Electronic Supplementary Information

Three-Dimensional Quantitative Analysis of Porosity Evolution and Inheritance from Biomass to Biochar through Pyrolysis

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Additional Experimental Section

Chemical and Materials

This tobacco is from Technology Center, China Tobacco Zhejiang Industrial Co. Ltd, Hangzhou, China.

Experimental methods

Prior to transmission electron microscopy (TEM) characterization, tobacco sample underwent a preprocessing step to ensure proper dispersion on the copper grid for the electron microscope imaging. The sample was initially ground in a mortar and pestle and then dissolved in an ethanol solution. After ultrasonic dispersion of the solution, the supernatant was dropped onto the copper grid. Upon natural evaporation of the alcohol, the sample achieved good dispersion on the copper grid. It is important to note that the supernatant should not be too concentrated; otherwise, it may lead to stacking of tobacco samples, affecting the observation. The copper grid was placed on the sample holder of the electron microscope and then introduced into the specimen chamber for electron microscope characterization.

For scanning electron microscope (SEM) imaging, the tobacco was cut into appropriate sizes and then affixed using conductive adhesive to ensure conductivity and stability.

Before characterization by nitrogen adsorption/desorption, tobacco samples underwent grinding treatment as well, similar to characterization by TEM.

Carbonization of tobacco was carried out according to the reported literature[1]: (1) Cleaning: Firstly, the tobacco leaves were cut into small pieces and soaked in pure water. They were then placed in an ultrasonic cleaner and sonicated for 30 minutes at room temperature. After ultrasonic cleaning, the precursor was filtered and collected, then dried in a vacuum oven at 60°C for 3 hours. (2) Pretreatment: After vacuum drying, 5 g of the precursor was transferred to an agate mortar and ground for about 20 minutes. Then, a solution containing 1 g of melamine in methanol (200 mL) was added, and the mixture was stirred at room temperature until the methanol completely evaporates. (3) Calcination: The pretreated precursor was loaded into a quartz boat, which was then placed in a tube furnace. The temperature was then raised to the carbonization temperature (at a heating rate of 1°C min^{-1} for 700℃ and 2°C min^{-1} for 900 ℃)

under a nitrogen (99.9%) atmosphere, and maintained at this temperature for 1 hour under a nitrogen atmosphere before being naturally cooled to room temperature under nitrogen flow. (4) Washing: Finally, the resulting carbonized samples were washed several times with 2 M HCl, 1 M HNO_3, and pure water successively, then dried in an oven at 80℃.

Materials Characterization

The microstructure of tobacco sample was observed by using Environmental Transmission Electron Microscopy (ETEM, Themis ETEM, 300kV). The micro-morphological structure and element distribution of tobacco were observed using a Field Emission Scanning Electron Microscope (ZEISS G500). Gas adsorption performance was determined using the BSD-PM High-Performance Specific Surface Area and Micropore Analyzer (Beijing Best Instrument Technology Co., Ltd.). Before testing, samples weighing 100 mg or more were first degassed at 200℃ for 8 hours. Surface area (SBET) was calculated based on nitrogen (N_2) adsorption data obtained using the Brunauer-Emmett-Teller (BET) method at -196℃.

Before conducting three-dimensional (3D) tomography, the tobacco samples were carefully placed onto narrow-slit grid carbon support membranes to ensure even distribution and adherence. The imaging was then performed using TEM with tilt series acquisition systematically carried out from -70° to 70° in precise 1° increments. Following data acquisition, a thorough alignment process was undertaken to correct any distortions or misalignments within the captured images. Subsequently, specific areas of interest, relevant to the desired structural features, were meticulously selected and cropped for further processing. The cropped data were then imported into Tomviz, a robust tomographic reconstruction software, to begin 3D reconstruction process. This involved the application of sophisticated algorithms, such as the TV Minimization algorithm, to reconstruct the volumetric structure from the series of 2D projections. Upon successful reconstruction, the resulting 3D volume underwent meticulous examination and analysis using dedicated 3D visualization software, enabling detailed exploration of the sample's internal structure. Furthermore, pore analysis was conducted within the sample, providing valuable insights into its microstructure and porosity distribution. This comprehensive workflow facilitated the detailed characterization and analysis of the tobacco and derived carbon materials at the nanoscale.

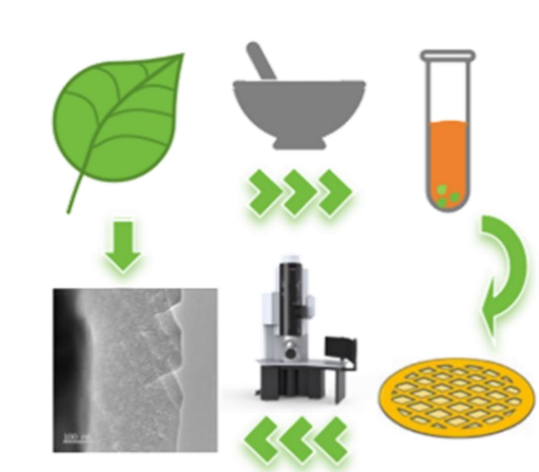
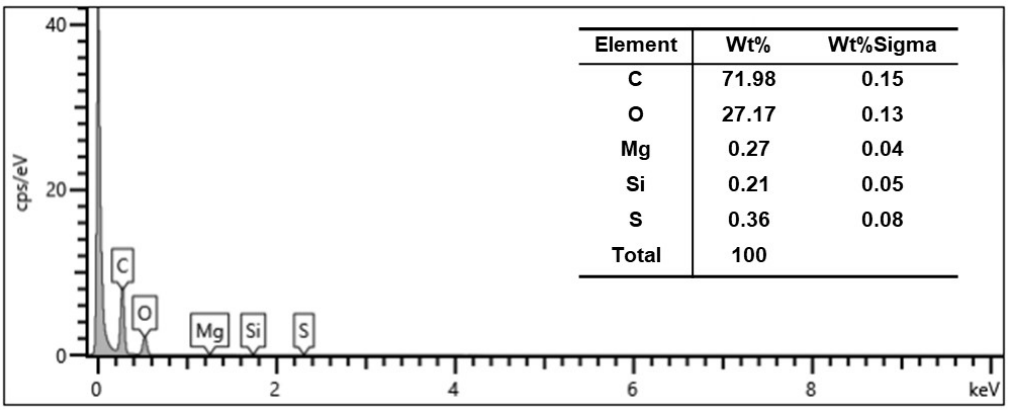


Figure S1. Model showing the pre-treatment of a tobacco sample for the TEM imaging process.



Element	Wt%	Wt%Sigma
C	71.98	0.15
O	27.17	0.13
Mg	0.27	0.04
Si	0.21	0.05
S	0.36	0.08
Total	100	

Figure S2. The EDX spectrum of tobacco.

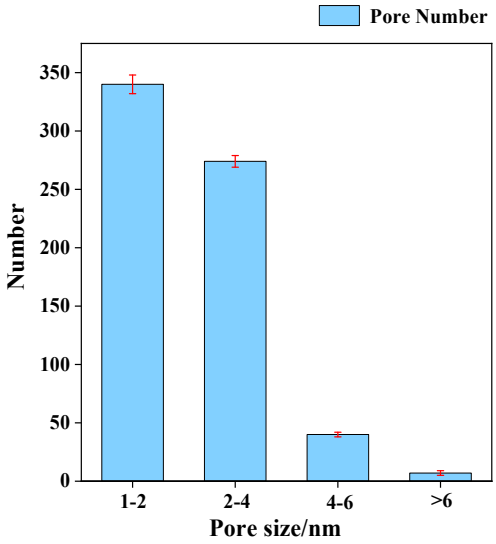


Figure S3. Statistical diagram of 2D pore size and number from TEM image in Figure 1c.

Pore analysis was conducted using the ImageJ software. First, the scale was calibrated by defining the size corresponding to each pixel, ensuring accurate dimensional analysis. This was done by using a known reference scale or calibration grid within the TEM images. After the calibration step, each individual pore within the tobacco samples was meticulously identified and labeled. This labeling process involved marking the boundaries of each pore to distinguish them from the surrounding matrix. Finally, the software was used to measure and export the size dimensions of each labeled pore, providing quantitative data on pore size distribution.

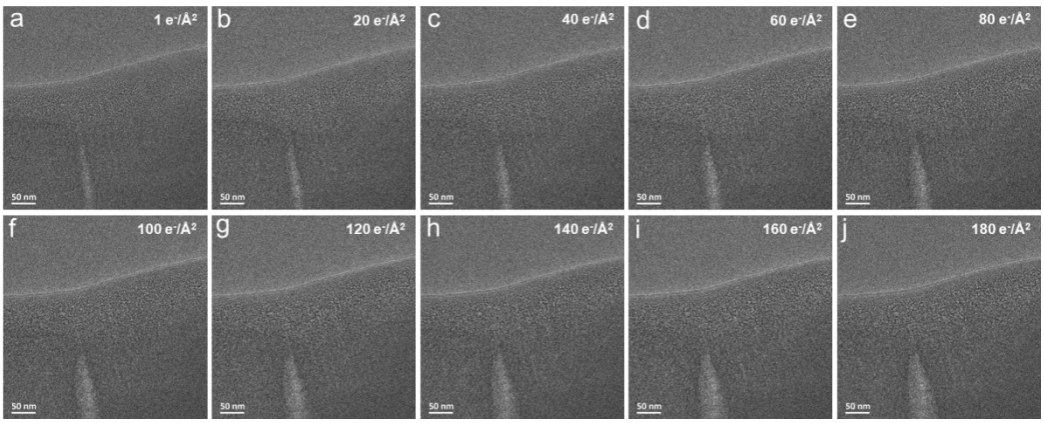


Figure S4. TEM images showing the electron irradiation damage of tobacco. The upper right inset of each TEM image is the corresponding cumulative dose.

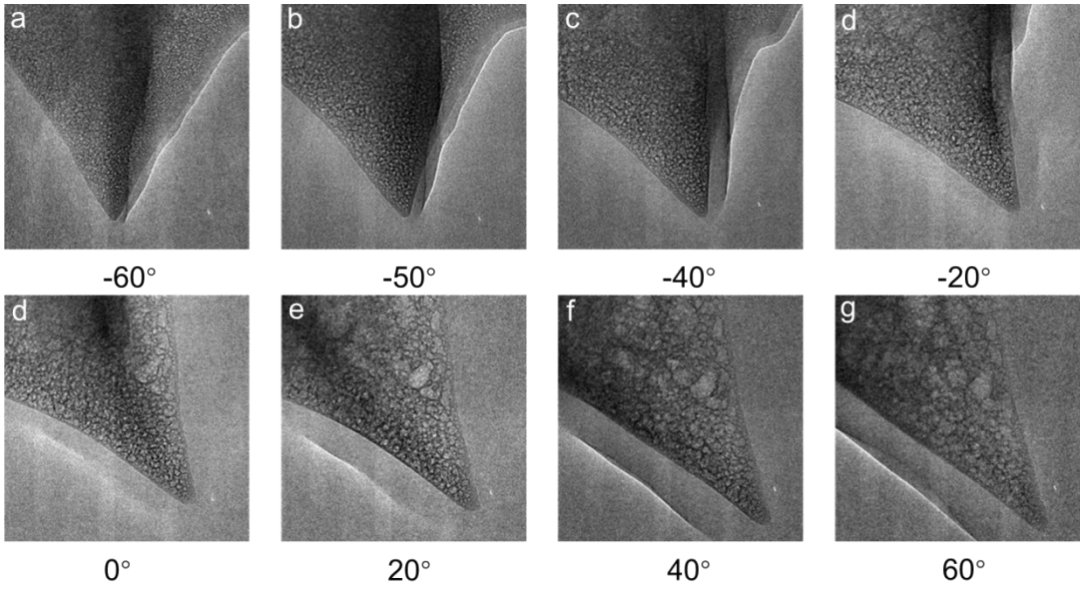


Figure S5. Representative TEM images that titled from -60° to 60°.

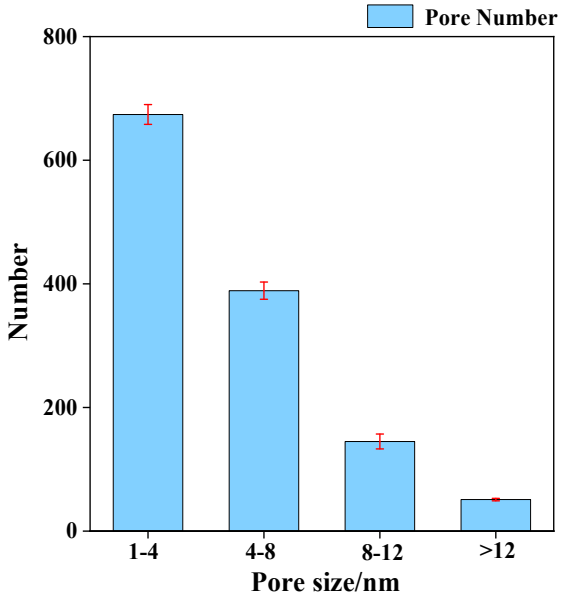


Figure S6. Statistical diagram of 3D pore size and number from electron tomography.

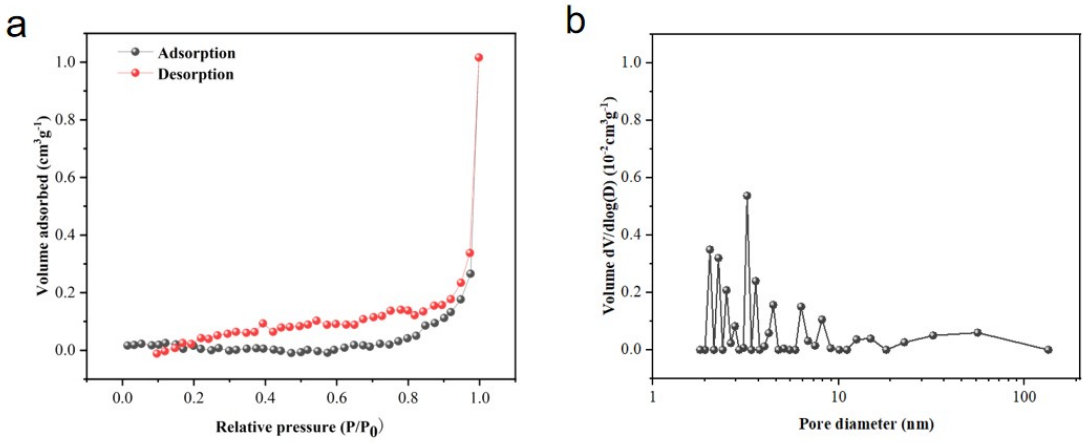


Figure S7. (a) N_2 adsorption and desorption isotherms of tobacco. (b) Corresponding pore size distribution.

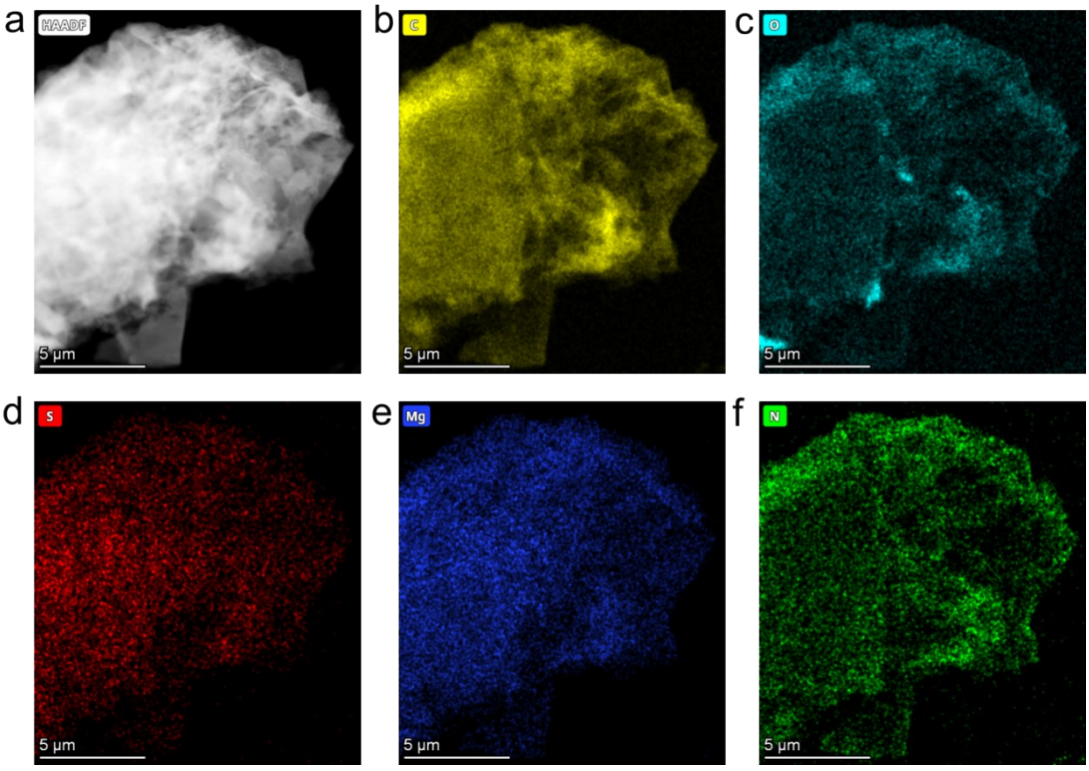


Figure S8. The EDX elemental mapping images of tobacco biomass after calcination at 900℃.

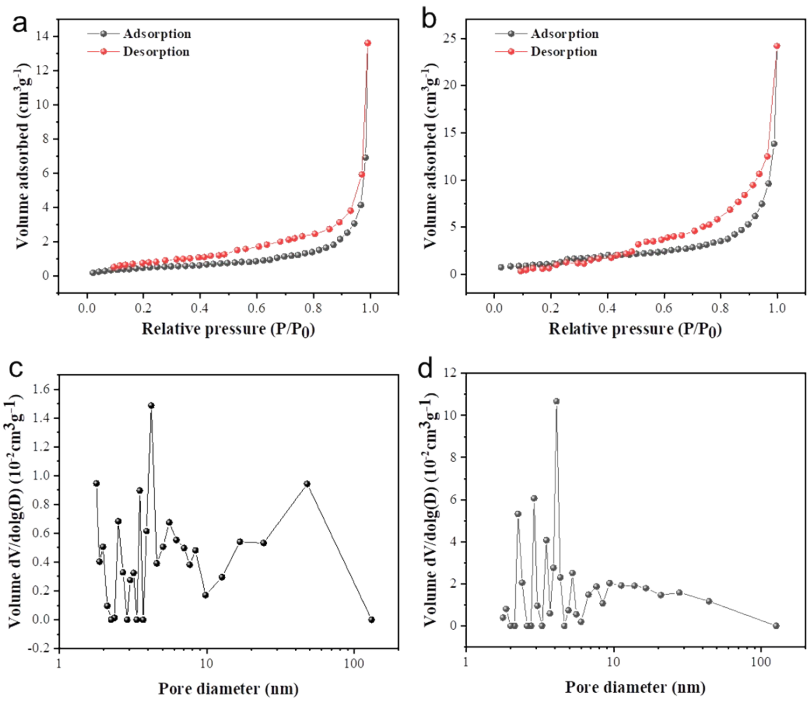


Figure S9. (a) N_2 adsorption and desorption isotherms and (c) corresponding pore size distribution of tobacco-derived carbon materials that prepared by calculation at 700℃. (b) N_2 adsorption and desorption isotherms and (d) corresponding pore size distribution of tobacco-derived carbon materials that prepared by calculation at 900℃.

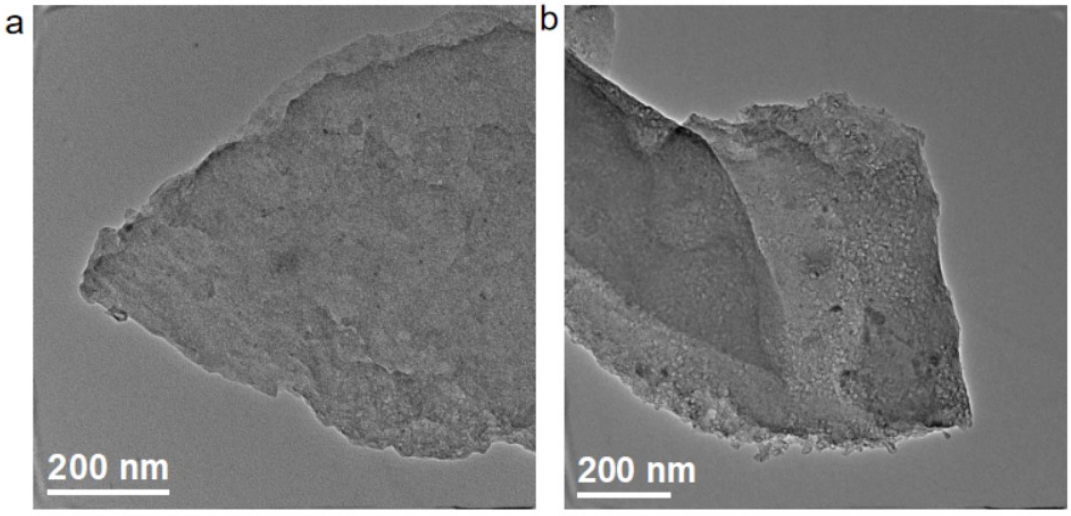


Figure S10. TEM images of tobacco biomass after calcination at (a) 700℃ and (b) 900℃.

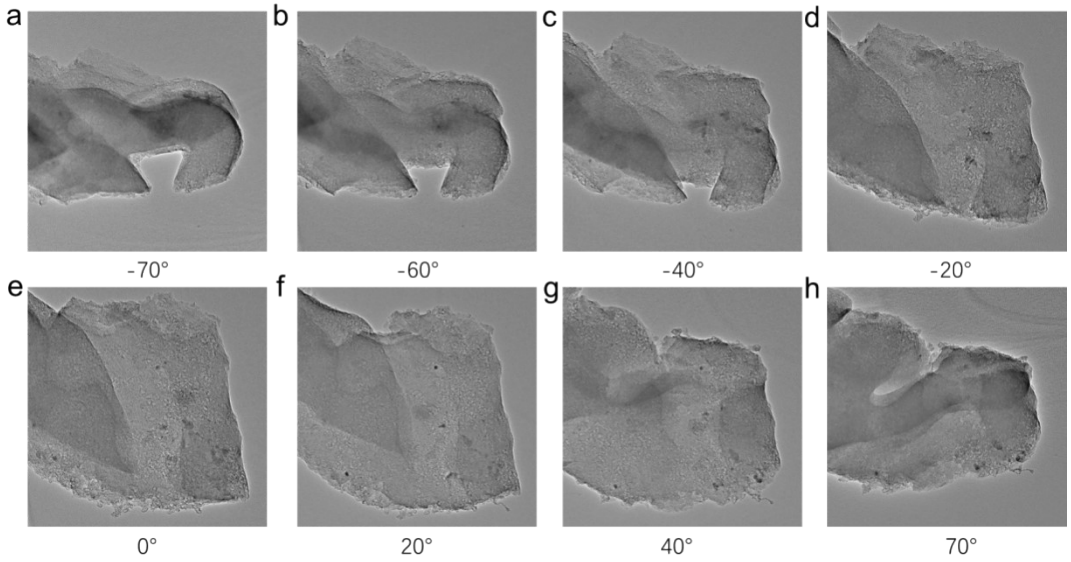


Figure S11. Representative TEM images that titled from -70° to 70°.

References

1. Y. Sha, J. Lou, S. Bai, D. Wu, B. Liu and Y. Ling, *Mater. Res. Bull.*, 2015, **64**, 327-332.