Supporting Information

1. Experimental Section

1.1 Physical characterization

X-ray diffraction (XRD) pattern were recorded to analyze the phase and crystal structure of the as-synthesized samples using a Shimadzu XRD-6100 operating in a 6 ° step at the range of 20-80 ° and using CuKα radiation (λ = 0.15405 nm). X-ray photoelectron spectroscopy (XPS) was performed on a Thermo VG Scientific Escalab 250 spectrometer with a monochromatic Al Kα excitation source. Scanning electron microscopy (SEM) images were obtained on an XL-30 (FEI COMPANY) equipped with an EDS spectrometer. The samples were examined with a Philips Tecnai G2 F20 High Resolution Transmission Electron Microscope (HRTEM) to obtain size/shape images of the nanostructured material. The magnetic properties of the synthesized samples were characterized using a vibrating sample magnetometer (VSM, Lake Shore 7404). The hysteresis curve was obtained by changing the magnetic field between + 17000 Oe and -17000 Oe.

1.2 Electrochemical characterization

Hydrogen Evolution Reaction (HER). All electrolysis measurements were performed in an N_2 saturated 1 M KOH solution in a CHI 650C electrochemical workstation. Typically, a mixture containing 735 μL of ultrapure water, 245 μL of ethanol and 20 μL of Nafion solution, 4 mg of catalyst and 1 mg of acetylene black was dispersed by sonication for 30 minutes. Then 10 μL of the homogeneous catalyst ink was dropped on a polished glassy carbon electrode having a diameter of 3 mm (0.57 mg·cm^{-2}) as a working electrode. Ni foil was used as a counter electrode and Hg/Hg_2Cl_2 electrode was used as a reference electrode. Linear sweep voltammetry was performed at a scan rate of 5 mV·s^{-1} to obtain a polarization curve. All potentials were referenced to a reversible hydrogen electrode (RHE) by adding a value of (0.24＋0.059×pH) V.

Electrochemically active surface area (EASA).[1] EASA was estimated from the electrochemical double-layer capacitance. The double layer capacitance (C_{dl}) was determined with a simple cyclic voltammetry (CV) method. The EASA is then calculated from the double-layer capacitance according to

$$EASA = \frac{C_{dl}}{C_s}$$

where C_s is the capacitance of an atomically smooth planar surface of the material per unit area under identical electrolyte conditions. An average value of C_s = 22 μF·cm^{-2} is used in this work.[2]

2. Supporting figures and tables

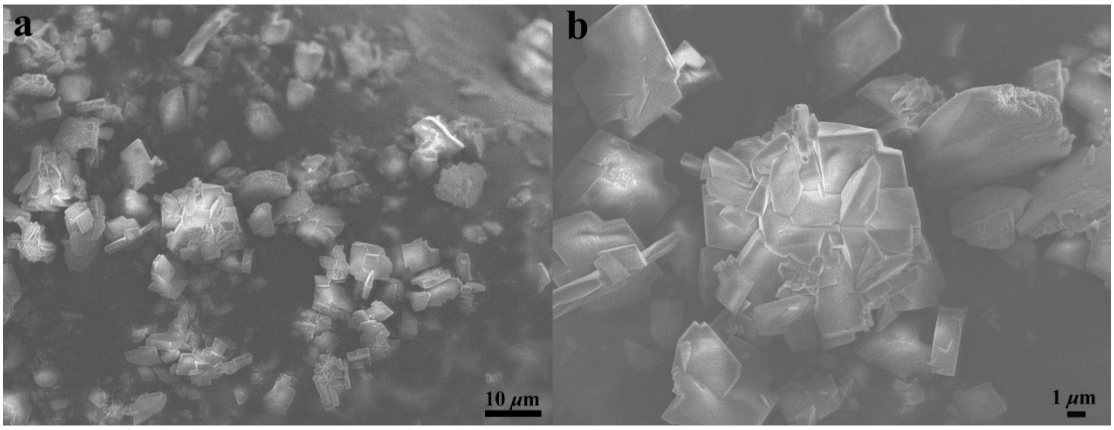

Fig. S1 SEM of iron oxalate dihydrate without PVP.

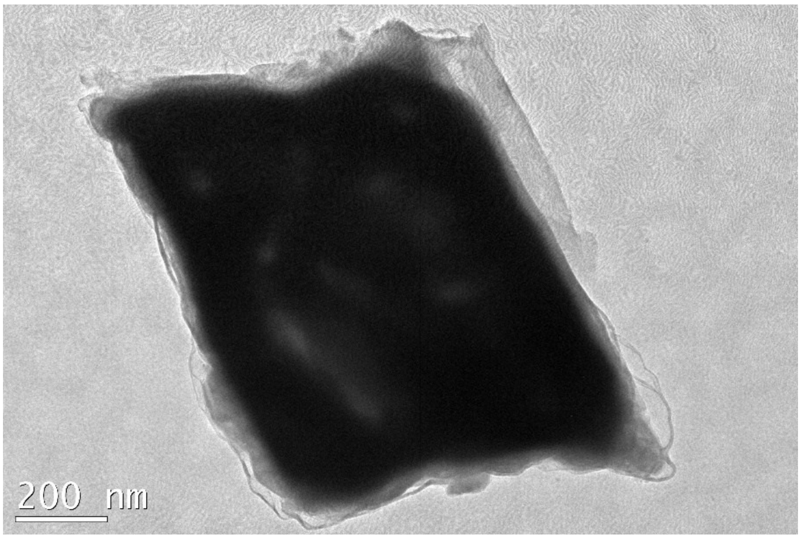

Fig. S2 Single particle magnification image of Fe_3C-620@NC materials.

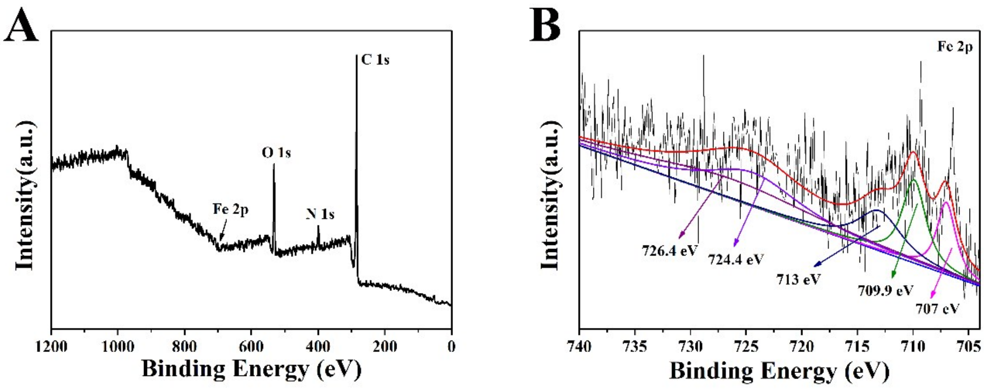

Fig. S3 (A) XPS full spectrum of Fe_3C-620@NC materials and corresponding high-resolution spectrum of the (B) Fe 2p.

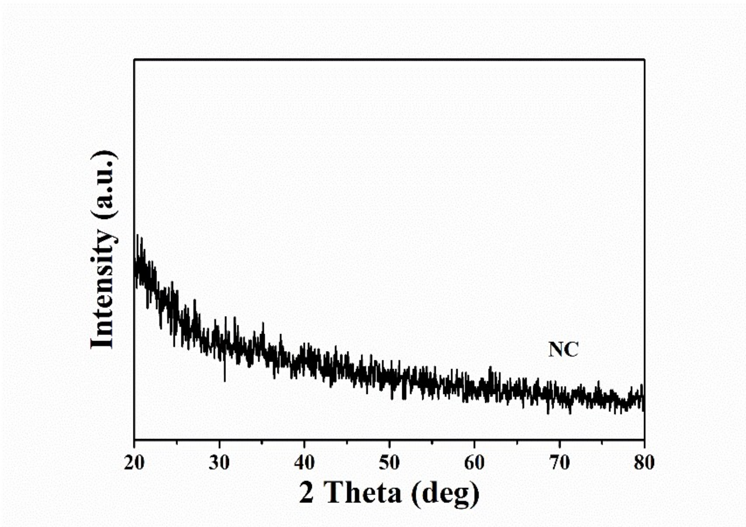

Fig. S4 XRD pattern of N-doped carbon (NC) by soaking Fe_5C_2-Fe_3C@NC catalyst in 0.5 M H_2SO_4.

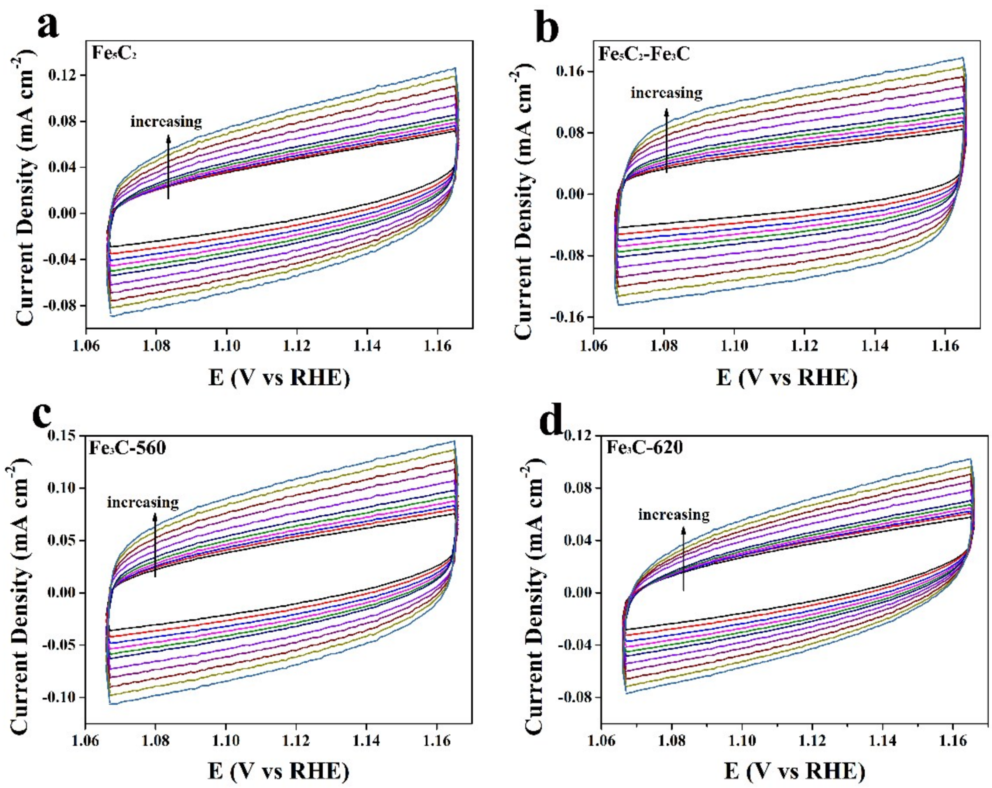

Fig. S5 CV curves of as-prepared ICs@NC catalysts under the potential window without faradaic processes.

Table S1 Content of elements on the surface of materials from the XPS analysis.

Sample	C (at%)	N (at%)	Fe (at%)	O (at%)
Fe_5C_2@NC	80.26	3.27	0.6	15.87
Fe_3C-620@NC	79.96	5.27	0.53	14.24

Table S2 Magnetism data of as-prepared samples.

Sample	M_S (emu·g^{-1})	M_r (emu·g^{-1})	H_C (Oe)
Fe_3O_4@NC	20.76	0.85	33.33
Fe_5C_2@NC	119.29	15.92	266.85
Fe_3C-560@NC	132.04	14.03	254.11
Fe_3C-620@NC	134.10	13.20	244.08

References

[1] Fan X, Peng Z, Ye R, et al. M3C (M: Fe, Co, Ni) Nanocrystals Encased in Graphene Nanoribbons: An Active and Stable Bifunctional Electrocatalyst for Oxygen Reduction and Hydrogen Evolution Reactions[J]. ACS nano. 2015, 9(7): 7407.

[2] McCrory C C L, Jung S, Peters J C, et al. Benchmarking Heterogeneous Electrocatalysts for the Oxygen Evolution Reaction[J]. Journal of the American Chemical Society. 2013, 135(45): 16977-16987.