Electronic Supplementary Information

Tungsten Nitride Nanocrystals on Nitrogen-Doped Carbon Black as an Efficient Electrocatalyst for Oxygen Reduction Reaction

Youzhen Dong[1,2], *and Jinghong Li*[2*]

1 Institute of materials science and technology
Nanjing University of Aeronautics and Astronautics, Nanjing 210000, China
2 Department of Chemistry, Key Laboratory of Bioorganic Phosphorus Chemistry and Chemical Biology, Tsinghua University, Beijing 100084, China
Fax: +86 10 6279 5290; Tel: +86 10 6279 5290; E-mail: jhli@mail.tsinghua.edu.cn

1. Chemicals

All chemicals were of analytical grade and used without further purification. Ammonium metatungstate $(NH_4)_6H_2W_{12}O_{40}.nH_2O$) and Nafion solution (5 wt%) are purchased by Alfa Aesar. Ammonia gas (NH_3) purity is 99.999%.

2. Synthesis of Tungsten Nitride Nanocrystals on Nitrogen-Doped Carbon Black (WN/N-Carbon black)

0.07 g ammonium metatungstate and 0.37 g carbon black were dispersed in 100 mL deionized water by ultrasonication. The obtained solution was heated at 70 °C for 2 h, and then steamed to dry at 100 °C. Finally, the power was carbonized at 450 °C in air for 3 h and 700 °C in an NH_3 atmosphere for 3 h.

3. Characterizations

XRD patterns were obtained via a D8 Advance (Bruker) X-ray diffractometer with

CuK a radiation (l=1.5418). SEM images were obtained by means of a JSM 7401F, 3 KV. TEM images were obtained with a Hitachi model H-800 transmission electron microscope operating at an accelerating voltage of 100 kV. X-ray photoelectron spectroscopy (XPS) measurements were performed on a PHI Quantera Scanning X-ray Microprobe using a monochromic Al-Kα (λ = 1486.7 eV) (Binding energy is calibrated with C 1s - 284.8 eV).

4. Electrochemical measurement

All experiments were performed at room temperature. Before every measurement, the glassy carbon electrode (GCE) surface was polished using 50 nm Al_2O_3 slurry and washed with ethanol and deionized water in ultrasonic bath. The electrochemical cell was assembled with a conventional three-electrode system: a glassy carbon working electrode, an Ag|AgCl/KCl (saturated) reference electrode, and a Pt wire counter electrode. The homogeneous ink was prepared by dispersing 1 mg catalyst 1 mL in Nafion solution (0.5 wt%, aq) with at least 30 min sonication. Then 6 and 20 mL of the catalyst inks were coated onto a clean GCE of 3 and 5 mm in diameter for CV and RDE measurements. Electrochemical measurements were performed using a CHI 830 electrochemical analyzer coupled with a RDE system (Princeton Applied Research, Model 616).

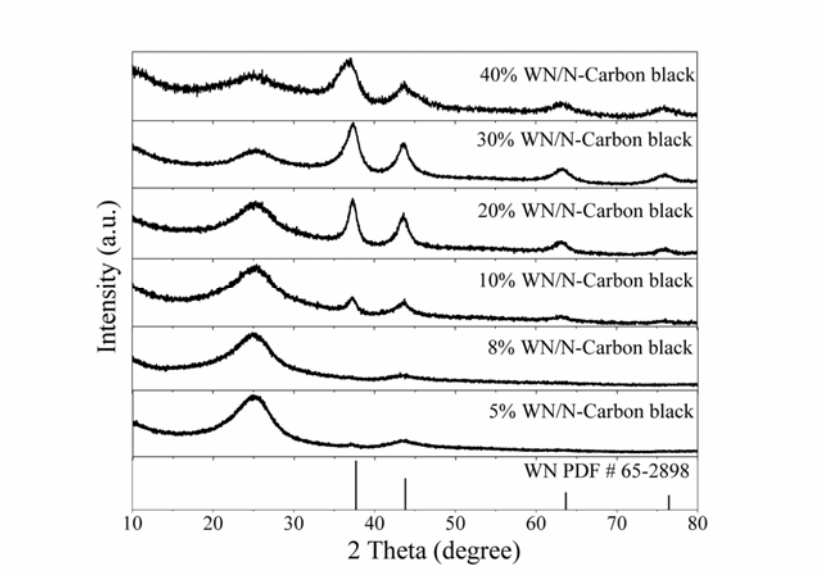

Figure S1. XRD parterns of WN/N-Carbon black with different contents of WN as indicated.

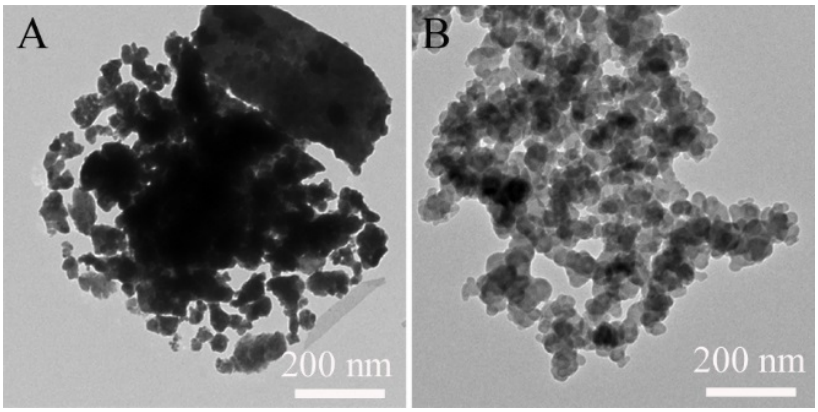

Figure S2. TEM images of pure WN and N-Carbon black.

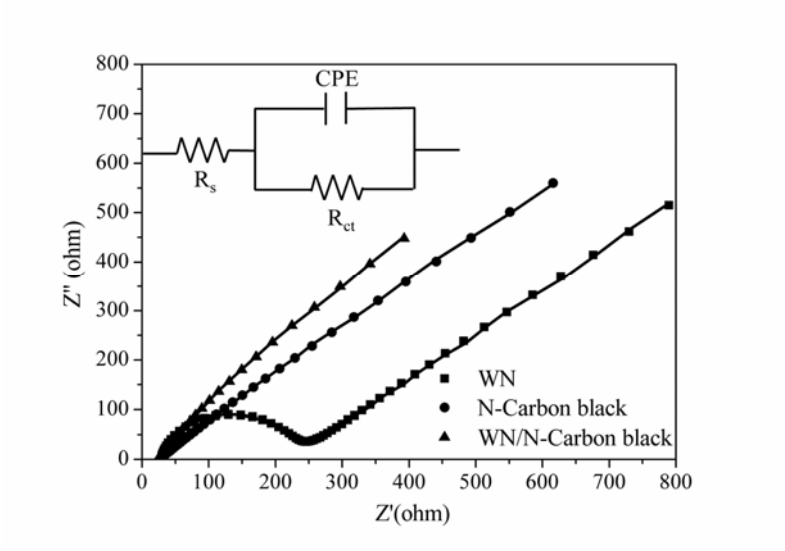

Figure S3. Electrochemical Impedance Spectra of WN, N-Carbon black and WN/N-Carbon black in 5 mM $Fe(CN)_6^{3-/4-}$ containing 0.5 M KCl from 0.1 Hz to 100 kHz with a signal amplitude of 10 mV. Inset is the equivalent circuit used to fit the impedance spectra. In the equivalent circuit, R_s, R_{ct}, and CPE were the electrolyte resistance, the electron-transfer resistance, and the chemical capacitance.

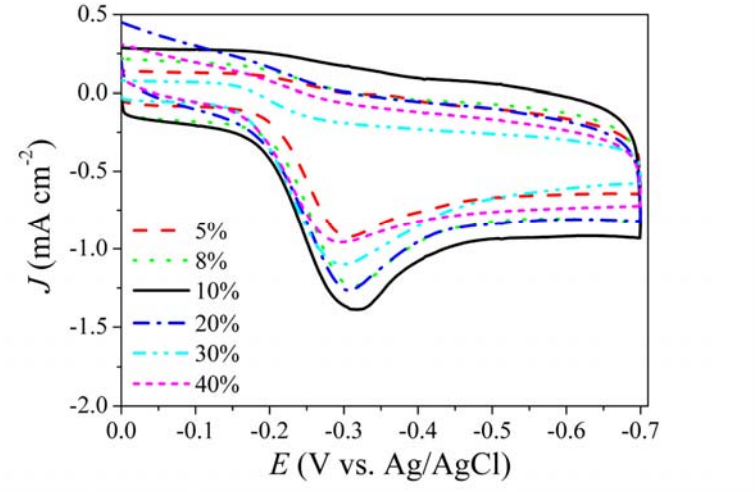

Figure S4. Cyclic voltammograms of WN/N-Carbon black with different contents of WN as indicated in O_2-saturated 0.1 M KOH solutions. Scan rate: 50 mV s^{-1}.

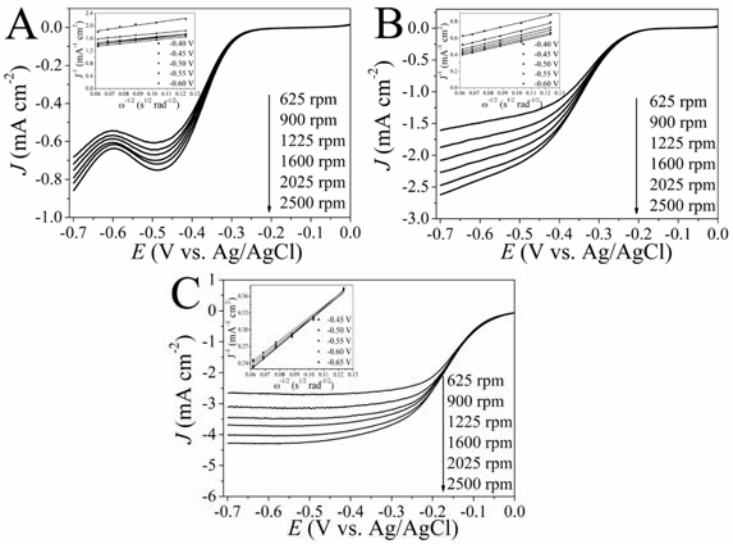

Figure S5. RDE voltammograms at different rotation rates of A) WN, B) N-Carbon and C) Pt/C in O_2-saturated 0.1 M KOH solutions. Sweep rate: 5 mV s^{-1}. Insets are the corresponding K-L plots at different potentials.

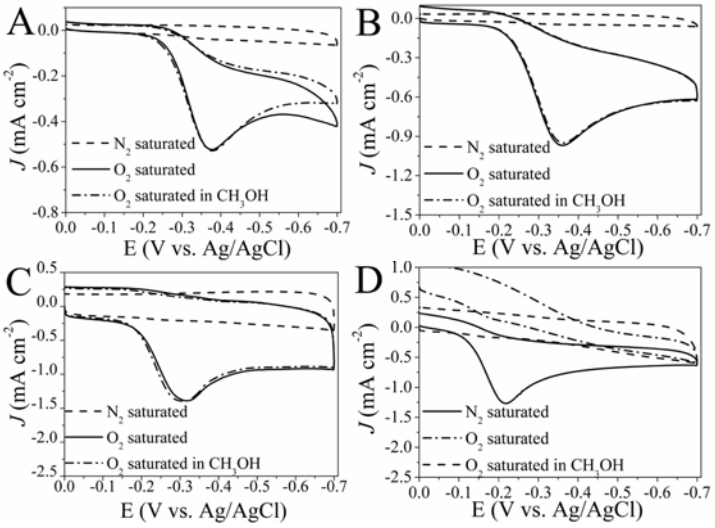

Figure S6. Cyclic voltammograms of A) WN, B) N-Carbon black, C) WN/N-Carbon black and D) Pt/C in N_2- and O_2-saturated 0.1 M KOH solutions as well as O_2-saturated 0.1 M KOH solution with 3 M methanol. Scan rate: 50 mV s^{-1}.