

Supplementary Information

A General Metal Acetate-Assisted Alcohol Thermal Strategy to Fabricate Flexible Carbon Nanofiber Film for Supercapacitor

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Experimental

Material Synthesis:

All chemicals used in the experiment are analytical grade and were from Macklin without any further purification. Firstly, polyacrylonitrile (PAN, 0.5 g) was dissolved in DMF (5 mL) and continuously stirred at room temperature for 12 h to form a uniform spinning solution. Electrospinning was performed at a voltage of 30 kV, and a distance of 18 cm, and the resulting PAN film was dried at 60 °C for 12 h to remove residual DMF. The PAN film was immersed in 0.05 M zinc acetate methanol solution and then transferred to a 50 mL high-pressure reactor at 150 °C for 7 h. After the reaction was cooled, the product was ultrasonically washed several times with methanol, and dried at 60 °C for 0.5 h. The product is denoted as CPAN-Zn, finally, carbonized at 900 °C for 3 h in a nitrogen atmosphere at a heating rate of 3 °C min⁻¹. The final product, the carbon nanofiber film, is denoted as CNF-Zn.

In the comparison experiment, only the alcohol thermal cyclization conditions were compared. Except for the comparison conditions, the other reaction conditions were unchanged. The comparison conditions included heating time (0 to 8 h), heating temperature (80 to 160 °C), and solution concentration (0.01 to 0.09 M) in addition. Different solvents containing zinc acetate (H₂O, methanol, and other linear alcohols), different zinc species dissolved in methanol (zinc acetate, elemental zinc, zinc nitrate, zinc chloride, and zinc sulfate), and methanol solutions containing other metal acetates (M(CH₃COO)_x, M: Cu²⁺, Zn²⁺, Cd²⁺, Tb³⁺, Mn²⁺, Pr³⁺, La³⁺, Ag⁺, Gd³⁺, Sm³⁺, Eu³⁺,

Ni²⁺, Dy³⁺, In³⁺, Y³⁺, Ce³⁺, Ho³⁺, Co²⁺, Er³⁺, Mg²⁺, Lu³⁺, Sc³⁺, Rh³⁺, Ru³⁺, Yb³⁺, Tm³⁺, Ca²⁺, Zr⁴⁺, Fe³⁺, Pd²⁺, Sr²⁺, Sn²⁺, Sb³⁺, Cr³⁺, Mo²⁺, Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺) were prepared into 0.05 M solutions. The mixture was poured into a 50 mL autoclave with PAN film and reacted at 150 °C for 7 h. After the reaction was cooled, the product was ultrasonically washed several times with methanol, and dried at 60 °C for 0.5 h. The corresponding cyclization product is denoted as CPAN-M, and the carbonization product is marked as CNF-M.

Material Characterization

X-ray diffraction (XRD) measurements were performed using X-ray powder diffraction (XRD, Rigaku Co, Japan, D/MAX- γ A) with Cu K α radiation ($\lambda=1.54056$ Å) at a scan rate of 8 ° min⁻¹. Raman spectra were tested using Confocal Laser MicroRaman Spectrometer (Via-Reflex/inVia-Reflex). Fourier transform infrared spectrum (FTIR) spectra were tested using a Fourier infrared spectrometer (Hyperion 2000). The Brunauer-Emmett-Teller (BET) surface area and pore size distribution of the product were measured by N₂ adsorption-desorption apparatus (Autosorb-IQ, USA). The X-ray photoelectron spectroscopy (XPS) was performed using (XPS, ESCALAB 250). The morphologies were systematically characterized by scanning electron microscopy (SEM, JEOL JSM-6700 M) and transmission electron microscopy (TEM, Hitachi H-800) coupled with energy dispersive X-ray (EDX) analysis. The tensile test was carried out on a Instron 5967, USA. All the prepared CNFs were subjected to tensile deformation at an extension rate of 2 mm min⁻¹ at ambient

temperature.

Calculation of the stereoregularity of polyacrylonitrile

As shown in the infrared spectrum of PAN (Fig. 1), the characteristic absorption peaks at 1250 cm^{-1} and 1230 cm^{-1} are attributed to the bending vibration of methine (CH) parallel to the molecular chain and the bending vibration of methylene (CH_2),¹ respectively. By measuring the intensity of the two peaks and substituting them into the following formula, the stereoregularity of PAN can be obtained.²

$$\frac{D(1230\text{cm}^{-1})}{D(1230\text{cm}^{-1}) + D(1250\text{cm}^{-1})} = 0.21 + 0.51X \quad (1)$$

Where D is the intensity of the absorption peak, and X represents the fraction of isotactic triad units. The calculated isotactic property of PAN is 56%, indicating that polyacrylonitrile is mainly isotactic and belongs to high stereoscopic PAN.

Electrochemical measurements

We used the electrode material with a size of $1\text{ cm} \times 1\text{ cm}$ (mass is about 1 mg, thickness is about 0.02 mm), AC (Vulcan XC-72 carbon, USA), and a Hg/HgO electrode as a working electrode, counter electrode, and reference electrode. Preparation of counter electrode: AC, acetylene black and polytetrafluoroethylene (PTFE) were mixed at a mass ratio of 7:2:1 to form a film with a thickness of about 0.1 mm and dried at $60\text{ }^\circ\text{C}$ for 5 h. The film is fixed on the nickel foam using a tableting machine. 6 M KOH solution was use as electrolyte. The assembly of symmetrical supercapacitor was made from the same two working electrodes as described above and tested in 6 M KOH electrolyte. Electrochemical testing was performed on a Chenhua

CHI660E electrochemical workstation, and cycling stability testing was performed on a LAND CT2001A.

The specific capacitance of the electrode material can be calculated based on **equation 2:**

$$C = \frac{I \times \Delta t}{m \times \Delta V} \quad (2)$$

Where C is the specific capacitance in F g^{-1} ; I is the discharge current in A g^{-1} ; t is the discharge time in s; m is the mass of the electrode material in g; and ΔV is the voltage difference in V.

The following equation calculates the energy density (E) and power density (P):

$$E = \frac{C \times \Delta V^2}{7.2} \quad (3)$$

$$P = \frac{E \times 3600}{\Delta t} \quad (4)$$

Where E is the energy density (Wh kg^{-1}) and P is the power density (W kg^{-1}).

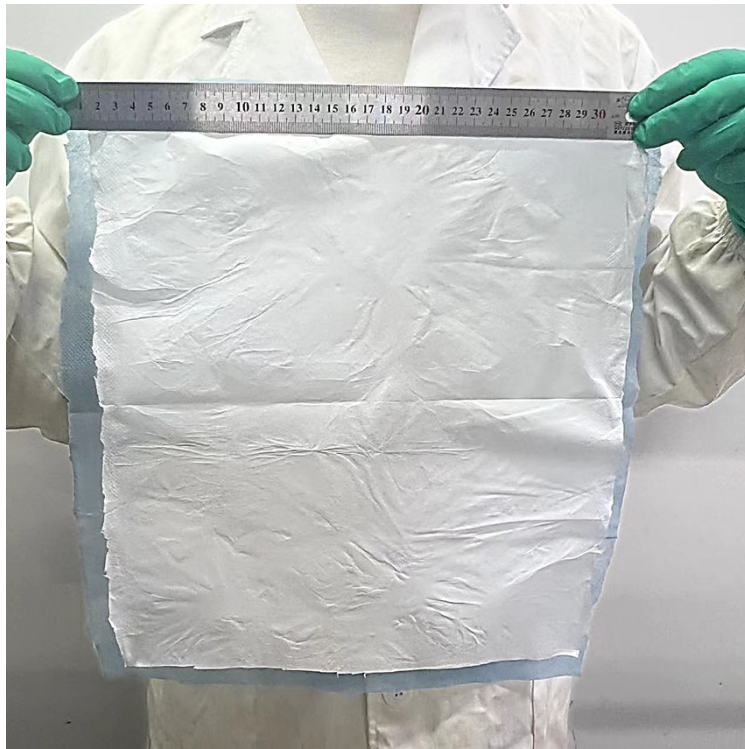


Fig. S1. Optical photograph of PAN film prepared by electrospinning.

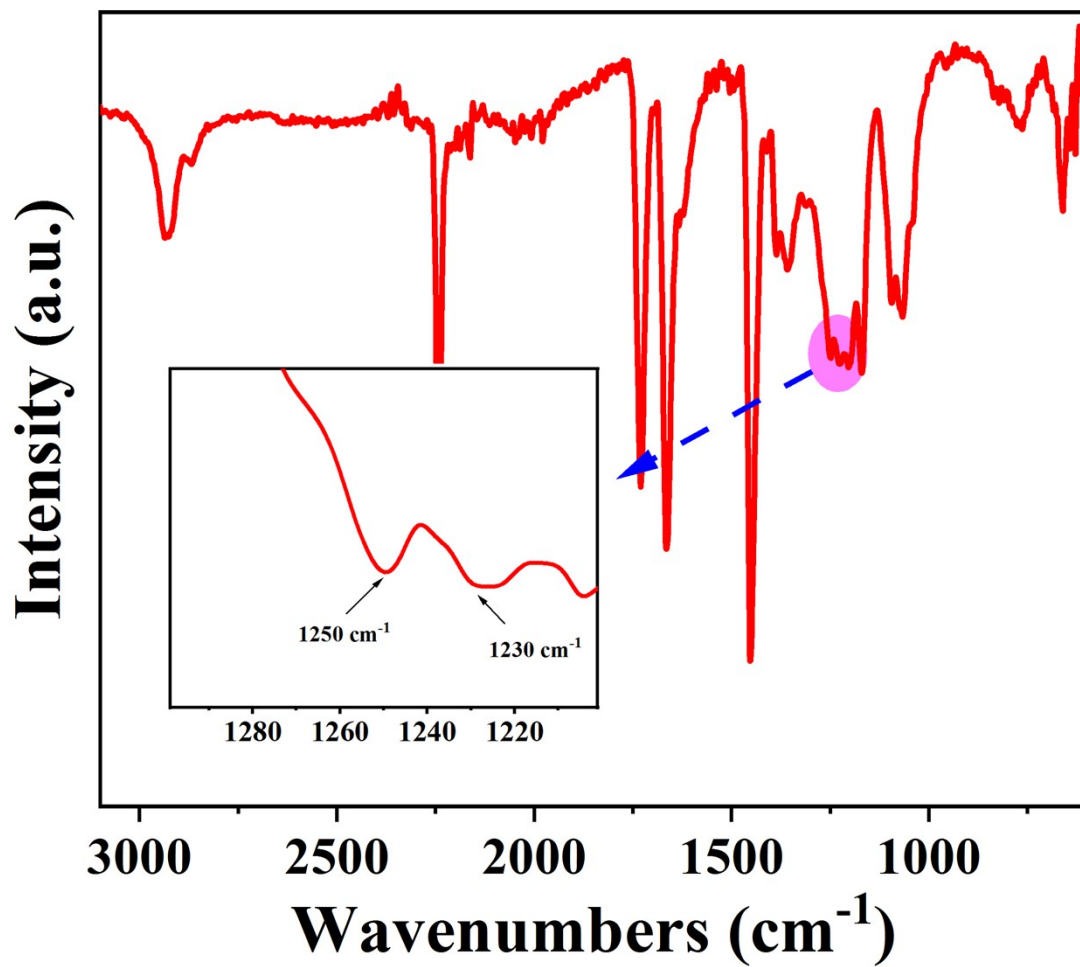


Fig. S2. FTIR spectra of PAN.

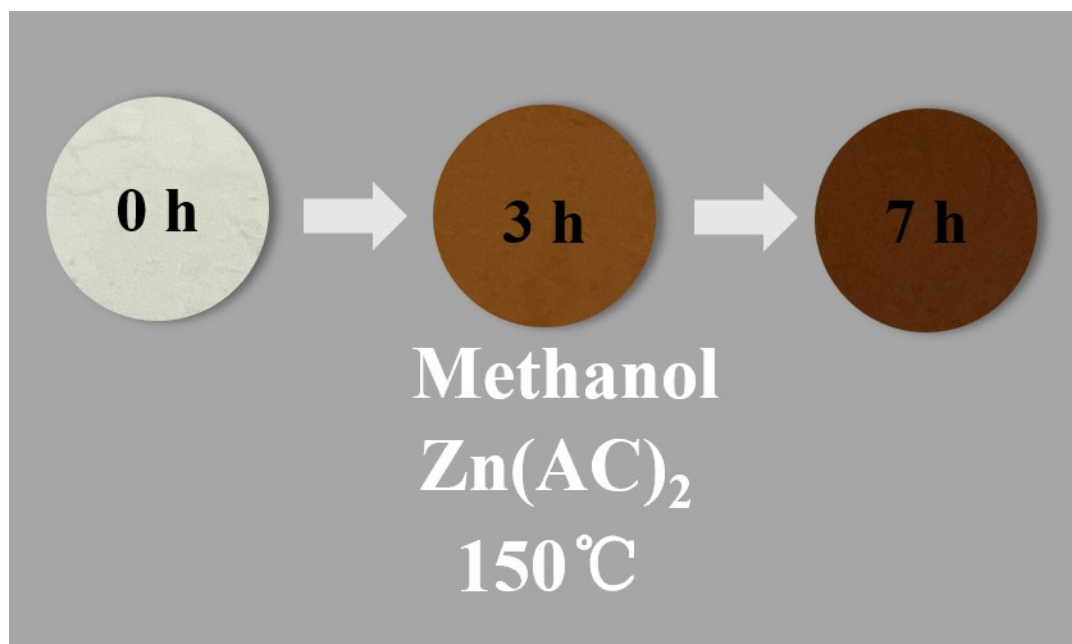


Fig. S3. Optical photographs of CPAN-Zn.

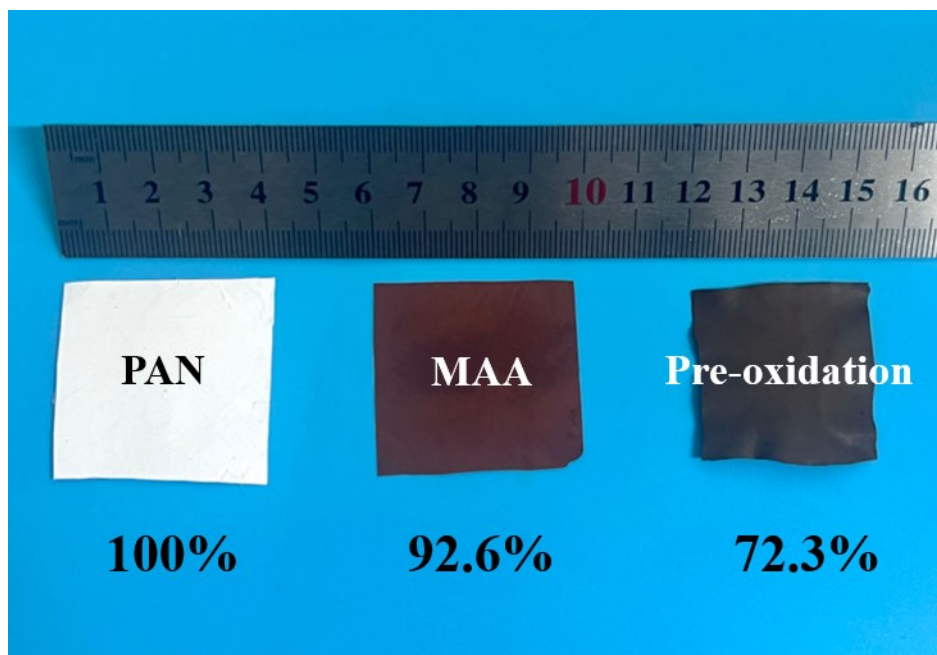


Fig. S4. Optical photographs of PAN, MAA-PAN, and pre-oxidation-PAN. (The number represents the preservation rate of the area.)

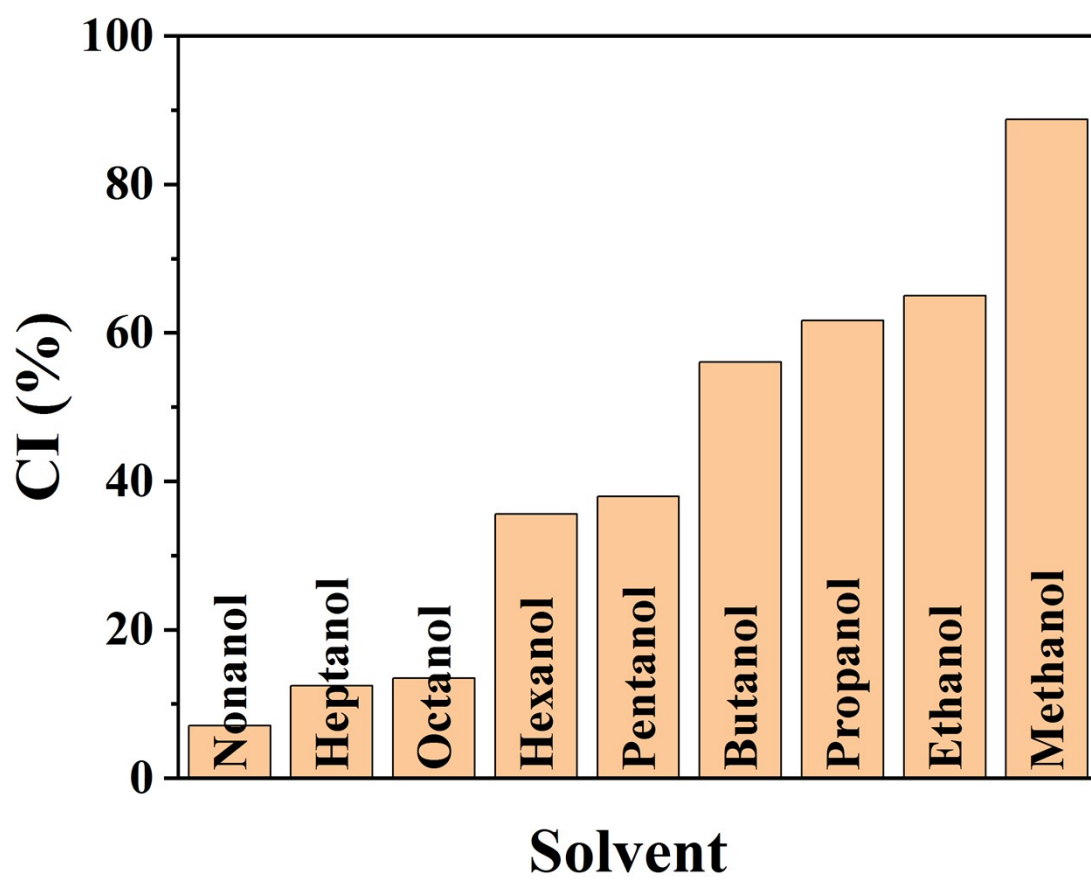


Fig. S5. The CI value of CPAN-Zn obtained by different reaction solvents.

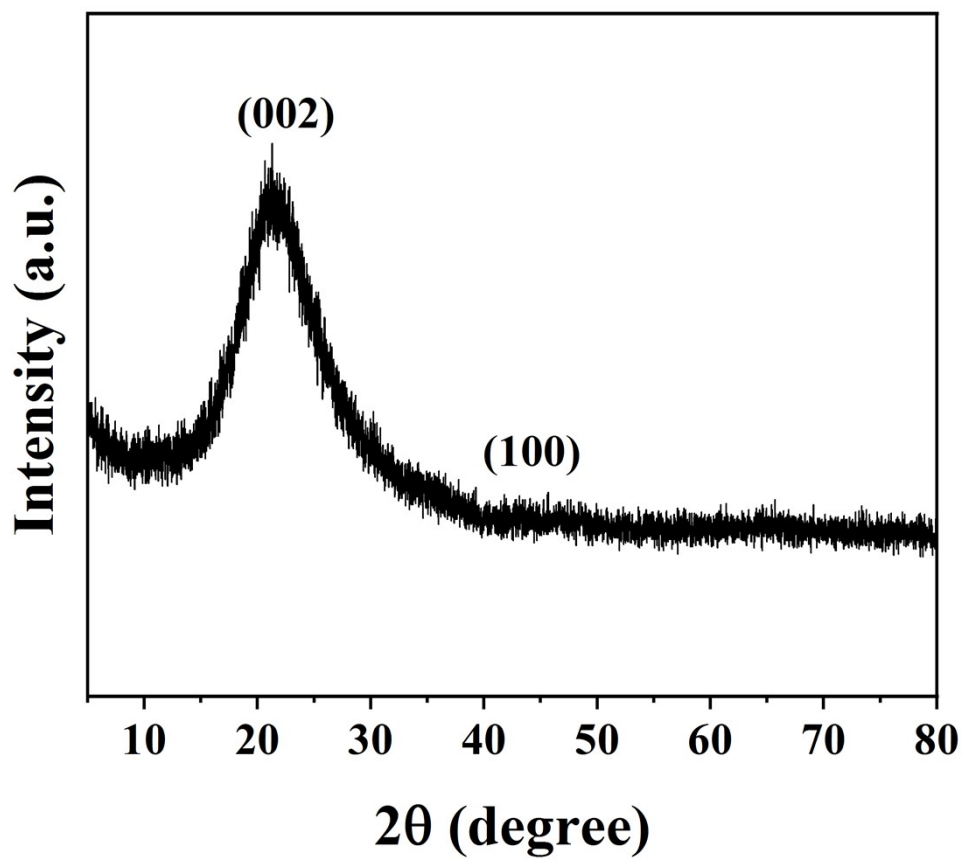


Fig. S6. The XRD pattern of CPAN-Zn after carbonization.

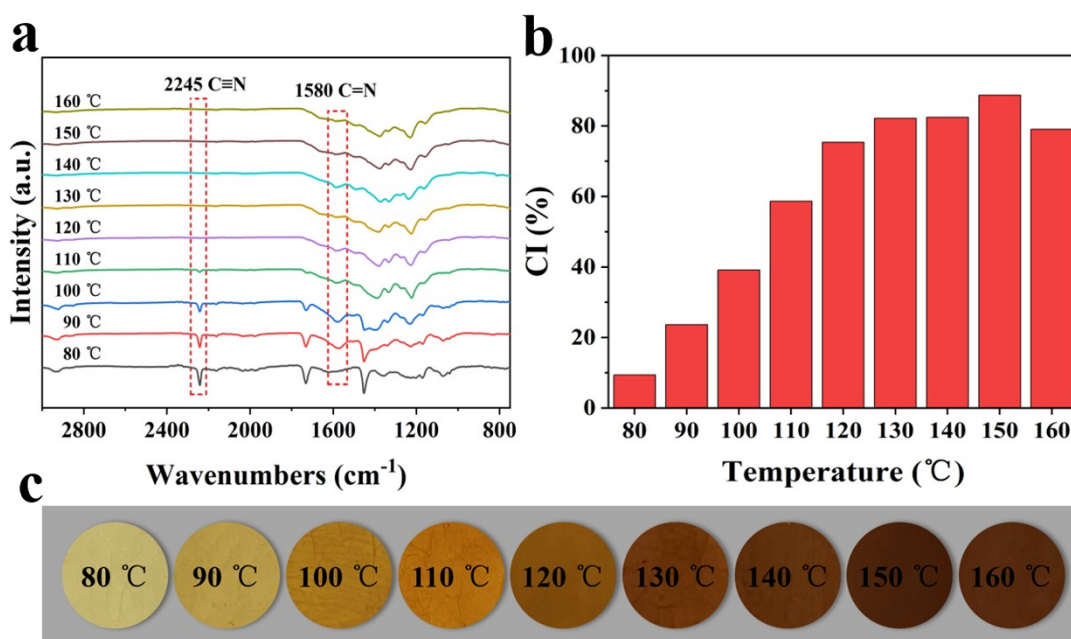


Fig. S7. The effects of different reaction temperatures on CPAN-Zn (7 h, methanol and zinc acetate). (a) FTIR spectra; (b) The CI value of CPAN-Zn; (c) Optical photographs of CPAN-Zn films with different reaction temperatures.

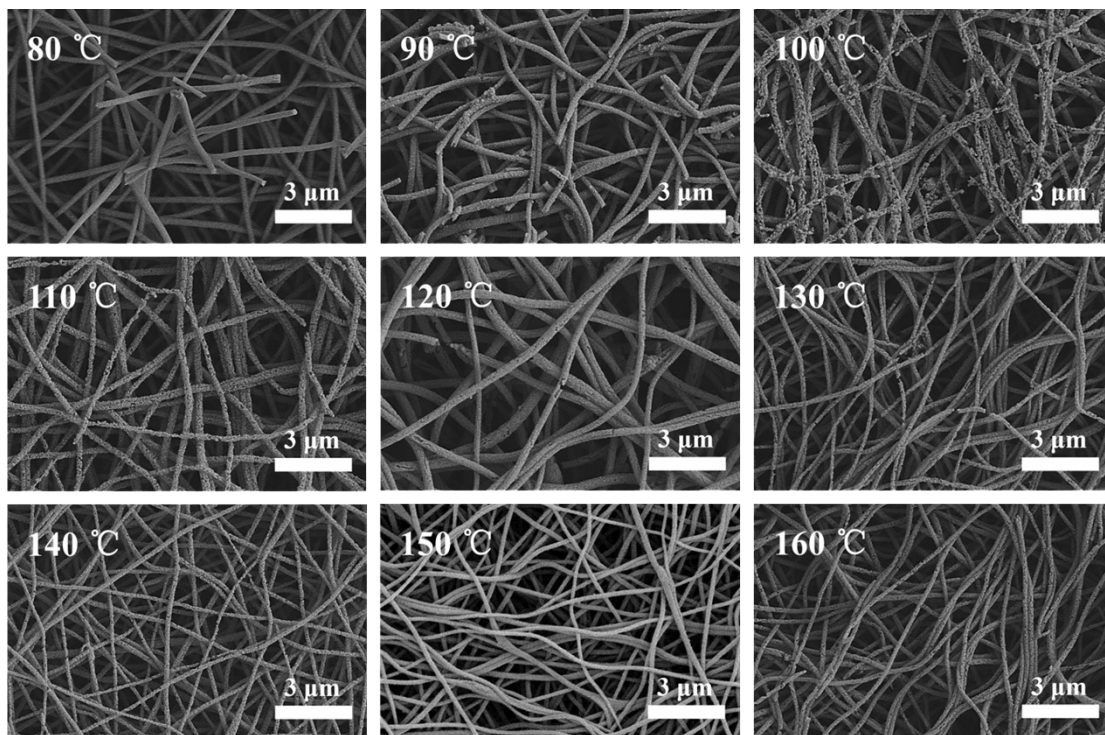


Fig. S8. SEM images of CNF-Zn (The temperature of the upper left corner represents the alcohol thermal reaction temperature of the precursor film of CNF-Zn).

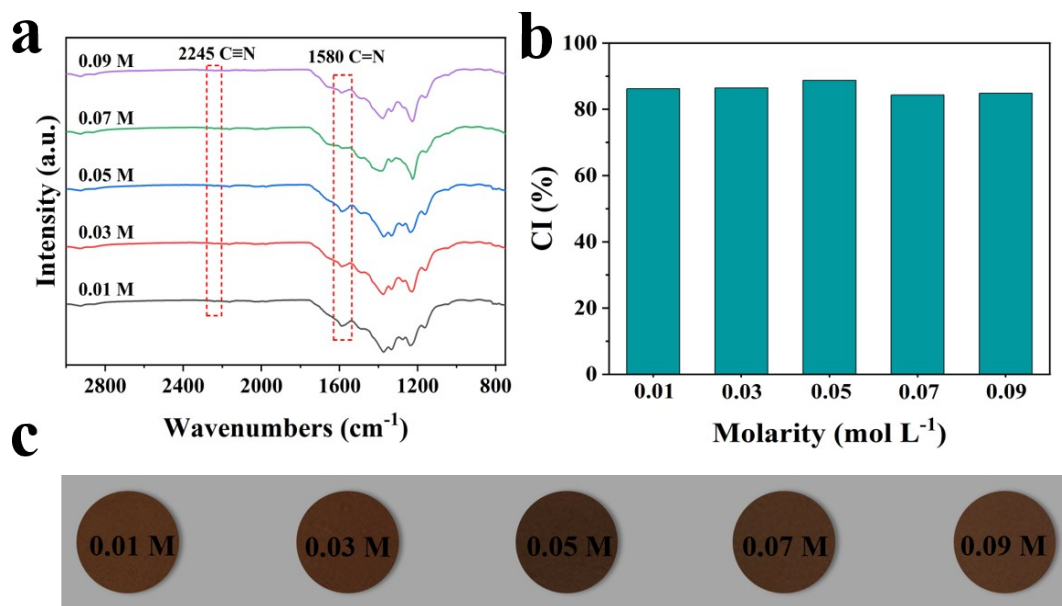


Fig. S9. The effects of different concentrations of zinc acetate on CPAN-Zn. (a) FTIR spectra; (b) The CI value of CPAN-Zn; (c) Optical photographs of CPAN-Zn films with different reaction concentrations.

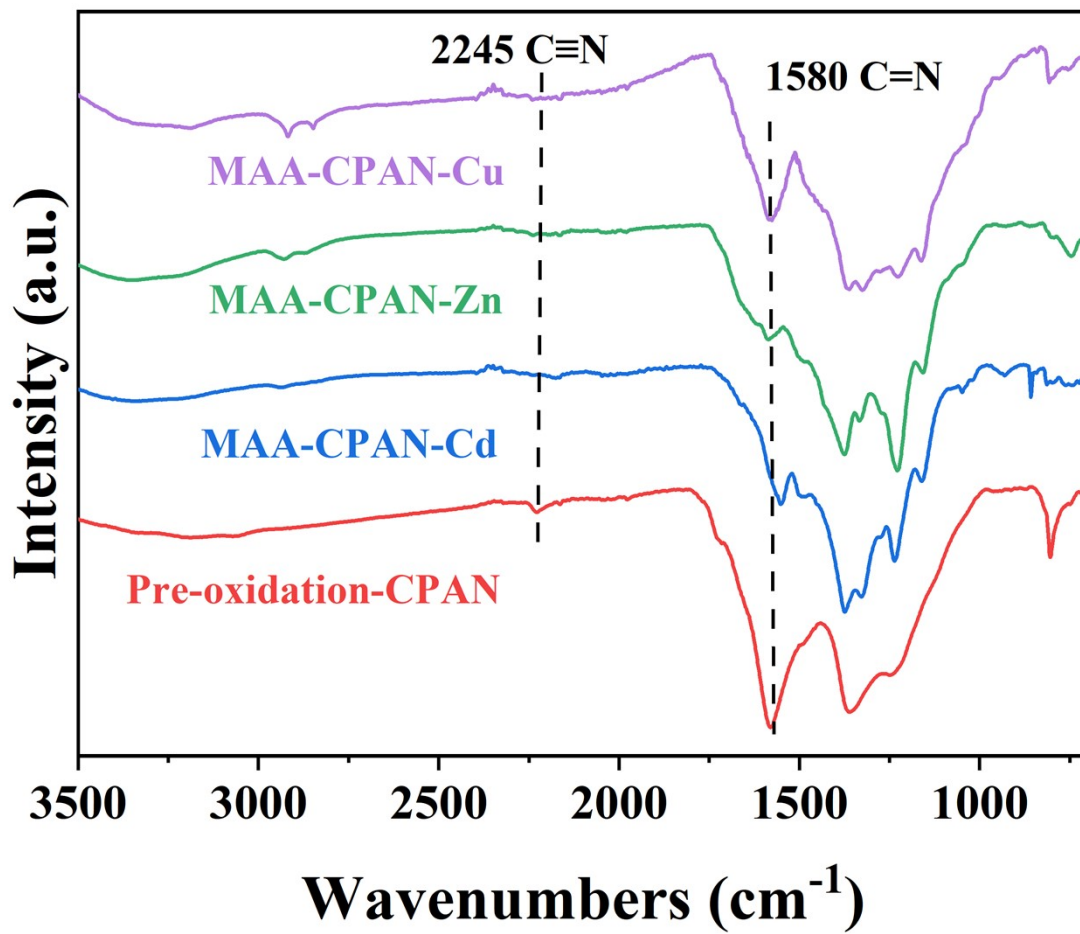


Fig. S10. The FTIR spectra of CPAN prepared by different methods.

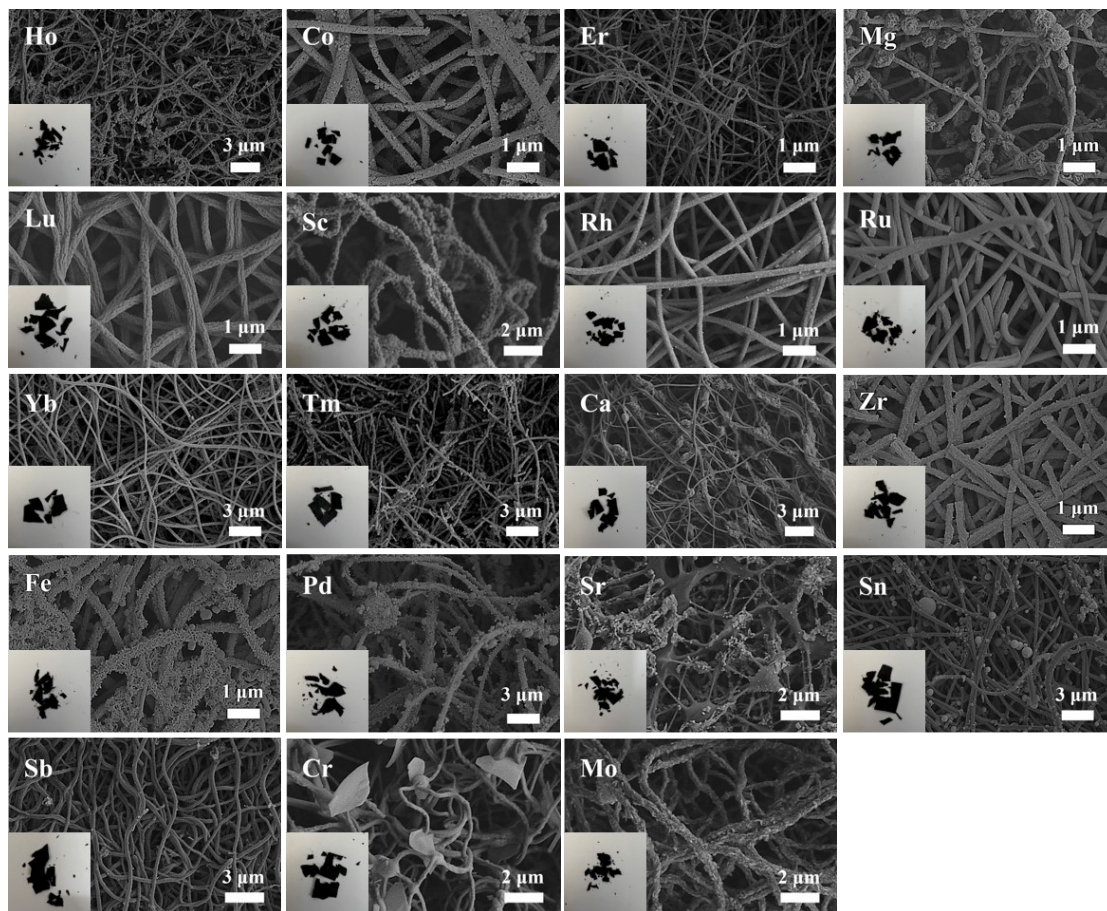


Fig. S11. SEM images of CNFs with poor mechanical properties. The insets are flexible displays of CNFs.

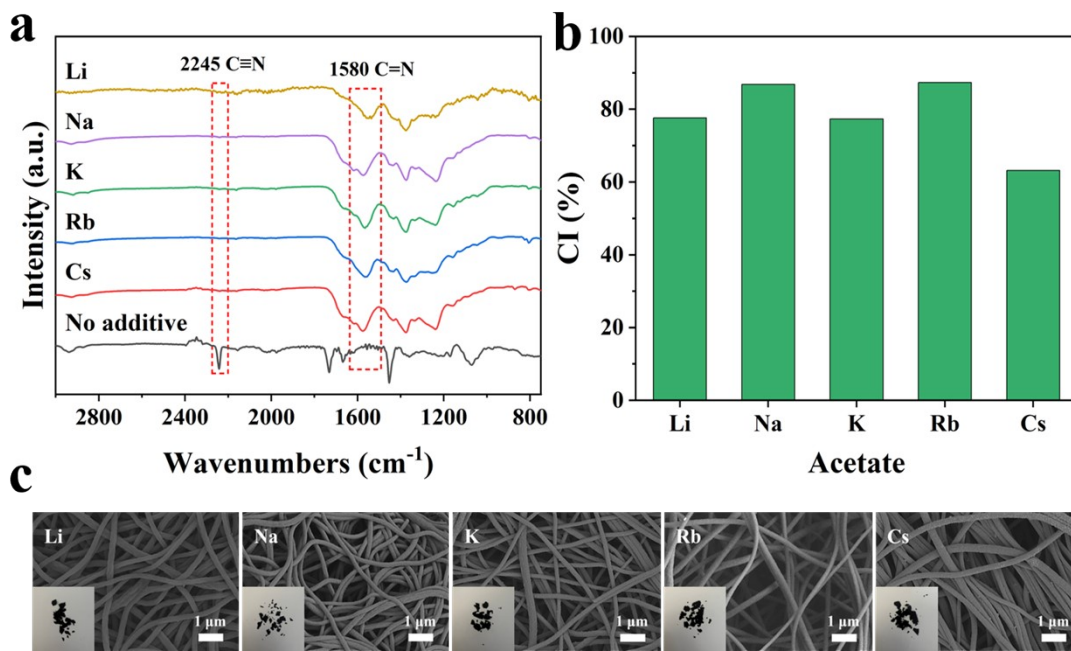


Fig. S12. The effects of acetates of alkali metal elements on CPAN. (a) FTIR spectra; (b) The CI value of CPAN; (c) SEM images of CNFs. The insets are flexible displays of CNFs.

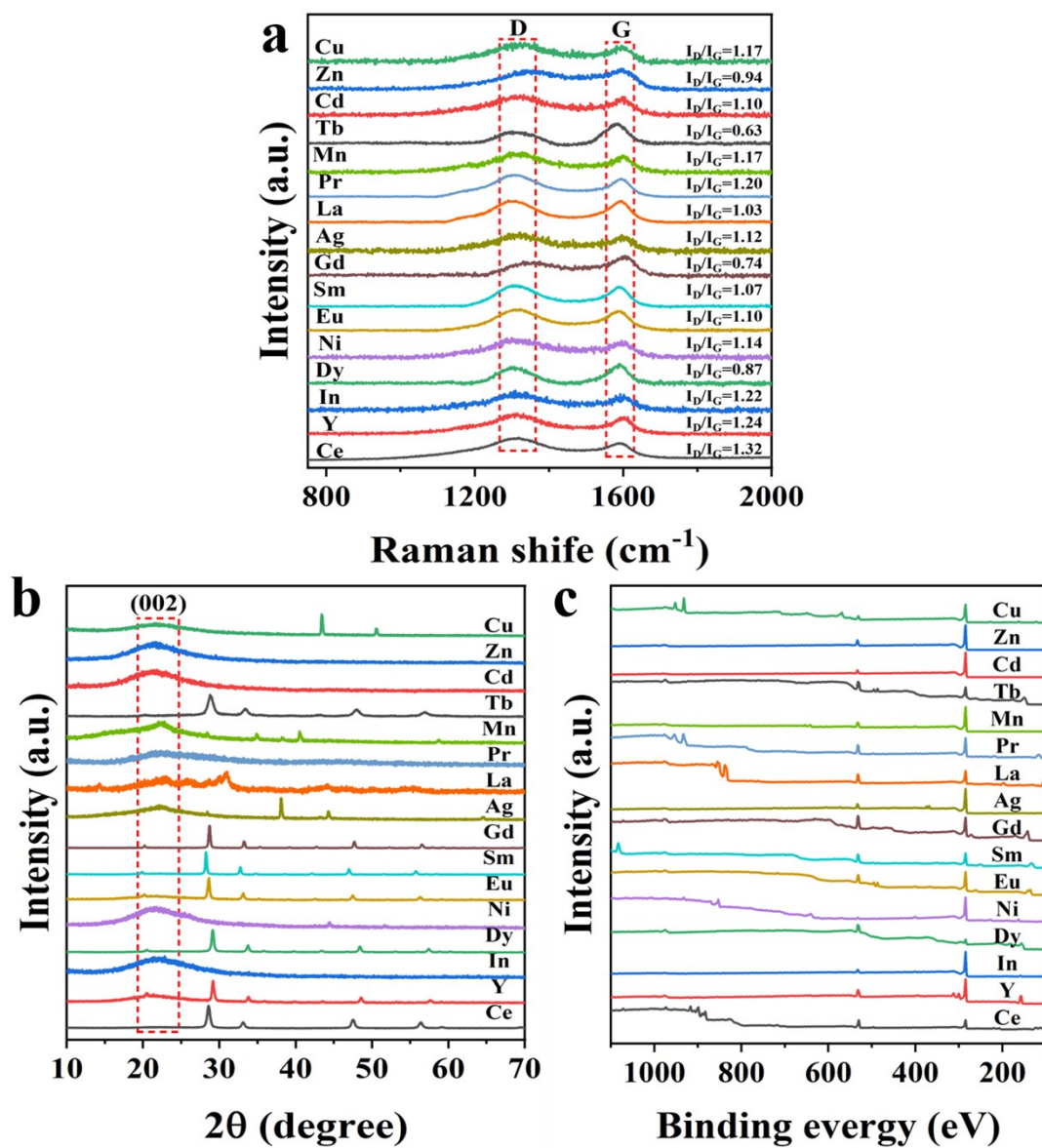


Fig. S13. CNFs with better mechanical properties: (a) Raman spectra; (b) XRD patterns; (c) XPS full spectra.

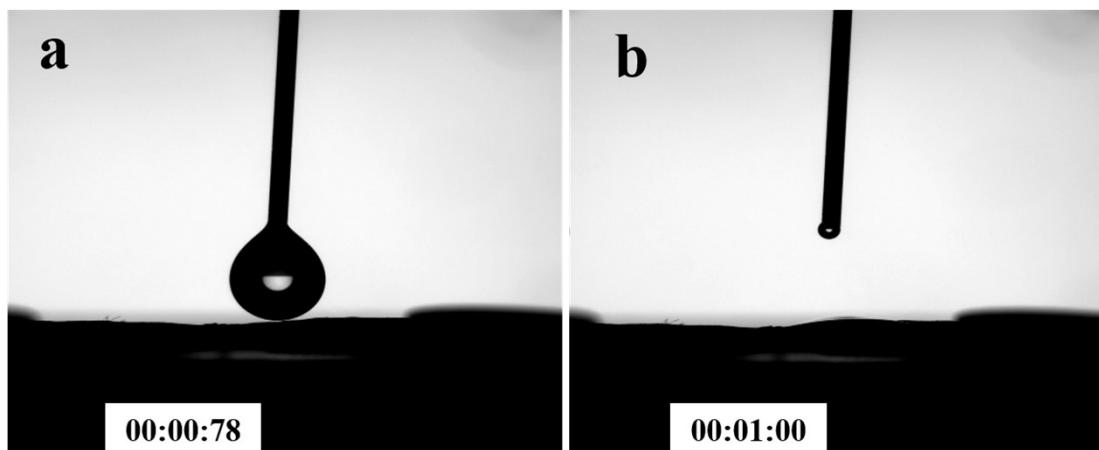


Fig. S14. Contact angle test of CNF-Zn.

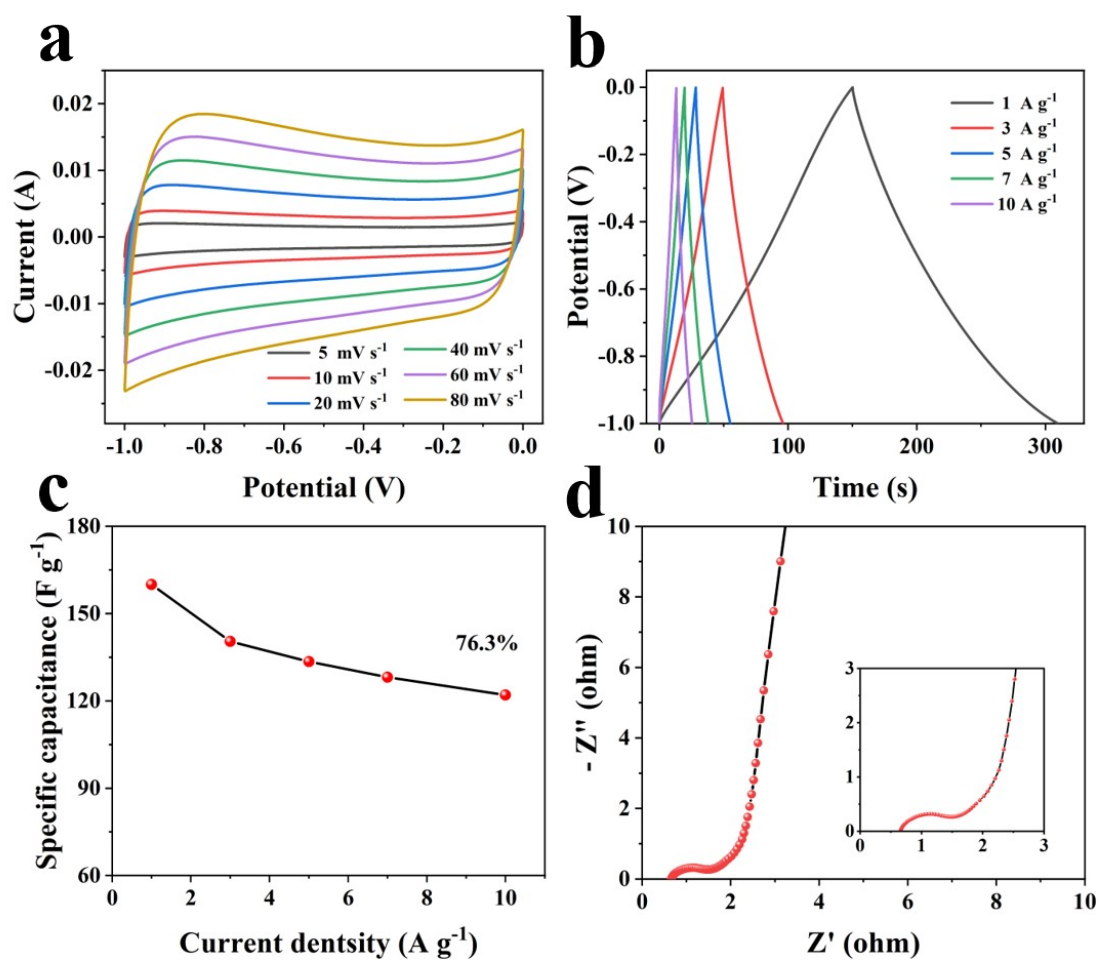


Fig. S15. Electrochemical performance test of CNF-Zn single electrode: (a) CV curves at different scanning rates; (b) GCD curves at different current densities; (c) Rate performance diagram; (d) Nyquist diagram (inset: magnified plot for the high frequency region).

References

1. M. Minagawa, K. Miyano, M. Takahashi and F. Yoshii, Infrared characteristic absorption bands of highly isotactic poly(acrylonitrile), *Macromolecules*, **1988**, *21*, 2387-2391.
2. D. Mathieu, M. Defranceschi, G. Lécayon and J. Delhalle, Insight into polyacrylonitrile molecular structure from calculated vibrational frequencies and infrared intensities of model oligomers, *Chem. Phys.*, **1994**, *188*, 183-195.