

**An easily accessible carbon material derived from  
carbonization of polyacrylonitrile ultrathin films: ambipolar  
transport properties and application in CMOS-like inverter**

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Electronic Supplementary Information  
(ESI)

## Electronic Supplementary Information

### Experimental Section

**Preparation of carbonized PAN ultrathin film:** 3.5 g Polyacrylonitrile (PAN, Sigma-Aldrich, Mw~150,000) was dissolved in 50 ml N,N-dimethylformamide (DMF) at 80 °C for 4 h under continuous agitation using a magnetic stirrer in an Erlenmeyer flask to form a 70 mg/ml solution. PAN solutions with concentration ranging from 10 mg/ml to 1 mg/ml were obtained via stepwise dilution. Si wafer with a 300 nm SiO<sub>2</sub> and quartz substrates (typically 1 cm × 1 cm) were rinsed successively with water, ethanol, and acetone, respectively. Afterwards the substrates were dried with N<sub>2</sub> stream and treated by O<sub>2</sub> plasma for 6 minutes. Under cleanroom conditions PAN with concentrations of 1, 1.5, 2, 3, 5 and 10 mg/ml was spin-coated onto the substrates at angular speeds between 5000 and 9000 rpm for 45 s. The precursor (PAN film) was oxidized in air at 300 °C for 4 h in a vacuum tube furnace with heating rate of 1 °C/min. Then the preoxidized film was carbonized under nitrogen at different temperatures (500 °C, 550 °C, 600 °C, 700 °C, 800 °C) for 4 h in vacuum tube furnace also with heating rate of 1 °C/min.

**Fabrication and Characterization of FETs and Inverters:** Bottom-gate top-contact FET devices and inverters were fabricated using n-Si wafer with a 300 nm SiO<sub>2</sub> served as the gate electrode and dielectric layer, respectively. After the PAN ultrathin film was carbonized, 30-nm thick gold source and drain contacts were deposited and patterned by a lift off technique. The channel length and width were 50 and 350 μm, respectively. The electrical transport measurements of the FET devices were carried out at room temperature using a Keithley 4200 semiconductor parameter analyzer in a glove box under nitrogen. The hole and electron mobilities were calculated from  $\mu = (L/WC_iV_{sd})(\Delta I_{sd}/\Delta V_g)$ , where L and W are the channel length and width, C<sub>i</sub> the areal capacitance of the dielectric, V<sub>sd</sub> the source–drain voltage, I<sub>sd</sub> the source–drain current and V<sub>g</sub> the gate voltage.  $\Delta I_{sd}/\Delta V_g$  were obtained from the respective linear regime of these transfer curves.

**Film characterization:** The morphology and thickness of the ultrathin films were measured using AFM (Nanoscope IV, Digital Instruments). UV-vis transmittance spectra of ultrathin films fabricated on quartz substrate were recorded on a JASCOV-570 spectrophotometer. X-ray diffraction (XRD) was measured on D/max2500 operated at 40 kV voltage and a 200 mA current with CuKα source ( $\kappa = 1.541 \text{ \AA}$ ). Raman spectra were taken with an iHR550 Jobin-Yvon spectrometer using an excitation wavelength of 473 nm. X-ray photoelectron spectroscopic (XPS) analysis was performed on an ESCALab220i-XL electron spectrometer from VG Scientific using 300W AlKα radiation. Ultraviolet photoemission spectroscopy (UPS) was performed by on an AXIS ULTRA DLD with a He I (21.2eV) source.

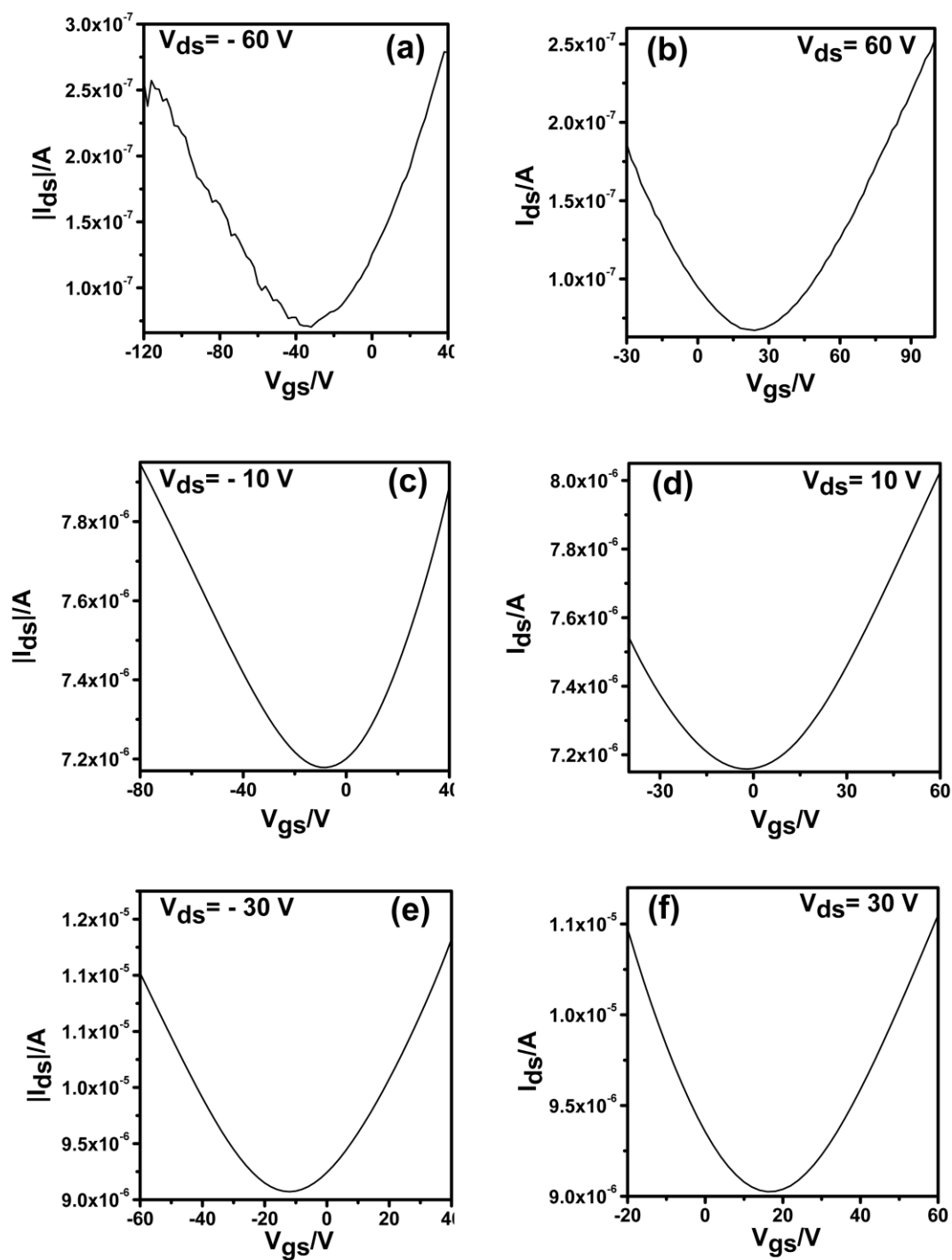


Figure S1. Transfer characteristics of FET devices with carbonized ultrathin PAN film semiconductor layer carbonized at (a, b) 500 °C; (c, d) 550 °C; (e, f) 600 °C.

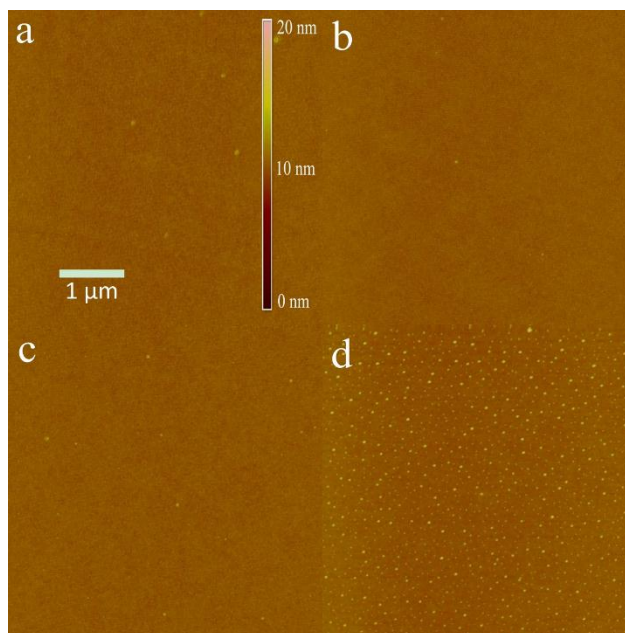


Figure S2. AFM images of carbonized PAN ultrathin films (3 mg/ml, 5000 rps) at different carbonization temperatures. (a) 500 °C (b) 550 °C (c) 600 °C (d) 700 °C

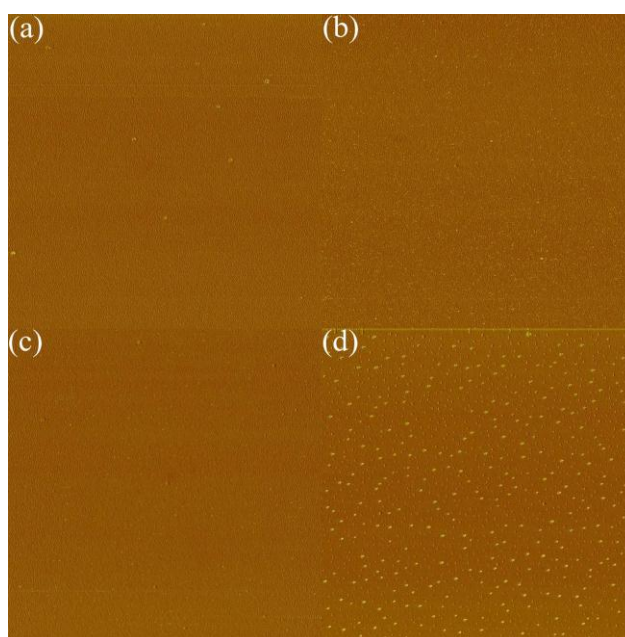


Figure S3. AFM Phase images of PAN ultrathin films carbonized at (a) 500 °C (b) 550 °C (c) 600 °C (d) 700 °C. All images have a scale bar of 5 μm.

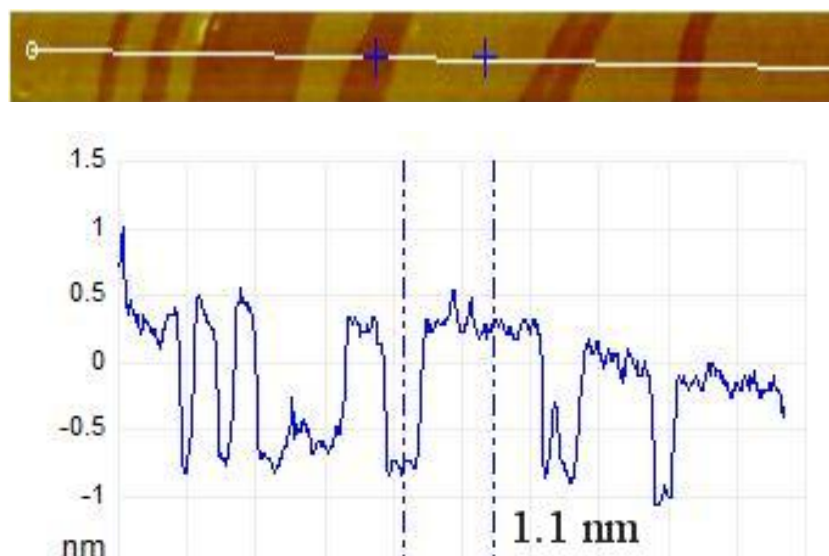


Figure S4. AFM cross section images of PAN ultrathin film carbonized at 700 °C. (2 mg/ml, 5000rpm)

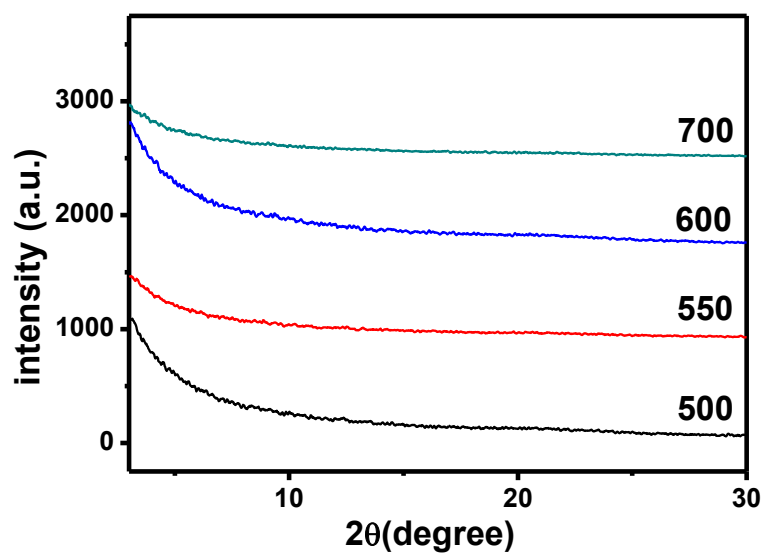


Figure S5. X-ray diffraction (XRD) patterns of carbonized PAN ultra-thin films in  $\theta$ - $2\theta$  configuration.

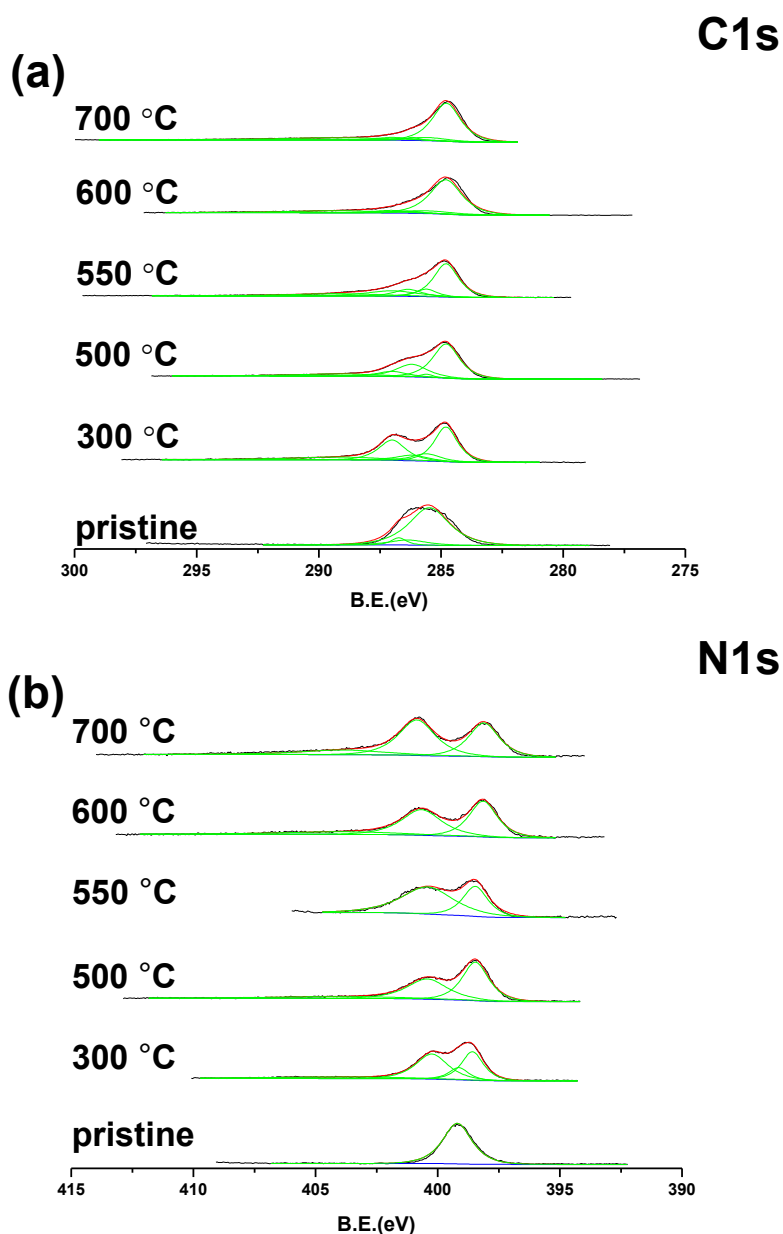


Figure S6. Comparison of XPS spectra for PAN ultrathin films on Si/SiO<sub>2</sub> substrate after treatment: (a) C1s peaks (b) N1s peaks.

**XPS Analysis:** X-ray photoemission spectroscopy (XPS) was performed to investigate the changes of chemical compositions during the thermal process. The XPS data in Figure S6 shows the high-resolution XPS spectra of C1s, N1s peak of PAN ultrathin film in each step. These changes are in agreement with previous proposed reaction mechanisms during preoxidization and carbonization. Before heat treatment, the C1s spectra of the PAN ultrathin film exhibits three distinct components, peaked at 285.48 (C\*H<sub>2</sub>CHCN), 286.35 (CH<sub>2</sub>C\*HCN) and 286.73 eV (CH<sub>2</sub>CHC\*N) respectively. The binding energy at 399.20 eV is typical N1s peak of CN in PAN. In the preoxidization step, the linear PAN molecules were converted to a cyclic structure and oxidized. C1s peaks located at 284.8, 285.6, 286.2, 287.0 and 289.2 eV represent C=C, C-N, C-O, C=O, C(O)O bond respectively. As for N1s, new peaks located at 398.46, 400.43 and 403.89 eV

appear, corresponding to C-N, C=N and pyridine-N-oxide. In the carbonization step, the cyclized structure starts to link up in the lateral direction by dehydration and denitrogenation. The content of C-C increases while C-O and C=O decreases as the carbonization temperature rising, this can be concluded from the peak area. At the same time, the relative amount of N atoms corresponding to graphitic-N (peak at 401 eV) increase compared to pyridinic-N (peak at 398.6eV).

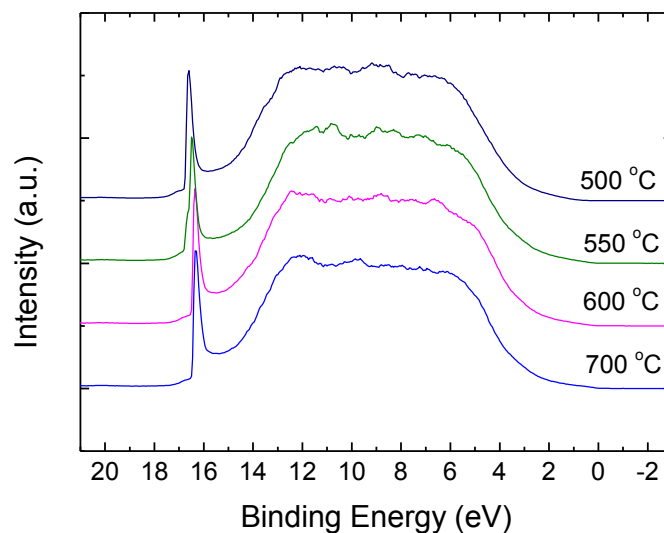


Figure S7. Ultraviolet photoelectron spectroscopy (UPS) of PAN ultrathin films on Si substrate carbonized at different temperatures.