Polynaphthoxazine-based 1D carbon nano-material: electrospun fabrication, characterization and electrochemical properties

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Microstructures of PNEM/PMMA fibers fabricated by electrospinning process

In our study, electrospinning of PMMA/PNEM nanofibers was achieved by using ethyl acetate (EAC)/DMF mixed solvent system. The PMMA/PNEM solution with increasing concentrations from 10-20 wt% were employed in the electrospinning process.

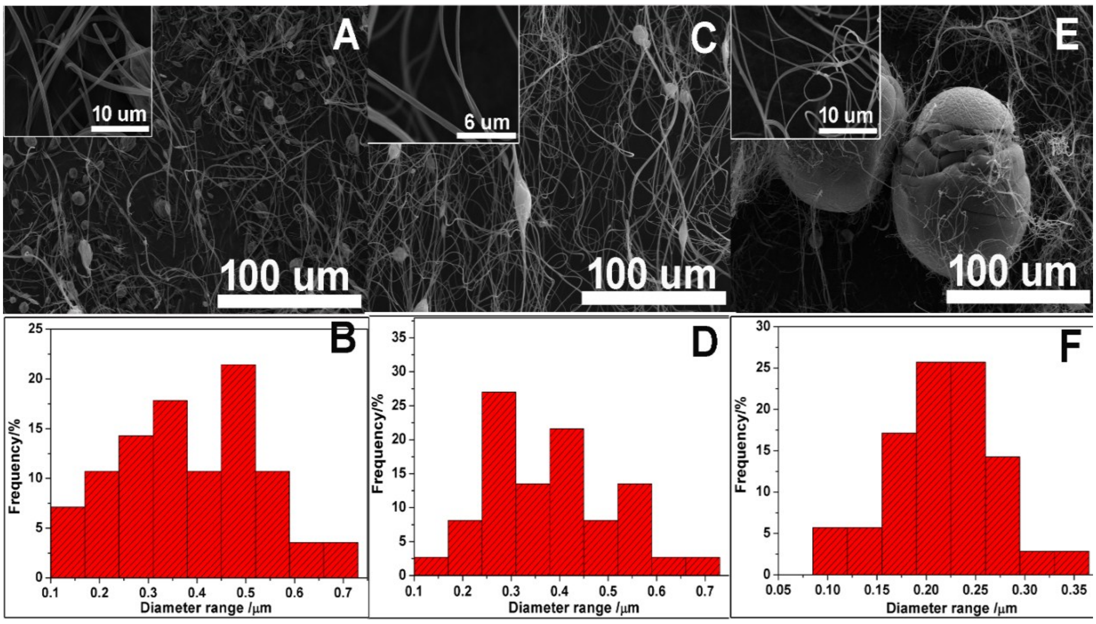

Figure S1 Representative SEM images and corresponding fiber diameter distributions of the electrospun nanofibers obtained from 10% (w/v) solutions of PMMA/PNEM where EAC/DMF (v/v) was 1:1 (A,B), 3:2 (C,D), 4:1 (E,F). Inset shows magnified view of a typical region.

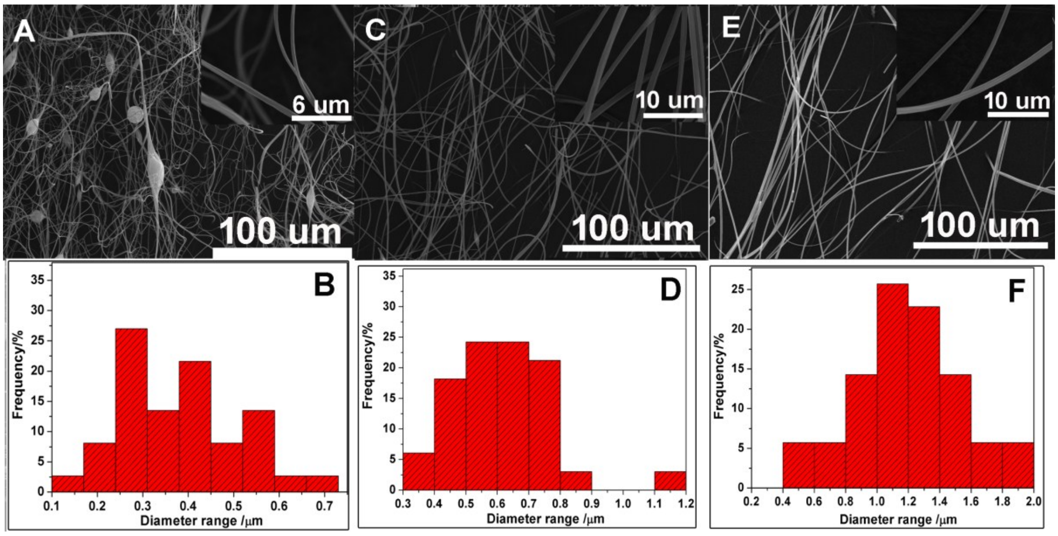

Figure S2 Representative SEM images and corresponding fiber diameter distributions of the electrospun nanofibers obtained from solutions of PMMA/PNEM where EAC/DMF was (A,B) 10%, (C,D) 15%, (E,F) 20%. Inset shows magnified view of a typical region.

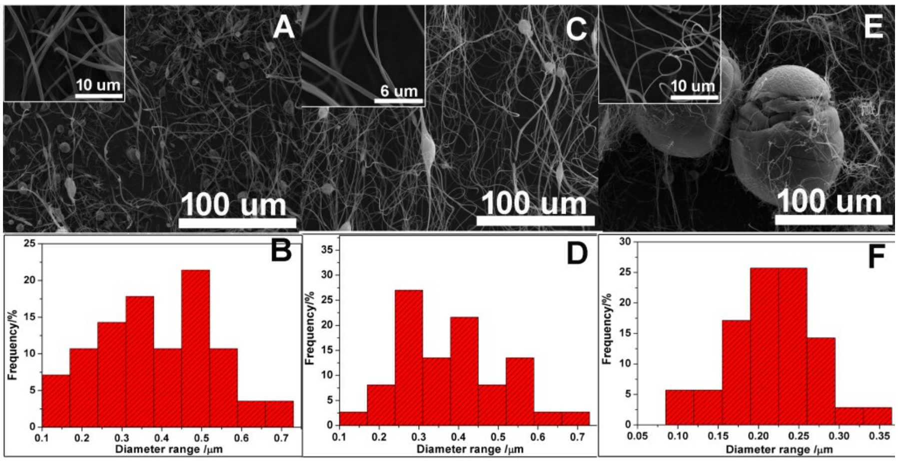

Figure S3 The SEM image of the film of PMMA/PNEM before (A) and after (B-D) selective etching of PMMA by acetone with different compositions: EAC/DMF=3:2, PNEM=10 wt%, `PMMA=10 wt % (A and C); EAC/DMF=3:2, PNEM=2 wt%, PMMA=8 wt % (B); EAC/DMF=1:1, PNEM=2 wt%, PMMA=8 wt % (D).

Thermal Properties of naphthoxazine-based samples

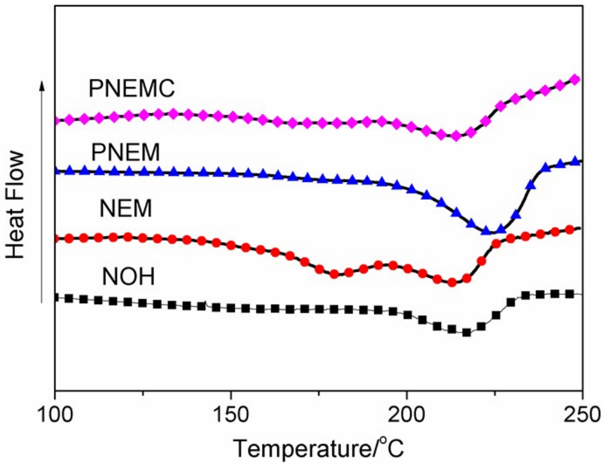

Figure S4 DSC thermograms of NOH, NEM, PNEM and PNEMC (PNEM with 1wt% PTS) under nonisothermal conditions at 10 °C/min.

Differential scanning calorimetry (DSC) was employed in order to determine the thermal properties of the products. The temperatures of maximum heat flow T_{peak} and the onset temperatures T_{onset} are listed in Table S1. As shown in Figure S4, an exothermic peak (215.3 °C) is observed for NOH, which originates from thermally activated ring-opening polymerization of naphthoxazines depending on the structure and concentration or nature. In the case of NEM, DSC profile had two exothermic major peaks, the first one has a maximum at 178.8 °C, which corresponds to thermal polymerization of methacrylic double bonds and the second exothermic peak emerging with a maximum at 213.4 °C belongs to ring-opening reaction of naphthoxazine units. However, the cure temperature increases to 223.4 °C after the polymerization reaction of the methacrylate-based naphthoxazine (NEM) initiator. It is possible that the high curing temperature is caused by relatively low ultimate elongation and restricted segmental motion of the PNEM compared with the NOH and NEM.

Obviously, this is one drawback for benzoxazine resin that the curing temperature is high leading to poor mechanical properties and bad processability. To overcome this problem, several ways have been proposed, like developing new reactive benzoxazines[1, 2] or the application of highly active initiators.[3-6] For example, p-toluenesulfonic acid (PTS) was investigated which lower the polymerization temperature dramatically for the conventional benzoxazines like 1,3-benzoxazine and bisphenol A-based one. The question arises whether this structure of sulfonic acid compounds may be suitable for ring opening polymerization of macromolecule with naphthoxazine unit. The promoting effect of PTS for the cure of naphthoxazine macromolecule was also studied by DSC (Figure S4). For the naphthoxazine-based polymer with PTS (PNEMC), the exothermic reaction peak for 213.7 °C, is lower than that of pure PNEM. Notably, the PNEMC also exhibits the much low curing onset temperature with 139 °C. This drastically decreased polymerization temperature was verified by thermostatic experiments.

Table S1 DSC thermograms data of NOH, NEM, PNEM and PNEMC

Samples	NOH(°C)	NEM(°C)	PNEM(°C)	PNEMC(°C)
T_{onset}	197.3	153.8	196.7	139.0
T_{peak}	215.3	178.8 214.3	223.4	213.7

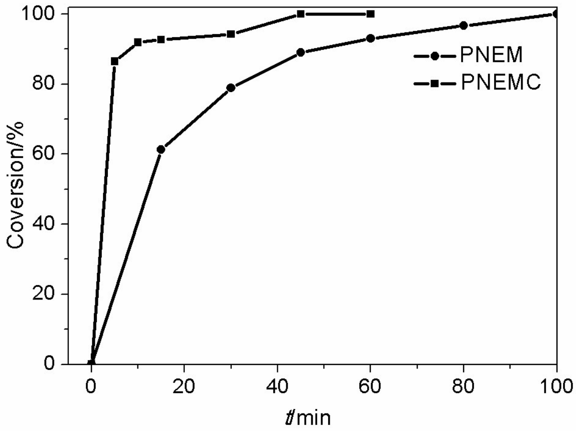

Figure S5 Time-dependence of polymerization conversion of naphthoxazine unit in PNEM and PNEMC (PNEM with 1wt% PTS) under isothermal conditions at 180 °C.

The ring-opening polymerization of naphthoxazine-based polymers without and with p-toluenesulfonic acid (PTS) was carried out at 180 °C for different times. The results are depicted in Figure S5. By heating PNEM with 10wt% PTS at 180 °C, 100% of naphthoxazine unit was consumed within 0.5 h. In comparison, naphthoxazine unit of PNEM did not convert to the corresponding polymers at 180 °C without any additives. These results demonstrated the remarkable promoting effect of the PTS on the cure of the naphthoxazine unit in PNEM macromolecule, which is very similar to that of conventional benzoxazines.

The weight composition and thermal degradation of the PNEM and corresponding cured PNEM (CPNEM) were also examined by TGA from room temperature to 800 °C at a heating rate of 10 °C/min under a nitrogen atmosphere. It can be seen that the PNEM shows multiple step decomposition to yield the related carbon materials. The final weight residue was 9.4 % due to partly crosslinking of PNEM during heating. In the case of CPNEM, the values of weight residue increased to 23.5% attributed to the ring-opening polymerization of naphthoxazine units in PNEM. The residue value of CPNEM is much higher than that of PNEM, suggesting that the naphthoxazine-based polymer can also be used as precursors to prepare carbon materials.

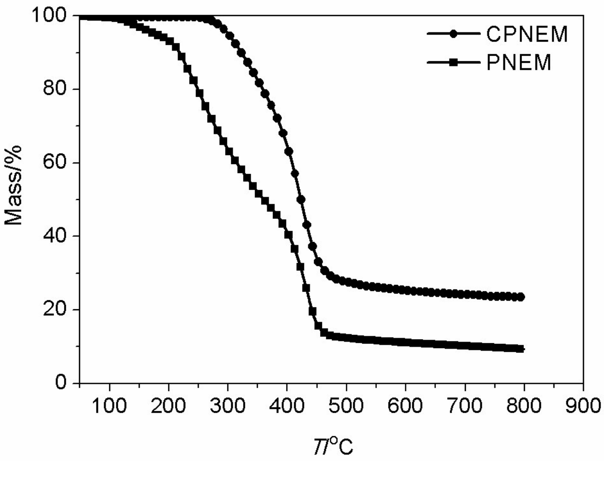

Figure S6 TG thermograms of PNEM and and corresponding cured PNEM (CPNEM).

Element data of naphthoxazine-based carbon nanofibers

Table S2 EDS element data of naphthoxazine-based nanofibers before and after carbonization

Element	**Carbon**	**Nitrogen**	**Oxygen**	**Others**
Before/wt%	49.5	2.2	29.9	18.4
After/wt%	69.6	2.7	27.4	0.3

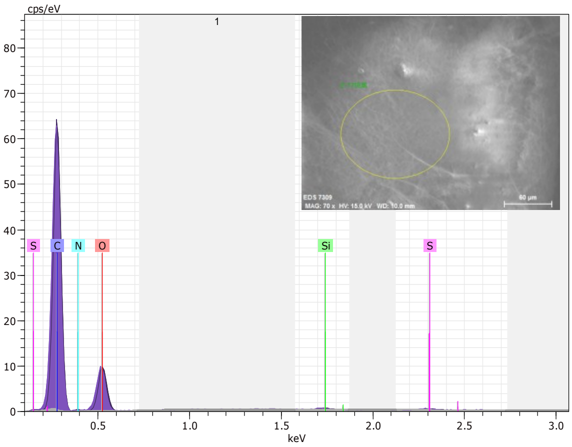

Figure S7 The SEM image and EDS element distribution of naphthoxazine-based nanofibers before carbonization

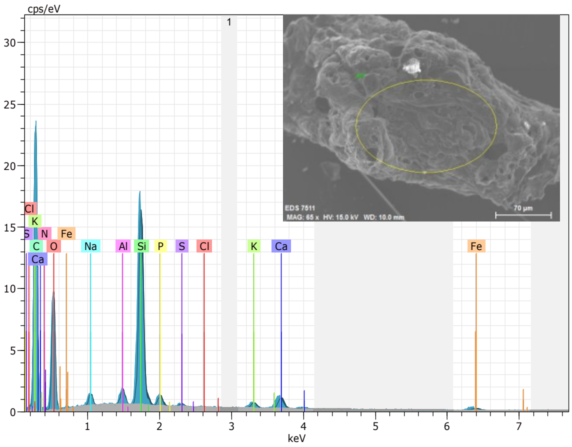

Figure S8 The SEM image and EDS element distribution of naphthoxazine-based nanofibers after carbonization

10. Reference for the Supplementary Information

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