, Adv. Mater., 2007, 19, 3353.
- 4 Y. Yang and M. Wan, J. Mater. Chem., 2002, 12, 897.
- 5 S. Weng, Z. Lin, L. Chen and J. Zhou, *Electrochim. Acta*, 2010, 55, 2727.
- 6 L. J. Zhang and M. X. Wan, Thin Solid Films, 2005, 477, 24.
- 7 H. J. Ding, M. X. Wan and Y. Wei, Adv. Mater., 2007, 19, 465.