Electronic Supplementary Material (ESI) for Faraday Discussions.

Electronic Supporting Information

Molten-salt treatment of waste biomass for preparation of carbon with enhanced capacitive properties and electrocatalytic activity towards oxygen reduction

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Experimental details :

Materials Characterizations. Powder X-ray diffraction (XRD) patterns were collected on a Shimadzu XRD-6000 by using irradiation of Cu Kα ($\lambda = 1.5406$ Å) at a scanning rate of 1°C min^{-1}. Surface functional groups were investigated with a Fourier transform infrared spectroscopy (FTIR) analyzer (NICOLET 5700 FTIR Spectrometer) by using the standard KBr method. Raman spectra were recorded by using WITEC CRM200 Raman System with the excitation source at 532 nm. X-ray photoelectron spectroscopy (XPS) spectra were measured on an ESCALAB 250Xi (Thermo Fisher) spectrometer with Al (Ka) source. The C 1s signal at 284.6 eV was taken as a reference for calibration. XPS Peak 4.1 software was employed to deconvolve the C 1s and O 1s peaks with a Gaussian and Lorentzian mix-product function (20% Lorentzian maximum contribution) after subtracting Shirley background. Brunauere-Emmette-Teller (BET) surface area was tested by using N_2 adsorption/desorption isotherms at 77 K (Micromeritics ASAP 2020 automatic analyzer). Microstructures of the samples were examined by using Field-emission scanning electron microscope (SEM, JEOL JSM-6700F microscope operated at 5 kV) and Atomic Force Microscopy at room temperature and under ambient conditions (AFM, MFP-3D, Asylum Research, USA, commercial Ti/Pt coated Silicon conductive tip). For AFM measurements, the samples were first ultrasonicated in absolute alcohol and the suspension was then pipetted and dropped onto a single-crystal silicon wafer and dried in air.

Electrochemical Measurements. All electrochemical tests were carried out by using an A Solartron Analytical 1470E CellTest System. For symmetric full-cell capacitors, the active material (i.e. MS-derived carbon powder), binder (polytetrafluoroethylene, PTFE) and conducting agent (super P) in a mass ratio of 8:1:1 were mixed together with the addition of several drops of ethanol.

The resulting slurry was rolled into film through a rolling machine. The film was cut into a circle with the diameter of 10 mm, which was then die-pressed over metallic Ti mesh under 3 tons. The electrodes were thoroughly vacuum dried at 120 °C overnight. Symmetric full cell in 1 M $MeEt_3NBF_4$ in acetonitrile ($MeEt_3NBF_4$/AN) of the materials was assembled into coin-cell configurations (CR-2016) in an Ar-filled glove box with the concentrations of moisture and oxygen below 1 ppm. Celgard 2400 was used as the separators. The active material is 2.3±0.2 mg in each single electrode. Electrochemical Impedance Spectroscopy (EIS) measurements were performed by applying an AC voltage of 5 mV amplitude at open circuit voltages in the 100 kHz to 100 mHz frequency range.

The gravimetric capacitance for a single electrode C_s (F g^{-1}) was calculated according to CVs or galvanostatic charge–discharge profiles with the following equation:

$$C_s = \frac{2Q}{Vm} \ \text{(F/g)}$$

Q (C) is the integrated charge for the discharge segment, *V* (V) is the cell voltage after ohmic drop; *m* (g) is the mass of active materials in a single electrode.

The energy density *E* (Wh kg^{-1}) and power density *P* (W kg^{-1}) (based on the total mass of active materials in the two electrode cell) were calculated based on the corresponding galvanostatic charge–discharge profiles according to:

$$E = \frac{1}{2}\frac{C_s}{4}V^2\frac{1}{3.6}$$

$$P = \frac{E}{t}$$

t is the discharge time (h).

For electro-catalytic activities towards the oxygen reduction reaction (ORR) in 0.1 M aqueous KOH, the carbon-modified glassy carbon rotating disk electrode (RDE, Pine Modulated Speed Rotator), Ag/AgCl and Pt wire were employed as the working, reference and counter electrodes, respectively. For preparation of the working electrode, 15 mg of catalyst (MS-derived carbon) and 0.5 mL of Nafion solution(1 mL of 5 wt% Nafion solution were dispersed in 50 mL of isopropanol) were ultrasonicated to form a homogeneous ink. Then 10 μL of the catalyst ink (containing 0.3 mg of catalyst) was loaded on a glassy carbon electrode with a diameter of 5 mm (loading ~ 1.529 mg cm^{-2}). Electrocatalytic activity of the samples towards ORR was tested in aqueous 0.1 M KOH (saturated by O_2) using linear sweep voltammetries (LSV) with a scan rate of 10 mV s^{-1} in different rotating rates. The ORR kinetics was analyzed by the Koutecky-Levich (K-L) equation [Eq. (1)]:

$$\frac{1}{J} = \frac{1}{J_k} + \frac{1}{B\omega^{0.5}} \qquad (1)$$

where $\boldsymbol{J_k}$ **(mA cm^{-2})** is the kinetic current density and $\boldsymbol{\omega}$ **(rpm)** is the rotating rate of the electrode. The parameter B could be determined from the slope of the K-L plots based on the Levich equation [Eq. (2)]:

$$B = 0.2nF(D_{O_2})^{2/3}\nu^{-1/6}C_{O_2} \qquad (2)$$

where $\boldsymbol{n}$ is the number of electrons transferred per oxygen molecule, $\boldsymbol{F}$ is the Faraday constant (F=96485000 mA s mol^{-1}), $\boldsymbol{D_{O2}}$ is the diffusion coefficient of O_2 in 0.1 M KOH (1.9*10^{-5} cm^2 s^{-1}), $\boldsymbol{\nu}$ is the kinetic viscosity (0.01 cm^2 s^{-1}), and $\boldsymbol{C_{O2}}$ is the bulk concentration of O_2 (1.2*10^{-6} mol cm^{-3}). The value 0.2 is employed when the rotation speed is expressed in rpm (revolutions per minute).

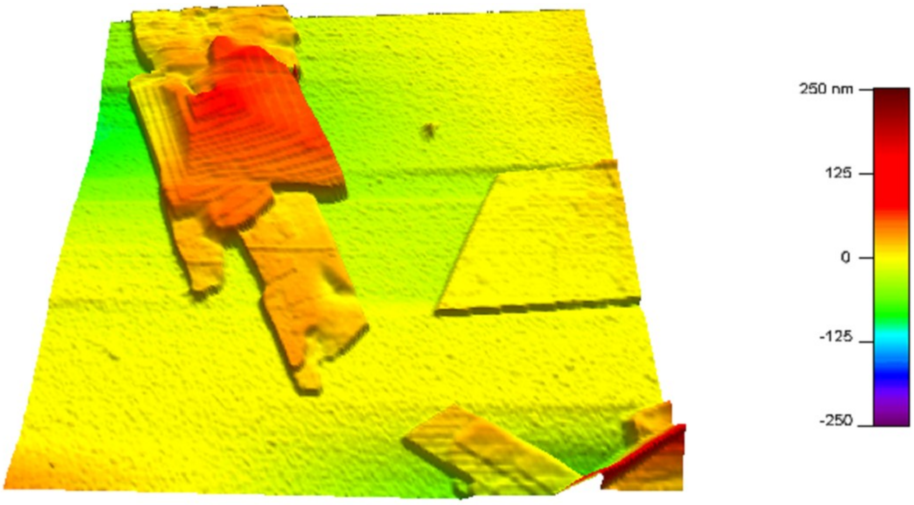

Figure S1. AFM images the samples after being treated in molten carbonates.