

Supporting Information

Synthesis of Heterocyclic Aramid Nanofibers and High Performance Nanopaper

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Experimental and Characterization Details

1. Materials

N-methyl-2-pyrrolidone (NMP), calcium chloride (CaCl_2) were purchased commercially and dehydrated before use. Terephthaloyl chloride (TPC, purity 99.99%), p-phenylene diamine (PPD, purity 99.99%) and 2-(4-Aminophenyl)-5-aminobenzimidazole (APBZ, purity 99.99%) were purchased commercially and used as received.

2. Preparation of heterocyclic aramid Nanofibers

In this work, HNF was prepared by polymerization-induced self-assembly method. 5g of CaCl_2 was added and dissolved in 100 ml of NMP at 100°C for 20 mins in a reactor under nitrogen atmosphere, rotating speed of stirring is 500 r/min. Then the reaction system was cooled down to 0~10°C using ice water bath. PPD and the third monomer APBZ (the total concentration 0.2 mol/L) were added and dissolved in NMP solution under stirring speed of 500 r/min for 30 mins. The addition ratio of APBZ in amines monomer was 20%, 40%, 50%, 60% and 80% respectively. Finally, 4.089 g of TPC was added subsequently into the system and start to react under high speed stirring of 1500 r/min. The reaction was stopped when the Weissenberg effect happened (generally 3~10mins).

10 g polymer gel was taken out and diluted by 100 ml NMP under stirring. Then, the diluent was added slowly into 1000 ml deionized water under a high shear homogenizer (Wiggen D500). The speed of homogenizer was 10000 rpm and after 5 minutes of homogenization, dispersion with a concentration of 0.1wt% of HNFs was obtained. The dispersion was filtered and thoroughly washed with water for three times and then dried in room temperature for further characterization.

3. Preparation of heterocyclic aramid papers

Process of the preparation of HNF paper is shown in fig.1. 1000ml HNF dispersion was poured into the sintered discs covered with a piece of filter paper. The residual NMP, CaCl₂, oligomer and unreacted monomers were filtered out assisted by vacuum and repeated three times of rinsing by deionized water. Finally, the wet HNF paper was transferred and fixed between two clean glass plates and dried in a vacuum oven at 70 °C under 3 kPa pressure for 48 h before characterization.

4. Characterization

A Fourier transform infrared spectrometer (FTIR, Nicolet6700, Nicolet) was applied for FTIR analysis of products. The nanofiber's morphology was observed by Transmission electron microscopy (TEM, Hitachi H-7650B). The surface morphology of HNF paper was characterized by field emission scanning electron microscopy (FE-SEM) (15 kV, Merlin Compact, Carl Zeiss, Germany). The thermal stability was analyzed by thermogravimetric analysis (TGA, TA Instruments Q5000IR) under a nitrogen atmosphere with a heating rate of 10 K/min from room temperature to 700°C. The tensile strength (TS) and elongation at break (EB) was detected by a Tensile Tester for Paper and Board (HK 202E, Hengke Inc., China) with a speed of 25 mm/min at room temperature. The electric insulation was measured by electrical breakdown strength (EBS) test using Resistance to Breakdown Voltage Tester (ZJC-20kV, China). The thickness of nanopaper is measured with a screw micrometer. Cut a square piece of paper (5cm×5cm), weigh it with a balance and calculate the surface density of paper.

5. Measurement of molecular weights of polymers

The inherent viscosity(η) obtained as following equation^[1] was used to measure the molecular weight of aromatic polyamide.

$$\eta_{inh} = \ln \left(\frac{\eta}{\eta_0} \right) / C$$

In this experiment, the inherent viscosity of heterocyclic aromatic polyamides in 98% sulfuric acid with concentration(C) at 0.5g/dL was measured by using an Ubbelohde viscometer (Beijing Midwest Group, 1.04–1.07 mm) at 30 °C. This data can be further converted to weight-average molecular weight as a reference.

$$M_w = 3902.4\eta^{1.556}$$

Table S1. The inherent viscosity and weight-average molecular weight of polymer

APBZ ratio	0%	20%	40%	50%	60%	80%
η_{inh}	3.2	3.7	3.4	3.5	4.5	4.1
$M_w/\times 10^4$	2.4	3.0	2.6	2.8	4.0	3.5

[1] H H. Yang, in Kevlar aramid fiber, J. Wiley, Chichester, 1993, pp. 23–46.



Fig. S1 Heterocyclic aromatic polyamide gel in reaction

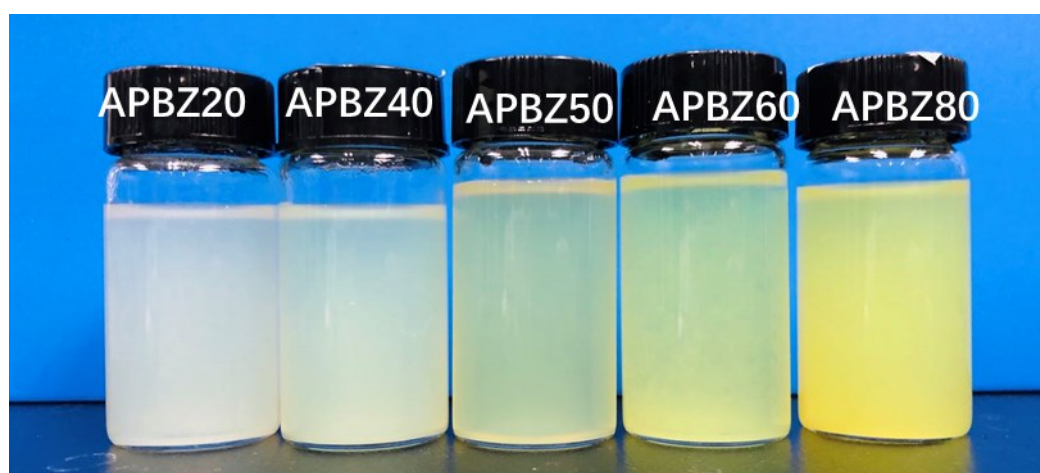


Fig. S2 HNF dispersions with different APBZ ratio.

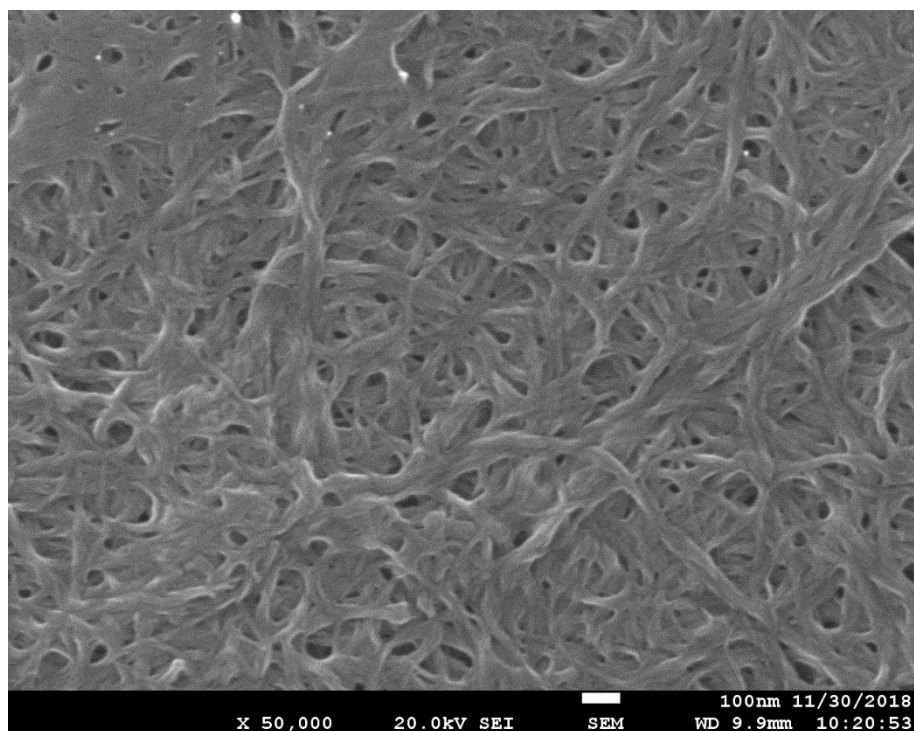


Fig. S3 SEM image of ANF paper surface.

6. Measurement of thermal stability and HNMR of polymers

Heterocyclic aromatic polyamides prepared in this work have excellent heat resistance and do not melt at high temperature. Usually, the polymers start to decompose at around 400°C~500°C. In previous research about aromatic polyamides, the TGA results might be more meaningful than DSC. In this work, the heterocyclic aromatic polyamides (HAP) cannot be dissolved in common solvents, but only in strong acids, such as concentrated sulfuric acid. So, we might not give the results of HNMR. The related references are listed below:

- [1] Tanner D, Fitzgerald J A, Phillips B R. The Kevlar story - an advanced materials case study[J]. *Angewandte Chemie*, 1989, 101(5):665-670.
- [2] Xin G L, Huang M R. Thermal Degradation of Kevlar Fiber by High-Resolution Thermogravimetry[J]. *Journal of Applied Polymer Science*, 1999, 71(4):565-571.
- [3] Luo L, Yuan Y, Dai Y, et al. The novel high-performance aramid fibers containing benzimidazole moieties and chloride substitutions[J]. *Materials & design*, 2018, 158(NOV.):127-135.