Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Electronic Supplementary Information (ESI) for:

An Assembly of Carbon Dots and Carbon Sheets from Plant Biomass for Excellent Oxygen Reduction Reaction

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Supplementary experimental section

Characterization methods. The optical properties of samples were accomplished on UV-NIR diffuse reflectance Spectrometer (Agilent, Cary 5000, USA) and Fluorescence Spectrophotometer (HITACHI, F4600, Japan). The morphologies of the as-prepared materials were studied by using transmission electron microscope (TEM, FEI Tecnai G^2 F20 S-TWIN electron microscope, operating at 200 kV), combined with energy dispersive X-ray spectroscopy (EDS), and field emission scanning electron microscope (SEM, ZEISS Sigma 500). The atom force micro analysis was conducted on a MFP-3D Infinity Asylum Research AFM (AFM, AIST-NT Instruments, USA). The phase structures of corresponding precursors and products were characterized with wide angle X diffraction (WAXD) and small angle X diffraction (SAXD) (XRD, Bruker D8 advance with Cu Kα, λ = 1.5418 Å). Raman spectra were recorded on a HR Evoltion Raman Spectrometer (Horiba Scientific, France) with excitation from the 514 nm line of an Ar-ion laser with a power of about 5 mW. X-ray photoelectron spectra (XPS) were recorded on a PHI quantera SXM spectrometer with an Al Kα = 1486.6 eV excitation source, where binding energies were calibrated by referencing the C1s peak (284.8 eV) to reduce the sample charge effect. The N_2 sorption isotherms were measured on surface area and pore size analyzer (ASAP2420-4MP, Micromeritics, USA) at 77 K. From the adsorption branch of isotherm curves in the P/P^o range between 0.05 and 0.35, the specific surface areas (S_{BET}) of BMNC are calculated by the multi-point Brunauer−Emmett−Teller (BET) method. The pore size distribution was evaluated by the non-localized density function theory (NLDFT).

Electrochemical measurements. All the electrochemical measurements were finished on a CHI760E electrochemical workstation in a three-electrode system, with a Pt wire as the counter electrode and Ag/AgCl electrode as the reference. The working electrodes, being from Pine company, are the rotating disk electrode (RDE) with a geometric surface area of 0.196 cm^2 or a rotating ring-disk electrode (RRDE) consisting of a glassy carbon (GC) disk surrounded by a Pt ring. The working electrode material was prepared by ultrasonication of mixture, consisting of 4 mg active materials, ethanol (720 μL) and Nafion (80 μL), for 40 min. The as-prepared solution (10 μL) was dropped onto glassy carbon of RRDE or RDE. 0.1 M

KOH solution and 0.1M $HClO_4$ solution were used as the electrolyte.

All potential values are converted to potential *versus* RHE according to the following equation (S1):

$$E_{vs.\ RHE} = E_{vs.\ Ag/AgCl} + E^{\theta}{}_{vs.\ Ag/AgCl} + 0.059pH \tag{S1}$$

All the samples were electrochemically cleaned by sweeping the potential from 0.20 to 1.20 V at 50 $mV\cdot s^{-1}$ in N_2 or O_2-saturated electrolyte until steady state cyclic voltammograms (CVs) were obtained. Linear sweep voltammetry (LSV) measurements were performed in an O_2-saturated electrode rotated at 10 $mV\cdot s^{-1}$ at different rotation speeds. The chronoamperometry (CP) were performed at 0.85 V for 15 h in O_2-saterated 0.1 M KOH solution on a RDE at 200 rpm for BMNC and at 0.92 V for 15 h for 20% Pt/C catalyst at the same conditions. The CP response of BMNC at 0.84 V and 20% Pt/C at 0.91 V were recorded with or without CH_3OH at 800 rpm, 4 mL CH_3OH for BMNC and 0.5 mL CH_3OH for 20% Pt/C being introduced into 100 mL of 0.1 M KOH solution at 400th second. Concentration of methanol is about 1 M and 0.125 M for BMNC and 20% Pt/C, respectively. The electrolytic solution was bubbled with either N_2 or O_2 at a flow rate of 40 sccm over 30 min before and during measurement. To get the current density, the as-obtained Faradaic current was normalized by the geometric surface area. The RRDE technology was conducted in 0.1 M KOH at 1600 rpm and the potential of ring is kept at 1.27 V (*vs.* RHE).

The % (H_2O_2) produced and the electron transfer number (n) were calculated according to reference.[S1] In this experiment, the collection efficiency of the ring electrode is 0.41. The value of N was obtained by testing $K_3[Fe(CN)_6]$ on CHI760E electrochemical workstation.[S2]

Preparation of homemade zinc–air battery. BMNC catalyst was loaded on carbon fiber paper to achieve the mass density of 1 mg cm^{-2}, functioned as the positive electrode. As the same time, the gas diffusion film (GDL) was trapped outside the positive electrode in order to allow oxygen to enter the contact cathode material. The electrolyte solution (6 M KOH and 0.5 M $Zn(OAc)_2$) was added in the middle of the positive and negative electrodes. Celgard 2340 microfibre filter was used as a separator and a polished high-purity Zinc plate was utilized as the negative electrode. All the tests proceeded under ambient atmosphere.

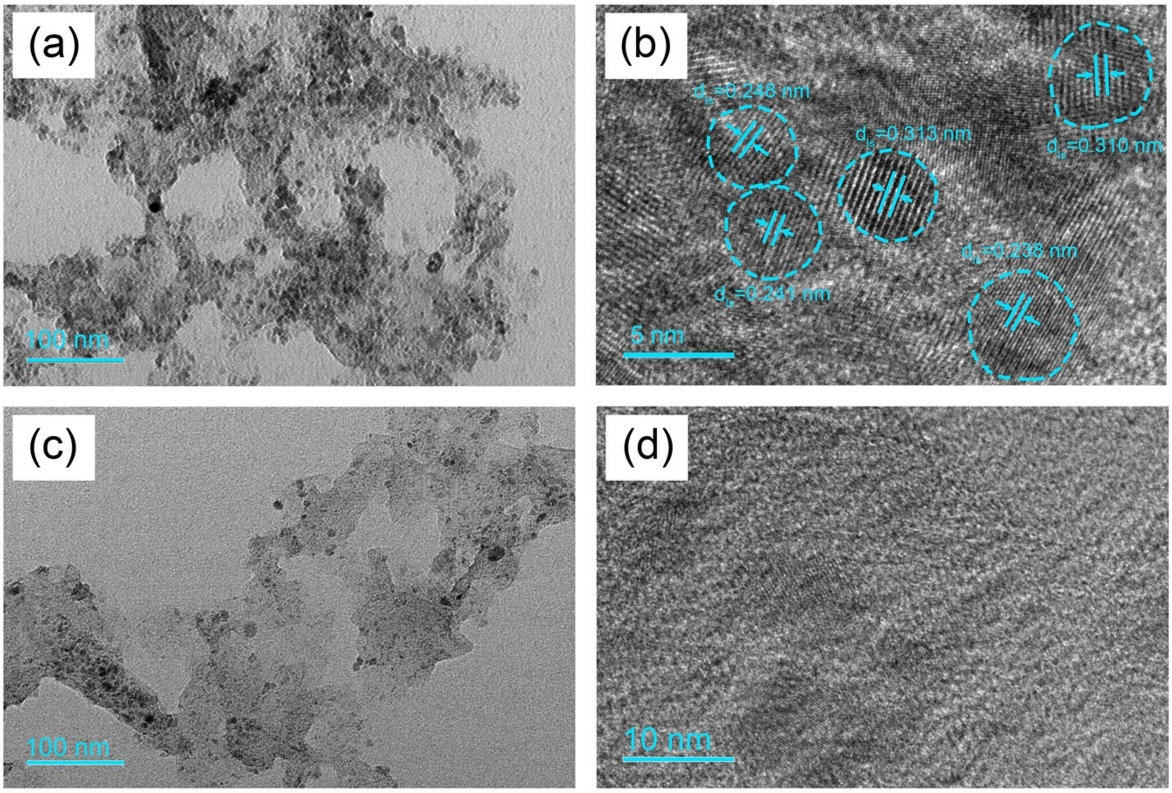

Fig. S1. The TEM images of (a, b) pre-CS; and (c, d) pre-HCS.

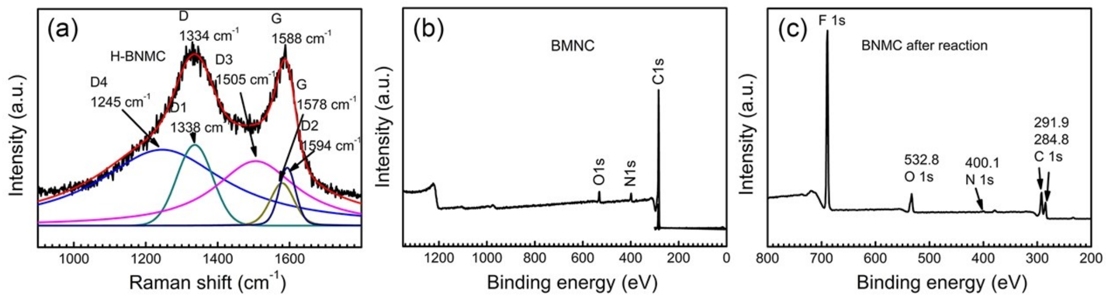

Fig. S2. (a) Raman spectrum of H-BNMC; and (b, c) XPS survey spectra of fresh BNMC and BNMC after reaction.

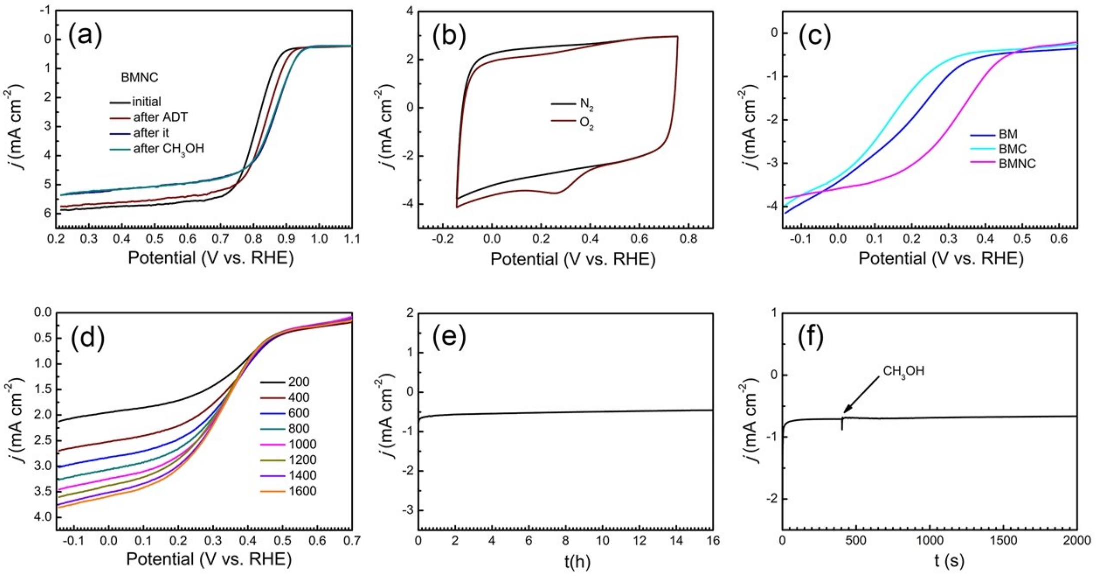

Fig. S3. The (a) LSV curves of BMNC initial, after ADT, after i-t and after addition of CH_3OH; (b) CV curves of ORR in O_2- or N_2-saturated 0.1M $HClO_4$; (c) LSV curves of ORR on BM, BMC and BMNC in 0.1M $HClO_4$; (d) LSV curves of ORR on BMNC at different rotation rates in 0.1M $HClO_4$; (e) CP curves on BMNC in 0.1M $HClO_4$; and (f) CP curves before and after addition of CH_3OH.

References

S1. Q. Zhao, Z. H. Yan, C. C. Chen and Chen, J. *Chem. Rev.* **2017**, *117*, 10121.

S2. U. A. Paulus, T. J. Schmidt, H. A. Gasteiger and R. J. Behm, *J. Electroanal. Chem.* **2001**, *495*, 134.