Supplementary Information

A metal-free catalyst: Sulfur doped and sulfur nanoparticales modified CMK-3 as electrocatalyst for enhanced N_2-fixtion

Jin Wang,[a] *Peng Wang,*[a] *Shuang Wang*[a, b, *] *and Jinping Li*[b, *]

[1] College of Environmental Science and Engineering, Taiyuan University of Technology, Jinzhong 030600, Shanxi, P.R. China,

[2] Shanxi Key Laboratory of Gas Energy Efficient and Clean Utilization, Taiyuan University of Technology, Taiyuan 030024, Shanxi, P.R. China

Materials

CMK-3 (99.6%) was purchased from Jiangsu XFNANO Materials Tech. Co., Ltd. (Nanjing China), ammonium chloride (NH_4Cl), salicylic acid ($C_7H_6O_3$), sodium citrate dehydrate ($C_6H_5Na_3O_7 \cdot 2H_2O$), pdimethylamino-benzaldehyde ($C_9H_{11}NO$), sodium nitroferricyanide dehydrate ($C_5FeN_6Na_2O \cdot 2H_2O$) and sodium hypochlorite solution (NaClO) were purchased from Aladdin Ltd. (Shanghai, China). Nafion (5 wt%) solution was purchased from Sigma-Aldrich Chemical Reagent Co., Ltd. Hydrochloric acid, sulfuric acid, hydrogen peroxide, hydrazine monohydrate ($N_2H_4 \cdot H_2O$) and ethyl alcohol (C_2H_5OH) were purchased from Sinopharm Chemical Reagent Co., Ltd, China. The ultrapure water used throughout all experiments was purified through a Millipore system. The high-purity nitrogen and argon gases used in the experiment came from Anxuhongyun technology development co. LTD. All reagents were analytical reagent grade without further purification.

S/CMK-3 preparation

A CMK-3 was dispersed in sodium thiosulfate solution ($Na_2S_2O_3$, 2.5 M, 50 mL) at the ambient temperature of 60℃ under magnetic stirring for 3 h. After the reaction, place the container in the refrigerator and pre-freeze for 0.5 h. The same pre-frozen (HCl, 1.0 M, 6 mL) was added to the solution drop by drop under magnetic stirring at 500 rpm. As obtained S/CMK-3 were washed several times by water and then subjected to oven drying at 60℃ overnight to obtain S/CMK-3.

Electrode preparation

2 mg of catalyst was dispersed in 960 μL (Vwater: Vethanol = 1:2) mixed solution and 40 μL Nafion solution (5 wt %) were sonicated for at least 20 min to form a homogeneous ink. Then, 50 μL of catalyst ink was drop-casted into carbon paper with a loading of 0.2 mg. The area of carbon paper electrode is 1.0×1.5 cm^2 and the practically immersing area in the electrolyte was 1.0×1.0 cm^2. Let dry naturally and leave to dry under a baking lamp for 1 h. Then dip in the prepared electrolyte for 1 h. The working electrode is ready to be used.

Characterizations

SEM images were collected from the tungsten lamp-equipped SU8010 scanning electron microscope at an accelerating voltage of 20 kV (HITACHI, Japan). The crystal structure of the synthesized samples was analyzed on a Rigaku Mini Flex II benchtop powder X-ray

diffractometer (XRD) with Cu-Kα radiation (40 kV, 40 mA, λ = 0.15418 nm) in the 2θ range of 5-80° with a scanning rate of 8°/min. Transmission electron microscopy (TEM) was tested on JEM-2100F. The X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo Fisher Scientific K-Alpha spectrometer with Al Ka (1486.6 eV) as the X-ray excitation source. N_2 adsorption–desorption isotherms are determined at 77 K using micromeritics asap 3020. Thermogravimetric (TG) analysis was carried out with a heating rate of 5 K/min from 303 K to 1273 K in N_2 on STA 449 F5 from NETZSCH company. The hydrophilic and hydrophobic properties of the material were accomplished on the Krüss contact angle analyser (DSA 100). The absorbance data of spectrophotometer were measured on PerkinElmer Lambda 650 ultraviolet-visible (UV-Vis) spectrophotometer.

Nafion 117 pre-treatment

The Nafion 117 membrane was boiled in 3% H_2O_2 solution for 30 min to remove organic impurities. The membrane surface of Nafion 117 was repeatedly cleaned with deionized water, and then boiled in 0.5 M H_2SO_4 solution for 1 h. The Nafion membrane is stored in deionized water for later use.

Electrochemical Measurements

The electrorhemical tests were carried out in a three electrode system on an electrochemical workstation (VERSASTAT3) at room temperature. Electrochemical reduction of N_2 to ammonia was performed in a two-compartment cell at room temperature, and the cells were separated by a Nafion 117 membrane. An Ag/AgCl (saturated KCl solution) electrode was used as the reference electrode, and a Platinum foil electrode was used as the counter electrode. The electrolyte volume in the two parts of H-cell is 70 mL. For electrocatalytic N_2 reduction, potentiostatic tests were conducted in N_2-saturated 0.05 M H_2SO_4 for 2 h, which was purged with N_2 for 30 min before the measurement. Pure N_2 was continuously fed into the cathodic compartment with a properly positioned sparger during the experiments.

Table S1 Properties of CMK-3[1]

Name	CMK-3
Average Length	1 μm
Purity	>99.6%
BET	⩾900 m^2/g
Vtotal	1.2-1.5 cm^3/g
Pore Size	3-5 nm

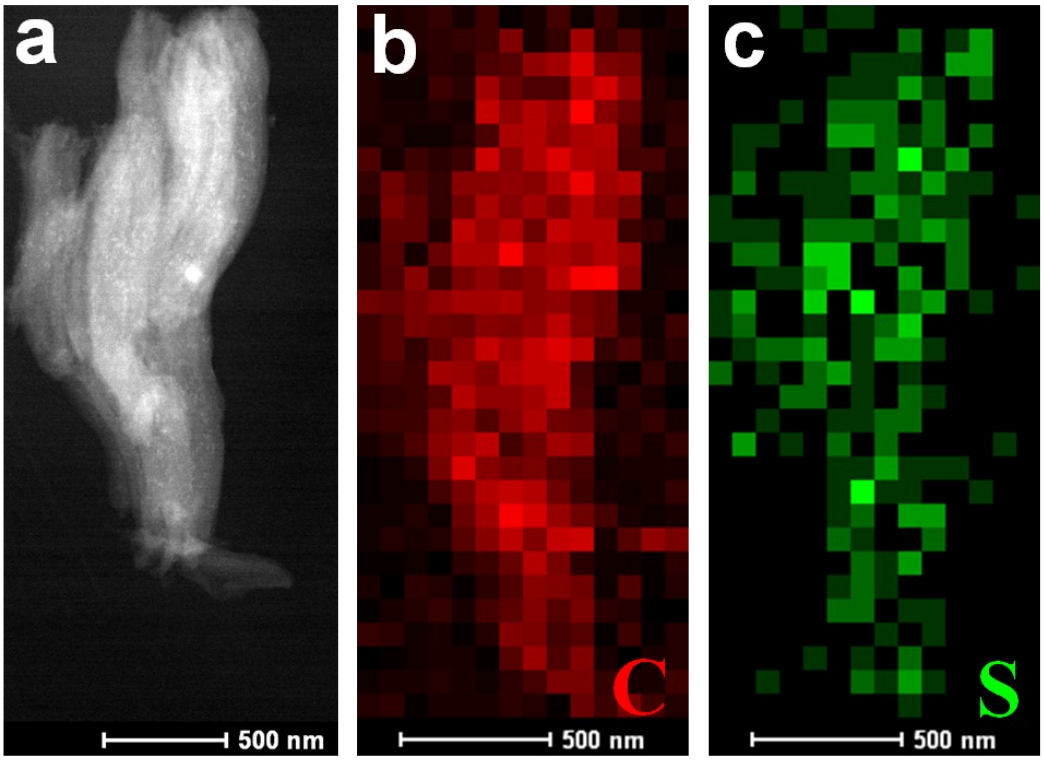

Figure S1. TEM image and the corresponding EDS elemental mapping images of S/CMK-3

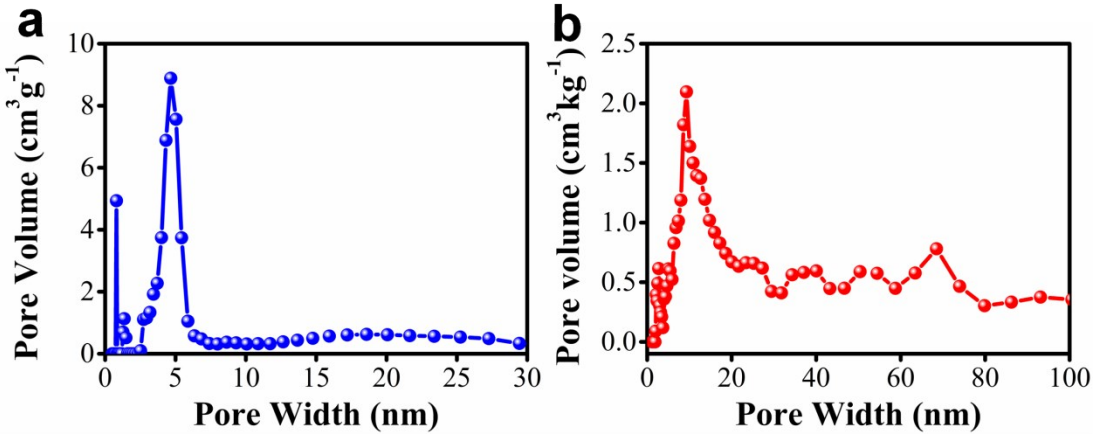

Figure S2. Pore size distribution of (a) CMK-3 and (b) S/CMK-3

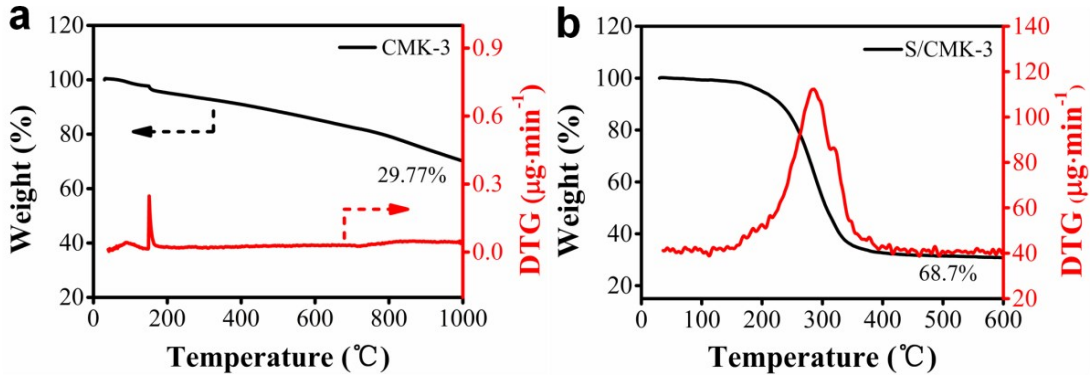

Figure S3. TGA and Differential Thermal Analysis (DTA) curves of (a) CMK-3 and (b) S/CMK-3

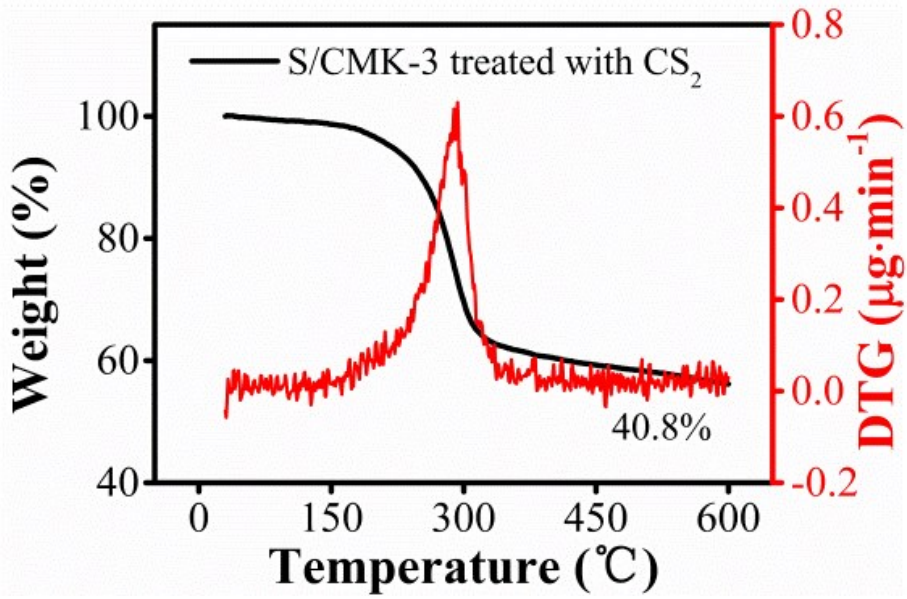

Figure S4 TGA and Differential Thermal Analysis (DTA) curves of S/CMK-3 treated with CS_2. (CS_2 was used to solubilize the sulfur nanoparticles of S/CMK-3 and then the supernatant containing sulfur is removed by centrifugation. The sample was then washed again with ethanol and water and dried overnight at 60°C.)

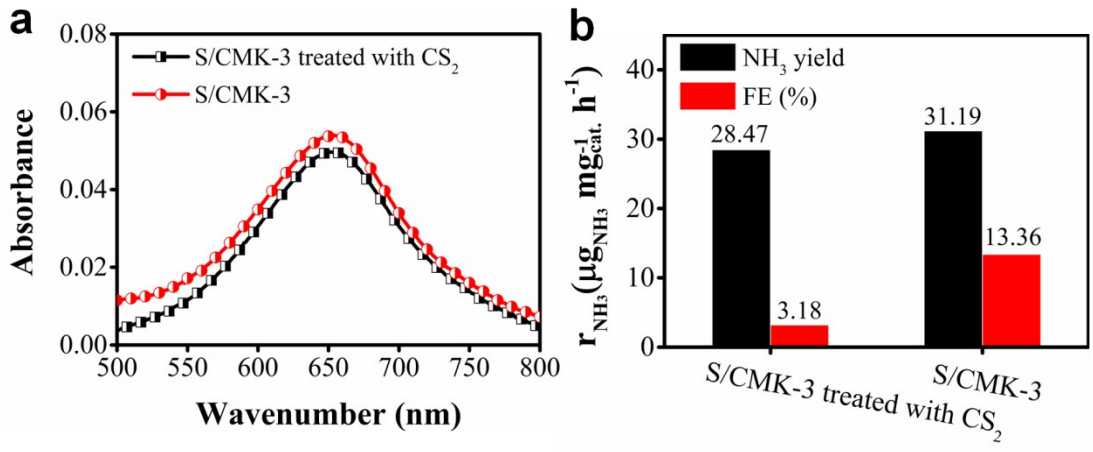

Figure S5 (a) UV/Vis absorption spectras of the electrolytes of S/CMK-3 treated with CS_2 and S/CMK-3 after electrolysis stained with indophenol indicator for 2 h. (b) NH_3 yields and corresponding FEs for S/CMK-3 treated with CS_2 and S/CMK-3

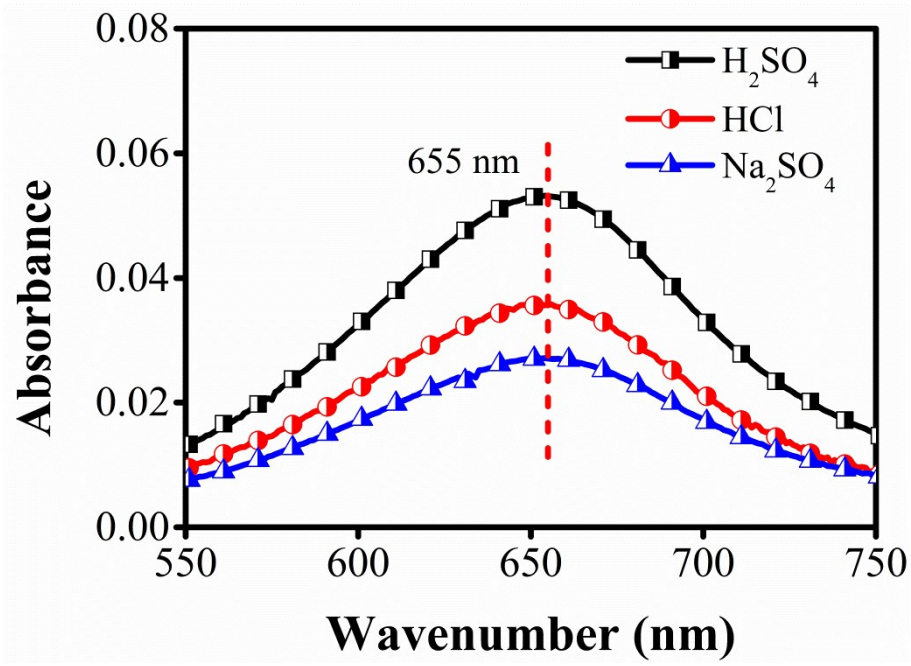

Figure S6. UV/Vis absorption spectra of the different standard electrolytes after electrolysis stained with indophenol indicator for 2 h

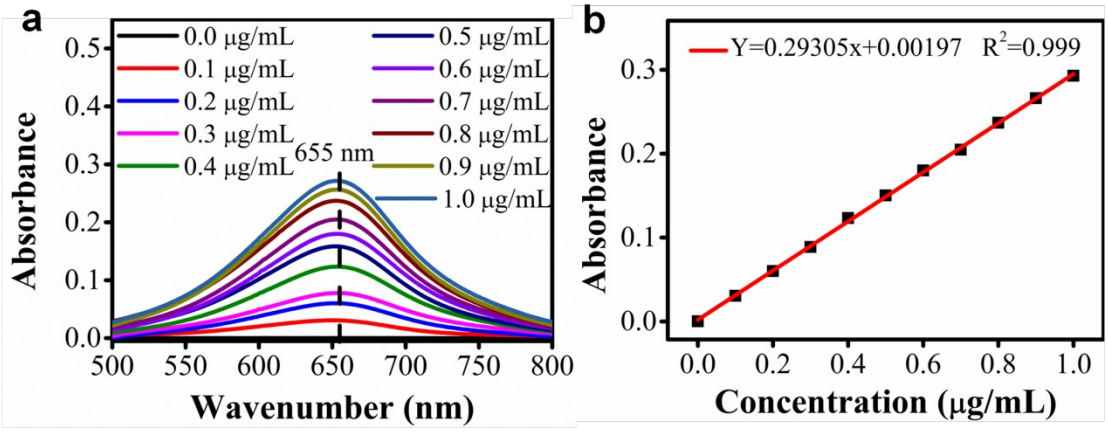

Figure S7. UV-vis curves (a) and (b) concentration-absorbance curve of NH_4^+ ions solution with a series of standard concentration. The absorbance at 655 nm was measured by UV-vis spectrophotometer. The standard curve showed good linear relation of absorbance with NH_4^+ ion concentration (y = 0.29305x+0.00197, R^2 = 0.999)

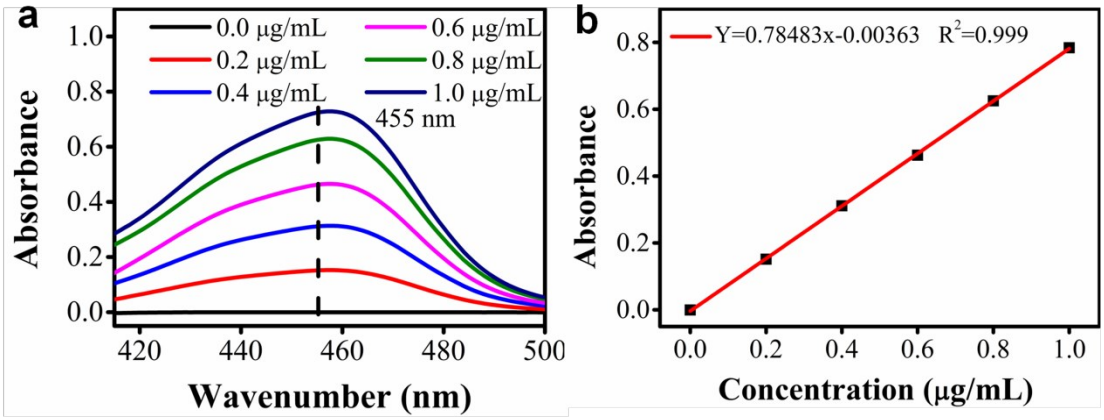

Figure S8. UV-vis curves (a) and (b) concentration-absorbance curve of N_2H_4 solution with a series of standard concentration. The absorbance at 455 nm was measured by UV-vis spectrophotometer. The standard curve showed good linear relation of absorbance with N_2H_4 concentration (y = 0.78483x+0.00363, R^2 = 0.999)

Reference

1 Jiangsu XFNANO Materials Tech. Co., Ltd. https://www.xfnano.com/Product/pro261.aspx