Supporting Information for
Subnano Amorphous Fe-based Clusters with High Mass Activity for Efficient
Electrocatalytic Oxygen Reduction Reaction

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S1. Materials

Synthesis of Fe subnano-cluster/3D-C. The monodisperse SiO₂ sphere templates were synthesized by a hydrolytic process. For the preparation of amino-SiO₂ templates, 1 g SiO₂ spheres were dispersed into a mixture of isopropanol (50 mL) and 3-Aminopropyl-triethoxysilane (3ml, APTES) via ultrasonic for 5 min, and then heated to 80 °C for 2 h under magnetic stirring to functionalize the silica sphere with -NH₂ radial group. Subsequently, these NH₂-SiO₂ spheres were washed with ethanol, and then dispersed again in a mixture solution of 50 mL ethanol and 10 mL deionized water. After that, 40 mg FeCl₃·6H₂O was dissolved into the above mixed solution under magnetically stirring, and this mixture solution was heated to 60 °C for 1 h to allow Fe ions fully adsorbing on the surface of NH₂-SiO₂ spheres. These Fe adsorbed silica spheres (Fe-SiO₂) were dispersed into another mixture solution of 20 mL polyaniline (PAni) and 10 mL deionized water under magnetic stirring for 30 min. Then, the above solution underwent a freezing dry process for overnight before the calcination at 800 °C for 2 h under nitrogen atmosphere. When naturally cooling down, the obtained black samples after calcination were dispersed into 40 mL Ammonium Fluoride (NH₄F) under magnetic stirring for 24 h to remove the SiO₂ templates. Finally, the precipitants were centrifugated and washed with deionized water several times to gain the Fe subnano-cluster/3D-C. The contrast sample of iron nanoparticle/hierarchical carbon framework (Fe NP/3D-C) was synthesized directly by dissolving 40 mg FeCl₃·6H₂O into a mixture solution of polyaniline (PAni) and
deionized water without SiO$_2$ sphere templates, then undergoing processes of freezing dry and calcination similar to that of Fe subnano-clusters/3D-C. For pure hierarchical carbon framework (3D-C), it was prepared in a method similar to that of Fe NP/3D-C without addition of FeCl$_3$.6H$_2$O.

**S2. Materials characterization**

Transmission electron microscopy (TEM), high-resolution TEM (HRTEM), and energy dispersive X-ray spectroscopy (EDS) measurements were performed on a JEM-2100F microscope in Material Test and Analysis Lab, Engineering and Materials Science Experiment Center, University of Science and Technology of China (USTC). The field emission scanning electron microscopy (SEM) images was taken on a FEI Sirion-200 scanning electron microscope. The X-ray diffraction (XRD) patterns were performed on Philips X’Pert Pro Super X-ray diffractometer with Cu K$_\alpha$ radiation. X-ray photoelectron spectra (XPS) were acquired at the Thermo ESCALAB 250Xi equipment with Al K$_\alpha$ (hv = 1486.6 eV) as the incident energy light at the structural measurement centers, university of science and technology of China (USTC). The binding energies obtained in the XPS spectral analysis were corrected for specimen charging by referencing C 1s to 284.6 eV. The specific surface areas of the samples were measured following the multipoint Brunauer-Emmett-Teller (BET) procedure from the N$_2$ adsorption/desorption isotherms using an ASAP 2460 M apparatus. The Fe absorption near-edge spectra (XANES) were measured at BL12B-a beamline of National Synchrotron Radiation Laboratory (NSRL, China) in the total electron yield (TEY) mode by collecting the sample drain current under a vacuum better than 5×10$^{-8}$ Pa.$^2$ The beam from the bending magnet was monochromatized utilizing a varied linespacing plane grating and refocused by a toroidal mirror. The energy range is 100–1000 eV with an energy resolution of ca. 0.2 eV.

Electrochemical measurements were performed using an electrochemical workstation (Model CHI760D, CH instruments, Inc., Austin, TX) with a standard three-electrode electrochemical cell and was used to record catalytic activity of samples in basic
solutions, where the as-prepared samples, a graphite rod and Ag/AgCl (saturated KCl) act as the working, auxiliary, and reference electrode, respectively. For the preparation of working electrodes, the as-prepared samples and the commercial catalyst powders (20 wt% Pt/C) were loaded on a rotating disc electrode (RDE) with loading mass of ~0.35 mg cm$^{-2}$ via drop casting of catalyst ink. The catalyst ink was a 1 mL mixture solution consisting of 2 mg of catalyst powder, 5 μL of Nafion (5%, Sigma Aldrich), 200 μL of ethanol, and 795 μL of distilled water. Tafel plots were obtained from the extrapolation of the linear region of a plot of overpotential versus current density. For the ORR kinetic measurements, the catalyst ink was carefully coated onto the polished rotating ring-disk electrode (RRDE). Chronopotentiometric measurements was recorded at E=0.7 V under rotating speed of 1600 rpm for 20 h. The mass activity ($A_{g\text{metal}^{-1}}$) was derived from the current density (mA cm$^{-2}$) that normalized by the actual mass loading of metal (mg cm$^{-2}$) in electrocatalysts at a special overpotential during ORR performance.

The relation between Ag/AgCl and RHE potential can be calibrated in the high purity H$_2$ saturated electrolyte with a Pt wire as the working electrode, resulting in calibration relation as following equation $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.0591*pH + 0.197V$ (at 25°C). Accordingly, in alkaline solution of 0.1 M NaOH, the relation used to convert the Ag/AgCl to RHE potential can be expressed as $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.965V$. All the final potentials were calibrated with respect to a reversible hydrogen electrode (RHE). The volume current density ($I_v$) of catalysts can be calculated based on the following equation$^{3,4}$:

$$I_v = 1.6 \times 10^{-19} \times \text{TOF} \times \text{SD}.$$

Where $1.6 \times 10^{-19}$, TOF and SD is the charge of an electron, turn over frequency on a single active sites and volumetric site density, respectively. As for the SD, it can be estimated in combination of average loading of Fe cluster on 3D-C and their corresponding volume.
**Figure S1.** (a) N K-edge and (b) Fe $L_{3,2}$-edge XANES spectra for Pre-Adsorbed, Fe-Adsorbed and PAni Coated samples.

**Figure S2.** TEM, HRTEM images for 3D-C (a,b) and Fe NP/3D-C (c,d).

**Figure S3.** BET specific surface area for 3D-C (a), Fe NP/3D-C (b), and Fe cluster/3D-C (c).
Figure S3 shows there is clear hysteresis loop in the isothermal N\textsubscript{2} adsorption-desorption curves of 3D-C, Fe NP/3D-C and Fe cluster/3D-C over the pressure (P/P\textsubscript{0}) range of 0.5-1.0, which indicates presence of rich macropores for all these samples. Moreover, the BET surface area of Fe cluster/3D-C is calculated to be 526 m\textsuperscript{2}/g, slightly larger than those of 3D-C (453 m\textsuperscript{2}/g) and Fe NP/3D-C (526 m\textsuperscript{2}/g).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.png}
\caption{Figure S4. Electrochemical CV measurements for Fe cluster/3D-C, Fe NP/3D-C and 3D-C.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.png}
\caption{Figure S5. Volumetric current density for Fe cluster/3D-C, Fe NP/3D-C and Pt/C.}
\end{figure}
Figure S6. (a) SEM image, (b) enlarged SEM image after ORR tests for Fe subnano-cluster/3D-C.

Figure S7. (a) TEM and (b) enlarged TEM images after ORR tests for Fe subnano-cluster/3D-C.

Figure S8. (a) Fe 2p XPS spectra after ORR tests and (b) FT Fe k-edge XAFS curves before and after ORR measurements for Fe subnano-cluster/3D-C.
Figure S9. LSV cyclic stability tests for Fe cluster/3D-C.

Figure S10. Fe $L_{3,2}$-edge XANES spectra for Fe NP/3D-C and Fe subnano-cluster /3D-C.

Figure S11. Electrochemical impedance spectroscopy (EIS) for 3D-C, Fe NP/3D-C and Fe subnano-cluster /3D-C.
To give a quantitative analysis, the fitting of Nyquist plot was carried out based on the equivalent circuit model shown in inset of Figure S11. The charge transfer barrier ($R_{ct}$) and surface reaction capacitance (CPE) of Fe cluster/3D-C is determined to be 800 ohm and 1.3 mF, much superior to those of Fe NP/3D-C (1750 ohm; 0.6mF) and 3D-C (2500 ohm; 0.1 mF), indicating fast electron transfer across electrode/liquid interface and accelerated reaction kinetics for surface oxygen reduction reaction.

**Table S1.** Summary of ORR performance of transition metal based hybrid catalysts

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Electrolyte</th>
<th>Onset potentials (vs RHE)</th>
<th>Half-wave potential (vs RHE)</th>
<th>Limited current density (mA/cm²) at 1600 rpm</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeO$_2$@Fe-NC</td>
<td>0.1M KOH</td>
<td>0.97</td>
<td>0.68</td>
<td>5.0</td>
<td>RSC Adv. 7, 14382(2017)</td>
</tr>
<tr>
<td>Fe-NC</td>
<td>0.1M KOH</td>
<td>0.91</td>
<td>0.81</td>
<td>6.0</td>
<td>ACS Appl. Mater. Interfaces 9, 4587(2017)</td>
</tr>
<tr>
<td>Fe-P-C</td>
<td>0.1M KOH</td>
<td>0.87</td>
<td>0.60</td>
<td>5.5</td>
<td>J. Am. Chem. Soc. 137, 3165(2015)</td>
</tr>
<tr>
<td>Fe-N-CC</td>
<td>0.1M KOH</td>
<td>0.94</td>
<td>0.83</td>
<td>4.5</td>
<td>ACS Nano 10, 5922(2016)</td>
</tr>
<tr>
<td>Fe-Fe$_2$C@NCNT</td>
<td>0.1M KOH</td>
<td>1.06</td>
<td>0.96</td>
<td>4.0</td>
<td>J. Power Sources 286, 495(2015)</td>
</tr>
<tr>
<td>Fe$_2$O$_3$@MoS$_2$-NGNS</td>
<td>0.1M KOH</td>
<td>0.95</td>
<td>0.85</td>
<td>6.2</td>
<td>ACS Appl. Mater. Interfaces 10, 2452(2018)</td>
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<tr>
<td>Co-WC</td>
<td>0.1M KOH</td>
<td>0.87</td>
<td>0.64</td>
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<td>Sci. Technol. Adv. Mater. 17, 37(2016)</td>
</tr>
<tr>
<td>CoNi$_2$NC</td>
<td>0.1M KOH</td>
<td>0.94</td>
<td>0.87</td>
<td>5.2</td>
<td>ChemCatChem 7, 1826(2015)</td>
</tr>
<tr>
<td>FeCo-N-C</td>
<td>0.1M KOH</td>
<td>0.84</td>
<td>0.74</td>
<td>5.5</td>
<td>J. Mater. Chem. A 6, 23445(2018)</td>
</tr>
<tr>
<td>CoPdNi-N-C</td>
<td>0.1M KOH</td>
<td>0.93</td>
<td>0.84</td>
<td>4.5</td>
<td>Appl. Catal. B Environ. 240, 112(2019)</td>
</tr>
<tr>
<td>LaNiO$_3$/S-N-G</td>
<td>0.1 M KOH</td>
<td>0.95</td>
<td>0.82</td>
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<td>Small 13, 1701884(2017)</td>
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<tr>
<td>Fe NP/3D-C</td>
<td>0.1M KOH</td>
<td>0.93</td>
<td>0.86</td>
<td>4.6</td>
<td>This work</td>
</tr>
<tr>
<td>Fe cluster/3D-C</td>
<td>0.1M KOH</td>
<td>1.01</td>
<td>0.92</td>
<td>5.9</td>
<td>This work</td>
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</table>

**Table S2.** Summary of key ORR parameters for all samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Onset-potential at 0.1 mA cm² (V vs RHE)</th>
<th>Half-wave potential (V vs RHE)</th>
<th>Mass loading (mg/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3D-C</td>
<td>0.85</td>
<td>0.67</td>
<td>0.35</td>
</tr>
<tr>
<td>Pt/C</td>
<td>1.03</td>
<td>0.95</td>
<td>0.35</td>
</tr>
<tr>
<td>Fe NP/3D-C</td>
<td>0.93</td>
<td>0.86</td>
<td>0.35</td>
</tr>
<tr>
<td>Fe cluster/3D-C</td>
<td>1.01</td>
<td>0.92</td>
<td>0.35</td>
</tr>
</tbody>
</table>

As shown in Table S2, the Fe cluster/3D-C could catalyze oxygen reduction at a
superior onset potential (at 0.1 mA cm$^{-2}$) of 1.01 V, slightly lower than that of Pt/C (1.03 V) and higher than those of Fe NP/3D-C (0.93 V) and 3D-C (0.85 V). Moreover, the half-wave potential of Fe cluster/3D-C for ORR is ~0.92 V, which is close to that of Pt/C (0.95 V) and clearly outperforming Fe NP/3D-C (0.86 V) and 3D-C (0.67 V). Based on the above results, the Fe cluster/3D-C is of potential as a promising ORR electrocatalyst with outstanding ORR activity, comparable to the benchmark commercial Pt/C.

S3. DFT calculation details

The first-principles density functional theory (DFT) calculations were performed using a plane wave basis set with the projector augmented plane-wave (PAW) method.$^{5,6}$ The exchange-correlation interaction was described within the generalized gradient approximation (GGA) in the form of PW91.$^{7}$ The energy cutoff was set to 400 eV, and the atomic positions were allowed to relax until the energy and force were less than $10^{-4}$ eV and $10^{-2}$ eV/Å, respectively. For modeling the experimental catalyst, a ball-like Fe$_{28}$N$_{26}$ cluster with size of around 1 nm in diameter was chosen to mimic the subnano amorphous Fe cluster and a ball-like Fe$_{54}$ cluster was used to mimic Fe particles. All the atoms in the model were fully released to optimize the model and the vacuum slab was set up to 15 Å.
References


