Atomically dispersed Fe-O_4-C sites as efficient electrocatalysts for electrosynthesis of hydrogen peroxide

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Methods

Synthesis of SA Fe/GO samples. SA Fe/GO was synthesized via the dispersion of 6.0 mg $FeCl_3$ and 50 mg graphene oxide (GO) in Millipore water (18.2 MΩ·cm) under ultrasonication for 30 min. The mixture was freeze-dried for 24 h to remove water, followed by thermal treatment in 5 vol% H_2 in N_2 at 300 °C for 2 h to form Fe nanoparticles (Fe NPs/ GO). Fe NPs/ GO was leached in 1M HCl for 12 h, and then 1M HNO_3 for 12 h to remove Fe NPs, the obtained sample named as SA Fe/GO. For comparison, GO was prepared through the same procedure without the addition of $FeCl_3$.

Structural characterization. XRD results were recorded by a powder XRD (GBC MMA diffractometer) with Cu Kα radiation at the scan rate of 2° min^{-1}. The XAS results of Co K-edge were collected at an XAS station of the Beijing Synchrotron Radiation Facility. EXAFS fitting is applied through Athena and Artemis software.[1] Wavelet transformation (WT) is also employed using the software package developed by Funke and Chukalina using Morlet wavelet with $\kappa = 10$, $\sigma = 1$.[2, 3] The morphological study of the newly developed catalysts was performed on an FEI Titan Themis Z microscope equipped with probe and image correctors at 300 kV.

Electrochemical measurements. The electrochemical performance of the resultant catalysts were carried out by using a three electrode system at an electrochemical workstation (CHI 760 E, CH Instrument, USA). A Pt wire was used as the counter electrode and a saturated calomel electrode was applied as the reference electrode. The working electrode was using a rotating risk-disk electrode (RRDE). The ring electrode was Pt ring with an outside diameter of 0.75 mm and inside diameter of 6.5 mm; the disk electrode was a glass carbon disk with the diameter of 5.0 mm. The slurry was prepared by adding 5.0 mg catalysts into a mixture of 50 μL Nafion and 950 μL ethanol, and then was sonicated for 1 h to form a homogenous dispersion. 5 μL of the ink was dropped on the disk electrode. All the tests were carried out in a O_2 saturated 0.1 M KOH solution at room temperature with a rotated rate of 1600 rpm. Linear sweep voltammetry (LSV) was performed at a scan speed of 10 mV/s, and the potential of ring electrode was set at 1.2 V (vs. RHE) to detect the production of H_2O_2. The potential (1.2 V vs. RHE) of the ring is set such that it can oxidize the H_2O_2 produced at the disk electrode, with the resulting current providing a measurement of the level of H_2O_2. In this potential, the Pt ring may be surface oxidized, and it can be readily recovered by rapid cyclic voltammetry at low potentials to reduce PtO_x.

The potential was calibrated to a reversible hydrogen electrode (RHE) by applied the following equation:

$$E\ (RHE) = E\ (SCE) + 0.224\ V + 0.0592\ pH$$

The selectivity, production and electron transfer number were calculated by the following equations:

$$H_2O_2 \text{ selectivity: } H_2O_2\ (\%) = 200\times(i_r/N)/(i_d + i_r/N)$$

$$H_2O_2 \text{ productivity (mg cm}^{-2}\text{ h}^{-1}) = ½ \times (i_r/N) \times M_{H2O2} \times 3600/\ (F/A)$$

$$\text{electron transfer number (n)} = \frac{4\,i_r}{i_r + i_d/N}$$

i_r was the ring current and i_d was the disk current, N is the current collection efficiency of Pt ring electrode (N = 0.26), M_{H2O2} is the molecular weight of H_2O_2 (M_{H2O2} = 34.01 g mol^{-1}), F is Faraday constant (F = 96485.3 C mol^{-1}), A is the area of disk electrode (A = 0.196 cm^{-2}). The collection efficiency of the electrode defined as the fraction of product from the disk to the ring is 0.26.

The stability test of these catalysts was performed by the chronoamperometric at a constant potential of −1.2 V (vs. RHE).

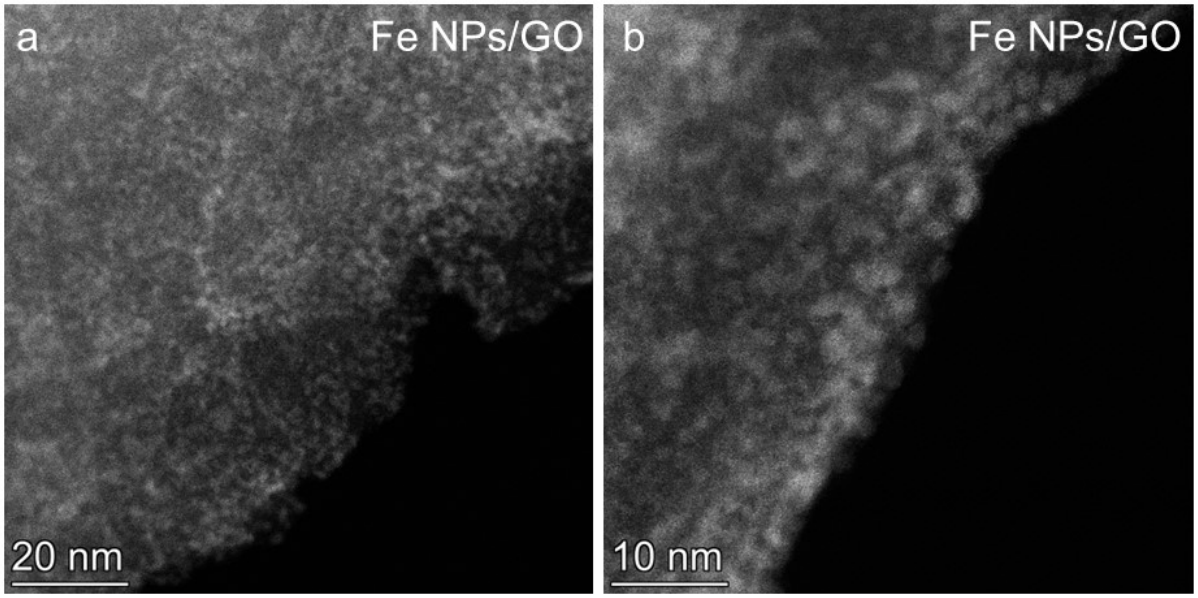

Figure S1. a-b, HAADF-STEM images of Fe NPs/GO.

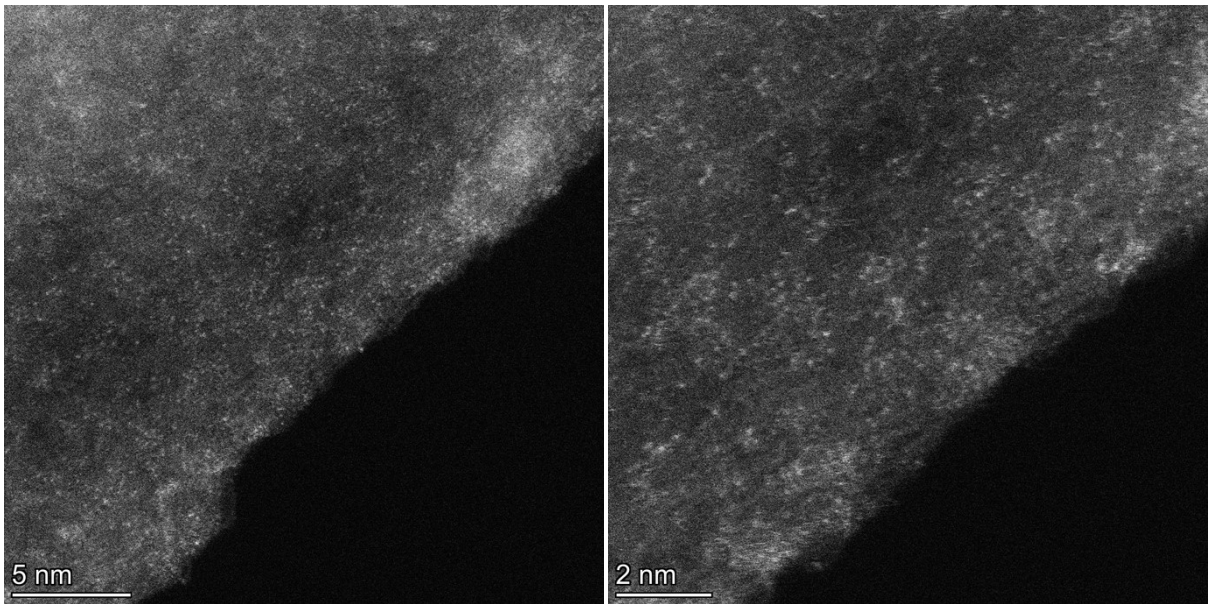

Figure S2. a-b, HAADF-STEM images of SA Fe/GO.

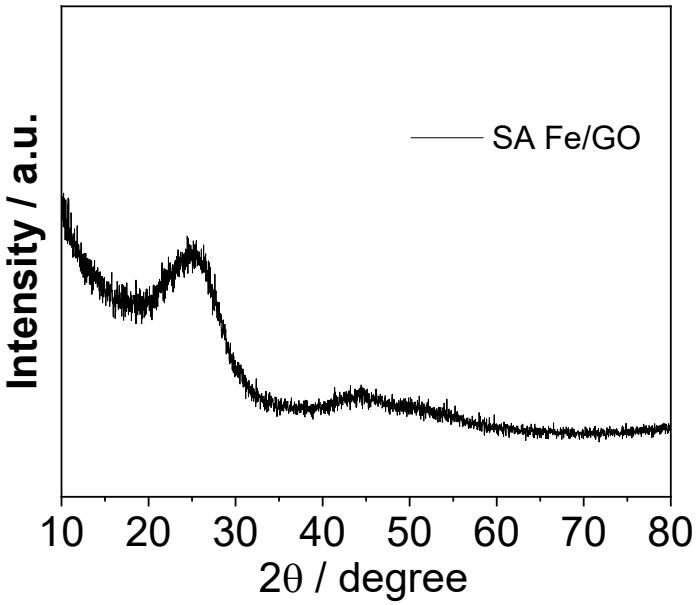

Figure S3. XRD patterns of the SA Fe/GO.

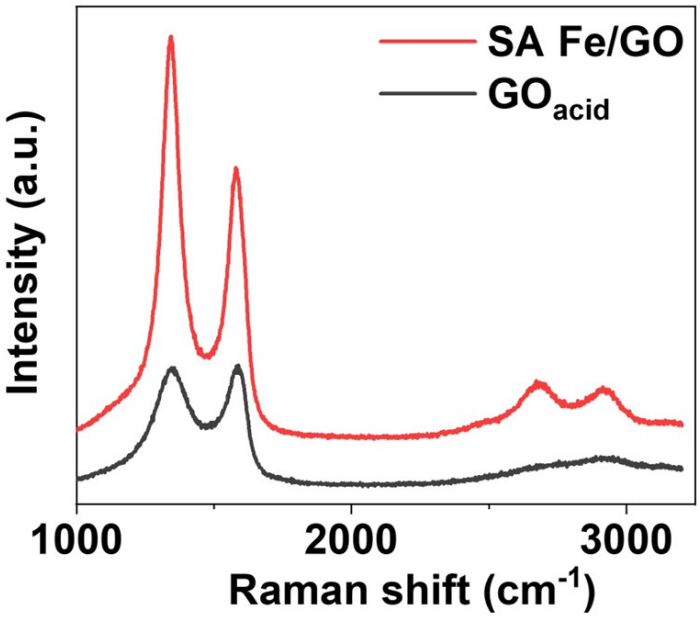

Figure S4. Raman spectra of GO_{acid} and SA Fe/GO.

Table S1. Fitting parameters for Fe K-edge EXAFS for the sample.

S_0^2 was obtained from Fe foil and fixed as 0.98. ΔE_0 was returned a value of -0.7780 ± 0.4972 eV. Data ranges $3.0 \leq k \leq 10.5$ Å^{-1}, $1.0 \leq R \leq 2.0$ Å. The number of variable parameters is 2, out of a total of 4.6563 independent data points, R factor for this fit is 1.08%. The Debye-Waller and ΔR are based on *guessing* parameters and fixed as 0.004 and 0.047.

Paths	CN	R	σ2
Fe-O	4.2±0.2	2.03	0.004

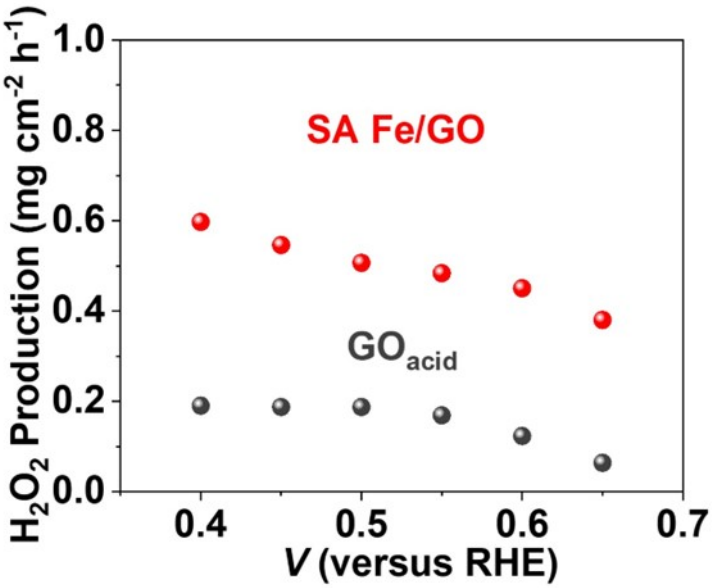

Figure S5. Electrosynthesis of H_2O_2 on GO_{acid} and SA Fe/GO in O_2-saturated 0.10 M KOH electrolyte.

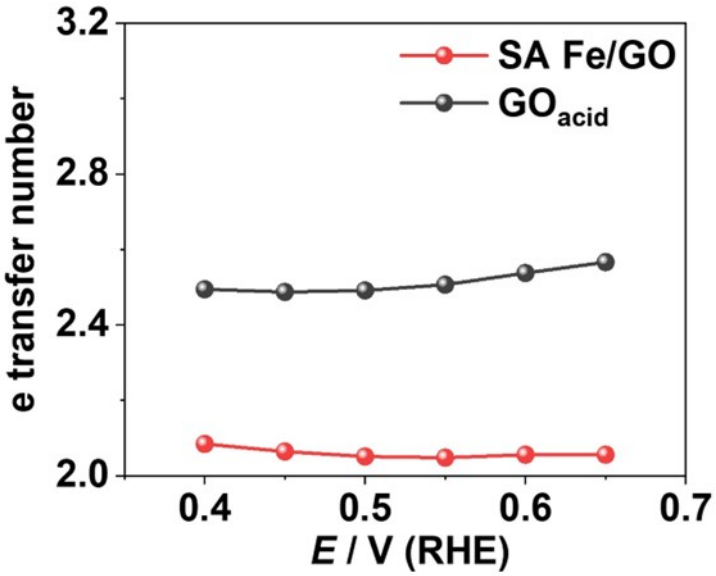

Figure S6. Calculated H_2O_2 electron transfer number during the potential sweep.

Table S2. Electrochemical performance comparison of the SA Fe/GO and other reported electrocatalysts for H_2O_2 electrochemical synthesis in alkaline environment.

Sample	Onset potential (RHE)	Selectivity	Electrolyte	Reference
SA Fe/GO	0.90 V	97% @0.6V	0.1 M KOH	**This work**
Pt-SA/rGO	0.96 V	90% @0.6V	0.1 M KOH	[4]
Co_1@NG(O)	0.8 V	72% @0.6 V	0.1 M KOH	[5]
Fe-CNT	0.82 V	94% @0.6 V	0.1 M KOH	[6]
Co-POC-O	0.84 V	81% @0.6 V	0.1 M KOH	[7]
Co_1@GO	0.91 V	81.4% @0.6 V	0.1 M KOH	[8]
Mo_1/OSG-H	0.78 V	95% @0.6 V	0.1 M KOH	[9]
O-CNT	0.77 V	90% 0.6V	0.1 M KOH	[10]
Meso C	0.75 V	78% @0.6 V	0.1 M KOH	[11]
N-CNF/Ni	0.78 V	70% @0.6 V	0.5 M KOH	[12]
$CoSe_2$ NS/CC	0.72 V	90% 0.6 V	0.1 M KOH	[13]
cCTN:Cl^-	0.7 V	85% 0.6V	0.1 M KOH	[14]
Fe_3O_4/ graphene	0.702 V	70% @0.6 V	1 M KOH	[15]

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