

Ru-Fe₄C nanoparticles loaded on N-doped carbon nanofibers as self-supporting high-efficiency hydrogen evolution electrocatalyst

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Experiment

1 Experimental materials

Ruthenium (III) chloride xhydrate (RuCl₃.xH₂O, 97%), Polyacrylonitrile (PAN, Mw=150000), N,N-Dimethylformamide (DMF, 99.9%) was purchased from Sigma-Aldrich, Potassium hydroxide (KOH) ,Pt/C (20%) and Iron chloride hexahydrate(FeCl₃.6H₂O,99%) were supplied by Shanghai Macklin Biochemical Co.,Ltd.

2 Synthesis of Ru-Fe₄C/NCNF

Ru-Fe carbon nanofibers were obtained by electrostatic spinning. The basic steps were as follows, 1.5 mmol FeCl₃ and 0.25 mmol RuCl₃ were dissolved into 11 g DMF, and 1.5 g PAN was added under the condition of magnetic agitation. Then, the precursor solution was magnetically stirred in a water bath at 40 °C to obtain mixed solution, which was then transferred to the needle cylinder for electrostatic spinning at 35 °C, voltage at 23 kV and spinning speed at 0.5 ml/h.

The precursor Ru-Fe nanofibers were pre-oxidized for 4 h at 230 °C in air, and then were carbonized for 3 h at 900 °C in argon atmosphere to obtain Ru-Fe₄C/NCNF with the heating rate was 5 °C min⁻¹. The carbon nanofibers were pyrolyzed at 800 and 1000 °C, respectively, to compare with the carbon nanofibers at different carbonization temperatures.

The other samples were prepared under the same condition except that 1 mmol FeCl₃ and 2 mmol FeCl₃.

3 Material characterization

The morphology and internal structure of the samples were characterized by field emission scanning electron microscope (ULTRA55, Zessi, voltage 3KV) and transmission electron

microscope (FEI Talos F200S). The crystal structure of the prepared samples was obtained by X-ray diffractometer (XRD, Bruker D8DIECOVER). At the same time, X-ray electron spectroscopy (XPS, Kratos Axis ULTRA DLD) was used to further investigate the elemental composition and chemical state of the sample surface.

4 Electrochemical measurements

All electrochemical tests were carried out by the Shanghai Chenhua electrochemical workstation, though a three-electrode system in 1M KOH with graphite rods as the counter electrode, Hg/HgO as the reference electrode and the prepared samples as a self-supporting working electrode directly. Linear sweep voltammetry (LSV) with 85% IR-compensation was used to test the sample polarization curve. Tafel slop was calculated from the LSV polarization curve by the formula: $\eta = b \log(j) + a$, where η , b and j were overpotential. Double-layer capacitance (C_{dl}) was calculated from the cyclic voltammetry (CV) scanning speed of 1-10mV s⁻¹, and the electrochemically active surface area (ECSA) was calculated by the formula: $ECSA = S_{geo} * C_{dl} / C_s$, where S_{geo} was the area of the prepared working electrode and C_{dl} was the corresponding value of the sample, C_s was an electrochemical double-layer capacitance with the value of 0.04 mF cm⁻² in an alkaline environment. And the stability test was investigated at a constant current density of 100 mA cm⁻² for 100 h.

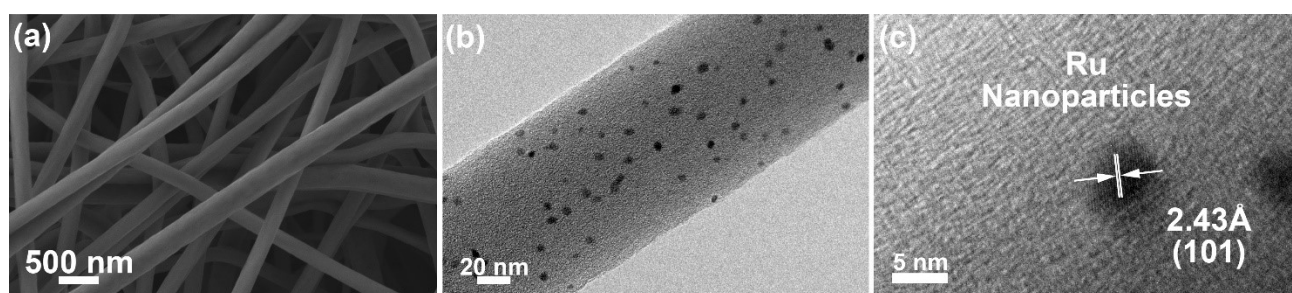


Figure S1 (a) SEM image of Ru/NCNF, (b) TEM image of Ru/NCNF, (c) HRTEM image of Ru/NCNF.

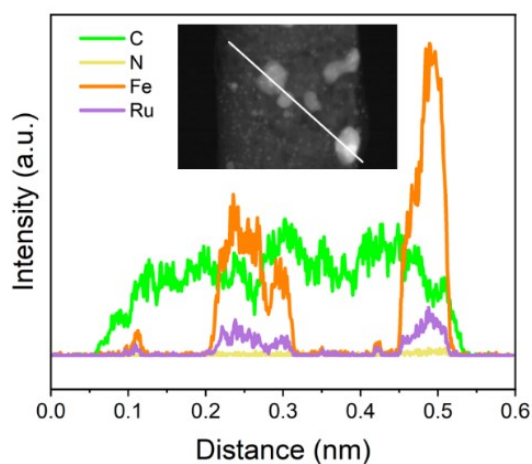


Figure S2 STEM-EDS EDX scan spectra of Ru-Fe₄C/NCNF.

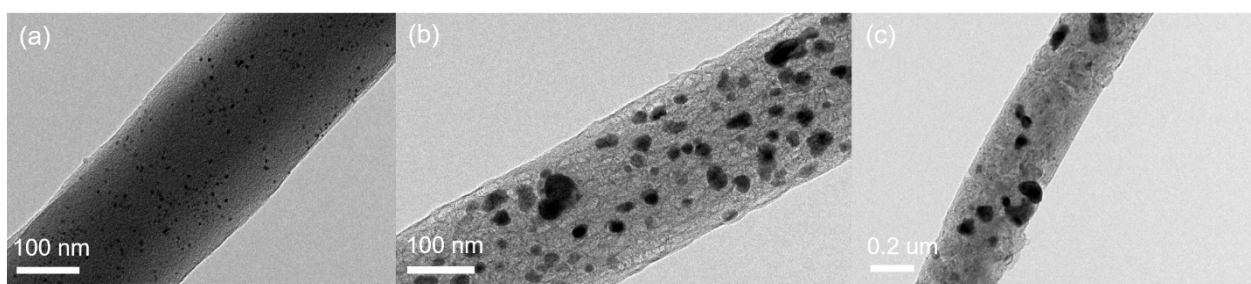


Figure S3 TEM images of Ru/NCNF, Fe₃C/NCNF, Ru-Fe₄C/NCNF.

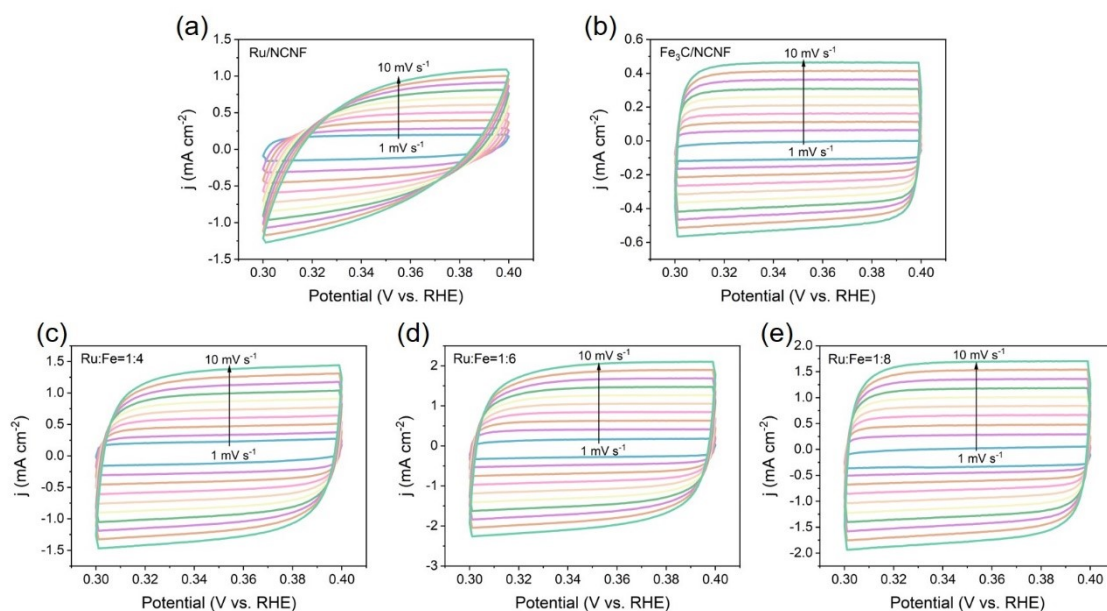


Figure S4 cyclic voltammety curves of Ru/NCNF, Fe₃C/NCNF, and Ru-Fe₄C/NCNF with different content of iron (Ru:Fe=1:4, Ru:Fe=1:6, Ru:Fe=1:8) at the scan rate of 1-10 mV s⁻¹ in 1 M KOH.

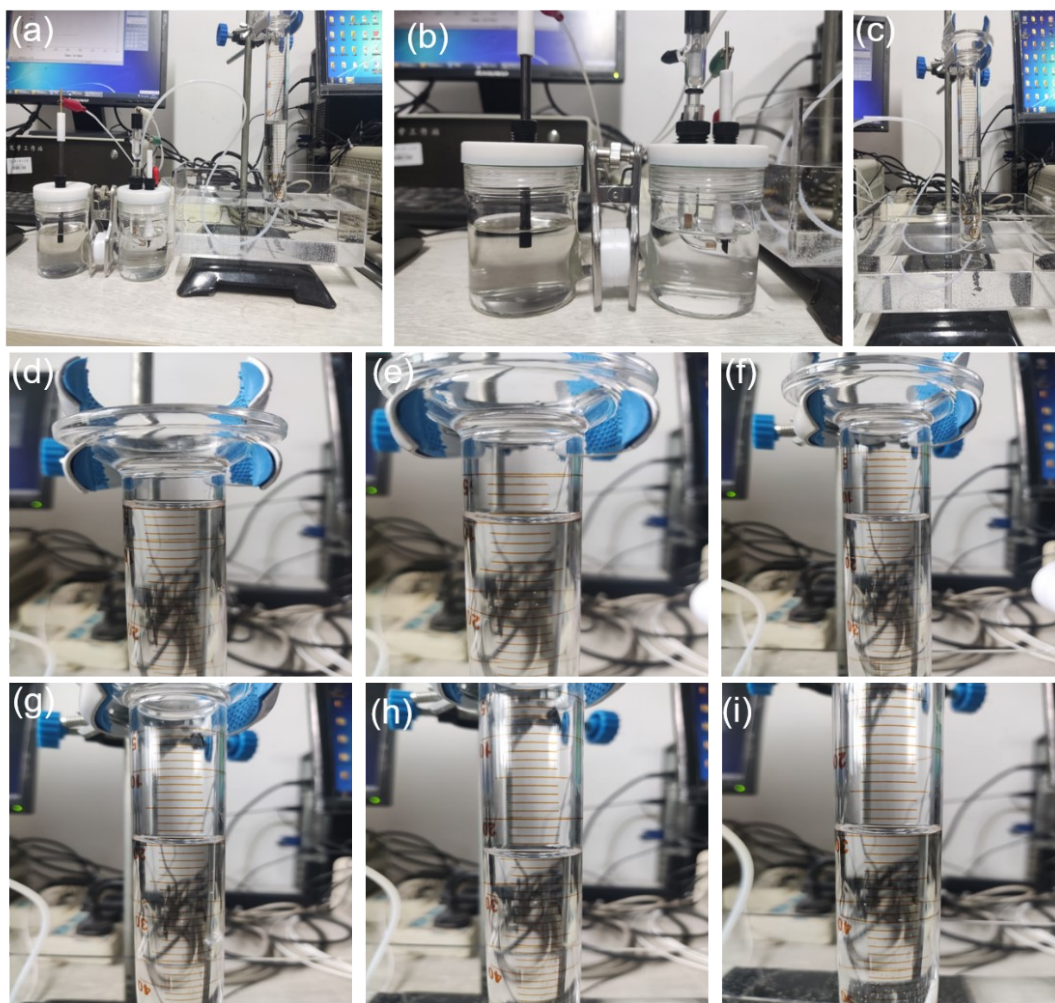


Figure S5 (a-c) H-type electrolytic cell, (d-i) the amount of hydrogen was collected at 10 minutes, 20 minutes, 30 minutes, 40 minutes, 50 minutes and 1 hour, respectively.