

# Multiscale carbon foam confining single iron atoms for efficient electrocatalytic CO<sub>2</sub> reduction to CO

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### ABSTRACT

Electrocatalytic  $CO_2$  reduction to CO is a sustainable process for energy conversion. However, this process is still hindered by the diffusionlimited mass transfer, low electrical conductivity and catalytic activity. Therefore, new strategies for catalyst design should be adopted to solve these problems and improve the electrocatalytic performance for CO production. Herein, we report a multiscale carbon foam confining single iron atoms prepared with the assistant of SiO<sub>2</sub> template. The pore-enriched environment at the macro-scale facilitates the diffusion of reactants and products. The graphene nanosheets at the nano-scale promote the charge transfer during the reaction. The single iron atoms confined in carbon matrix at the atomic-scale provide the active sites for electrocatalytic  $CO_2$  reduction to CO. The optimized catalyst achieves a CO Faradaic efficiency of 94.9% at a moderate potential of -0.5 V vs. RHE. Furthermore, the performance can be maintained over 60 hours due to the stable single iron atoms coordinated with four nitrogen atoms in the carbon matrix. This work provides a promising strategy to improve both the activity and stability of single atom catalysts for electrocatalytic  $CO_2$  reduction to CO.

## **KEYWORDS**

CO2 reduction, electrocatalysis, multiscale structure, carbon foam, single iron atoms

# **1** Introduction

The increased utilization of fossil fuels has put an enormous amount of CO<sub>2</sub> into the atmosphere, which has caused a series of environmental issues. Therefore, converting CO2 into carbon-based fuels through renewable energy sources is one promising strategy to turn the waste into treasure [1-5]. Electrocatalytic CO<sub>2</sub> reduction reaction (CO2RR) to CO using renewable electrical energy has attracted extensive interest [6-9], since CO is the essential reactant in the classical Fischer-Tropsch synthesis, which is an important process to produce chemicals and fuels [10, 11]. Thus it is necessary to rationally design active and stable electrocatalysts for electrocatalytic CO<sub>2</sub>RR to CO. Recently, single atoms confined in an appropriate support have shown excellent performance in thermocatalysis [12-14], electrocatalysis [15-17] and photocatalysis [18, 19]. The coordinatively unsaturated single atoms and its stable confining environment can endow the highly catalytic performance. Additionally, the dispersed single atoms can maximize the atomic utilization efficiency. These properties make them great potential as candidate catalysts for electrocatalytic CO<sub>2</sub>RR [20-25]. However, the diffusion-limited mass transfer, low electrical conductivity and catalytic activity have hindered the reaction for efficient CO production. Therefore, rational catalyst design from macro-scale to atomic-scale may realize the multiscale structural modulation to systemically promote the electrocatalytic  $CO_2RR$  to CO [26].

In this work, we demonstrate the multiscale structural modulation of carbon foam confining single iron atoms for efficient electrocatalytic CO<sub>2</sub>RR to CO: (i) At the macro-scale, the pore-enriched environment facilitates the transfer of reactant (CO<sub>2</sub>) and product (CO), and increases the surface area of catalyst for the accessibility with reactant; (ii) at the nano-scale, the graphene nanosheets as the support can promote the charge transfer; (iii) at the atomic-scale, single iron atoms confined in the carbon matrix enhance the intrinsic activity for electrocatalytic CO<sub>2</sub>RR to CO. Such catalyst exhibits efficient electrocatalytic activity and durability. The maximum CO Faradaic efficiency of 94.9% is achieved at the potential of -0.5 V vs. RHE, and maintains stability for over 60 hours.

# 2 Experimental procedures

#### 2.1 Chemicals

Iron phthalocyanine (FePc) and SiO<sub>2</sub> colloidal dispersion (30 wt.% in ethylene glycol) were purchased from Alfa Aesar. KHCO<sub>3</sub> (99.7%) and N, N-Dimethylformamide (DMF) were respectively acquired from Sigma Aldrich and Sinopharm Chem. Reagent Co. Ltd. All chemicals were used without further purification in this study. Carbon fiber paper (AvCarb GDS3250) was acquired from Fuel Cell Store. Ultrapure water (Millipore, 18.2 M $\Omega$ ·cm) was used throughout all the experiments.



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#### 2.2 Catalyst preparation

The carbon foam confining single iron atoms (Fe-N<sub>4</sub>/CF) was prepared by a template-assisted method. Firstly, 80 mL DMF was used as solvent to disperse and mix 1 g FePc and 12 g SiO<sub>2</sub> colloidal dispersion, and then the solution was stirred in an oil bath at 80 °C to volatilize the solvent. To remove the liquid solvent completely, the mixture was dried under 80 °C in a vacuum oven. After that, the gained solid was ground to a fine powder. Then, 1 g powder was subjected to thermal treatment at 5 °C·min<sup>-1</sup> temperature ramp rate in an 80 mL·min<sup>-1</sup> Ar atmosphere. The temperature rose to 800 °C and maintained for 2 h. After pyrolysis, SiO<sub>2</sub> template was leached using 5% HF aqueous solution with stirring under room temperature, followed by washing with deionized water for several times and drying at 80 °C. To obtain the final catalyst, a second thermal treatment was carried out at 800 °C for 2 h with the same condition as the first thermal treatment. Different pyrolysis temperatures (900 and 1,000 °C) were also carried out to investigate the impact of pyrolysis temperature on the electrocatalytic CO<sub>2</sub>RR performance. The resulting samples were denoted as Fe-N<sub>4</sub>/CF-800, Fe-N<sub>4</sub>/CF-900 and Fe-N<sub>4</sub>/CF-1,000, respectively. For comparison, FeNC@1,000 was synthesized with the same method by direct pyrolysis of FePc at 1,000 °C, followed by dealing with 5% HF aqueous solution, and then pyrolysis again at 1,000 °C to get the final sample.

#### 2.3 Characterization

Scanning electron microscopy (SEM) was performed on Hitachi S5500. Transmission electron microscopy (TEM), higher resolution TEM (HRTEM) analyses were conducted with a FEI Tecnai F20 microscope operated at an accelerating voltage of 200 kV. The highangle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and corresponding energy-dispersive X-ray (EDX) mapping were carried out on a FEI Talos F200S microscope operated at an accelerating voltage of 200 kV. Atomic resolution HAADF-STEM images were obtained by using a JEOL ARM200F microscope, equipped with a probe-forming aberration corrector and operated at 200 kV. The powder X-ray diffraction (XRD) measurements were performed on a Rigaku Ultima IV diffractometer with Cu Ka radiation  $(\lambda = 1.5418 \text{ Å})$  at 40 kV and 30 mA. Raman spectra were taken on a Jobin-Yvon Horiba Xplora confocal Raman system by using the 532 nm excitation laser at a power of about 0.3 mW. Nitrogen adsorption-desorption isotherms were measured on a Micromeritics Tristar 3020, where the Brunauer-Emmett-Teller (BET) and density functional theory (DFT) methods were used to characterize the specific surface areas and pore size distribution. Inductively coupled plasma optical emission spectroscopy (ICP-OES) was performed on PerkinElmer Optima 7300DV to measure the content of Fe in each sample. The X-ray photoelectron spectrum (XPS) was performed on the Thermo Fisher Scientific ESCALAB 250 system used Al Ka X-rays as the excitation source (1,486.68 eV). The binding energies were referenced to the C 1s peak (284.6 eV). X-ray absorption nearedge structure (XANES) profiles and extended X-ray absorption fine structure (EXAFS) spectra were performed at the BL14W1 beamline of the Shanghai Synchrotron Radiation Facility (SSRF). <sup>1</sup>H nuclear magnetic resonance (NMR) was performed by a Bruker 500 MHz NMR instrument.

#### 2.4 Electrochemical measurements

Electrochemical measurements were carried out by an electrochemical workstation (CHI760E). A custom-made gas-tight H-cell separated by Nafion 115 was used to analyze the electrocatalytic performance. Anode and cathode, respectively, contained 45 mL 0.5 M KHCO<sub>3</sub> with around 45 mL headspace. Pt net and Ag/AgCl (saturated KCl) were employed as counter electrode and reference electrode, respectively. The sample was supported on the carbon fiber paper as the working electrode. To fabricate the working electrode, the

sample was firstly dispersed with ethanol, and then brush onto the carbon fiber paper with 1 cm  $\times$  1 cm work area to form 2 mg·cm<sup>-2</sup> with 10% Nafion content. All potentials were referenced to the reversible hydrogen electrode (RHE). RHE was calculated by the conversion E (vs. RHE) = E (vs. Ag/AgCl) + 0.1989 V + 0.059 × pH. Linear sweep voltammetry (LSV) was carried out in Ar- (pH = 8.8)and  $CO_2$ -saturated (pH = 7.2) 0.5 M KHCO<sub>3</sub> solution without stirring at a scan rate of 5 mV·s<sup>-1</sup>. The Faradaic efficiency of various reduction products were analyzed by the controlled potential electrolysis in CO2-saturated 0.5 M KHCO3 electrolyte. CO2 was continuously bubbling into the anode and cathode electrolytes at a rate of 10 mL·min<sup>-1</sup> controlled by the mass flow meters. The electrolytes were slightly stirred to facilitate the diffusion. The gaseous reduction products were analyzed by online gas chromatography (GC-2014) every 30 min, and the liquid reduction product was detected by using <sup>1</sup>H NMR after 2 hours electrolysis at a given potential.

#### 2.5 Faradaic efficiency calculation

The calculation for Faradaic efficiency of  $H_2$  and CO at a given potential as follows

$$i_{\rm H_2 \, or \, CO} = v_{\rm H_2 \, or \, CO} \times V \times \frac{2Fp_0}{\rm RT}$$
$$\rm FE_{\rm H_2 \, or \, CO} = \frac{i_{\rm H_2 \, or \, CO}}{i_{\rm total}} \times 100\%$$

 $i_{\rm H_2 \ or \ CO}$ : partial current density for H<sub>2</sub> and CO;

 $v_{\rm H_2 \, or \, CO}$ : volume fraction of H<sub>2</sub> or CO based on the calibration curves from GC peak areas;

*V*: gas volume flow rate controlled by a mass flow meter;

*F*: Faraday constant;  $p_0$ : pressure; *R*: ideal gas constant; *T*: temperature; FE<sub>H<sub>2</sub> or CO</sub>: Faradaic efficiency for H<sub>2</sub> or CO production;

 $i_{\text{total}}$ : total current density.

## 3 Results and discussion

All Fe-N<sub>4</sub>/CF materials of this study were prepared with FePc and SiO<sub>2</sub> nanospheres as precursor and template, respectively. Although FePc owns well-defined Fe-N<sub>4</sub> structure, the performance of CO<sub>2</sub>RR to CO is poor due to the difficulty for \*CO desorption during our previous work [27]. To enhance the activity of electrocatalytic CO<sub>2</sub>RR, an appropriate support should be adopted to modulate the coordination environment of Fe-N<sub>4</sub> active centers and thus improve the activity of the single Fe-N<sub>4</sub> sites. Carbon nanomaterials have shown excellent mechanical and unique electronic properties for electrocatalytic applications [28, 29], which could be an excellent support to confine and further modulate the single Fe-N<sub>4</sub> sites. Therefore, FePc was carbonized by a SiO<sub>2</sub> template-assisted method to synthesize Fe-N<sub>4</sub>/CF-800, Fe-N<sub>4</sub>/CF-900 and Fe-N<sub>4</sub>/CF-1,000 according to the synthetic temperature, as shown in the schematic illustration (Fig. 1).

The SEM and TEM images of Fe-N<sub>4</sub>/CF samples exhibit that the porous framework was well fabricated after removing the template of SiO<sub>2</sub> nanospheres (Figs. 2(a) and 2(b), Figs. S1(a), S1(b), S2(a), and S2(b) in the Electronic Supplementary Material (ESM)). The SEM images show that the pore size of the framework is mainly in a range of 40–90 nm, which agrees with the size of the SiO<sub>2</sub> nanospheres. The HRTEM (Fig. 2(c), Figs. S1(c) and S2(c) in the ESM) images show no iron clusters or nanoparticles were found in the framework of Fe-N<sub>4</sub>/CF samples. A typical lattice spacing of 3.5 Å (Fig. 2(c)) represents the (002) lattice plane of graphitic carbon, which indicates that the carbon foam was composited with graphene nanosheets. These graphene nanosheets will be favorable to promote the electron transfer during the reaction. The EDX spectra for elemental mappings



Figure 1 Schematic illustration of the synthesis of multiscale carbon foam confining single iron atoms.



**Figure 2** Morphology characterization of Fe-N<sub>4</sub>/CF-1,000. (a) SEM image. (b) TEM image. (c) HRTEM image. (d) Atomic resolution HAADF-STEM image showing the atomic dispersion of iron atoms in Fe-N<sub>4</sub>/CF-1,000.

(Fig. S3 in the ESM) show that the distribution of Fe and N are homogeneous in the carbon foam. Furthermore, the atomic resolution HAADF-STEM images for Fe-N<sub>4</sub>/CF (Fig. 2(d), Figs. S1(d) and S2(d) in the ESM) exhibit homogeneously bright spots corresponding to single iron atoms across the entire carbon foam.

The detail structural parameters of Fe-N<sub>4</sub>/CF were further analyzed in Fig. 3. XRD patterns exhibit no characteristic peaks of iron-based nanoparticles (Fig. 3(a)). Only two diffraction peaks at around 25.8° and 43.7° represent (002) and (101) lattice planes of graphitic carbon, which are consistent with the HRTEM and atomic resolution HAADF-STEM results (Figs. 2(c) and 2(d), Figs. S1(c), 1(d), S2(c), and S2(d) in the ESM). Raman spectra (Fig. S4 in the ESM) exhibit characteristic D and G bands of graphite carbon at approximately

1,350 and 1,603 cm<sup>-1</sup>. The  $I_D/I_G$  ratios in these samples prepared with different temperature is almost similar, suggesting that these samples have similar defect densities. The N2 adsorption-desorption isotherms indicate these samples also have the similar pore size distribution and specific surface areas in the range of 1,009–1,059 m<sup>2</sup>·g<sup>-1</sup> (Fig. S5 and Table S1 in the ESM). The porous framework and high specific surface areas, fabricated by the template of SiO<sub>2</sub> nanospheres, can efficiently enhance the transfer of reactant (CO<sub>2</sub>) and product (CO) during the electrocatalytic CO<sub>2</sub>RR. In contrast, FeNC@1,000 synthesized without SiO<sub>2</sub> template did not form the foam structure, but exhibit some nanoparticles embedded in the carbon matrix instead according to the SEM and TEM images (Figs. S6(a) and S6(b) in the ESM). The HRTEM image exhibits Fe<sub>3</sub>C nanoparticle with the interlayer spacing value of 2.0 Å is encapsulated in carbon shells (Fig. S6(c) in the ESM), which has been further demonstrated by XRD pattern (Fig. S7 in the ESM). Furthermore, the Fe content of FeNC@1,000 is much higher than that of Fe-N<sub>4</sub>/CF-1,000 (Table S1 in the ESM), while the specific surface area of FeNC@1,000 is only 220 m<sup>2</sup>·g<sup>-1</sup> which is quite lower than that of Fe-N<sub>4</sub>/CF-1,000 (Table S1 in the ESM).

The chemical composition and electronic properties of the catalysts were investigated by XPS, ICP and X-ray absorption fine structure (XAFS). The XPS spectra of Fe-N<sub>4</sub>/CF samples (Fig. S8 in the ESM) show that carbon, nitrogen and oxygen are the main species. The peak of iron is not obvious due to the low content, which has been tested by ICP (Table S1 in the ESM). The high-resolution N 1s spectra (Fig. 3(b)) can be fitted into five peaks: pyridinic N (398.2 eV), Fe-N<sub>x</sub> (399.1 eV), pyrrolic N (400.7 eV), graphitic N (401.4 eV), and N–O<sub>x</sub> (403.4 eV) species, respectively [30, 31]. All the N contents decreased with the increase of synthetic temperature, while the pyridinic N decreased by the most. The surface iron content (Fig. S9 in the ESM) also has the same trend with the total N content. The high-resolution Fe 2p spectra can be fitted into Fe<sup>2+</sup> (710.5 eV) and  $Fe^{3+}$  (714.3 eV). The  $Fe^{2+}$  in Fe-N<sub>4</sub> could be oxidized to  $Fe^{3+}$  in the form of O<sub>x</sub>-Fe-N<sub>4</sub> when the samples expose to the air [32, 33]. XANES profiles (Fig. 3(c)) indicate no significant change for all Fe-N<sub>4</sub>/CF samples, these near-edge structure of which is quite similar to the FePc reference. EXAFS spectra (Fig. 3(d) and Fig. S10 in the ESM) reveal that all the three Fe-N<sub>4</sub>/CF samples show a prominent



**Figure 3** Structural analyses of Fe-N<sub>4</sub>/CF samples. (a) XRD patterns. (b) XPS N 1s spectra. (c) Fe K-edge XANES profiles. (d) Fourier transformed EXAFS spectra in the R space.

peak for the Fe-N coordination, while no characteristic peak for Fe-Fe coordination can be found, which also agrees with the FePc reference. Furthermore, the Fe-N coordination numbers for these samples are 4.4, 4.2, and 4.4 according to the fitting results (Table S2 in the ESM). These results indicate that all the iron atoms in the Fe-N<sub>4</sub>/CF samples remain the atomic dispersion with a form of Fe-N<sub>4</sub> central structure even after high temperature pyrolysis.

The electrocatalytic CO<sub>2</sub>RR performance was carried out by using a H-type three-electrode cell with 0.5 M KHCO3 electrolyte. LSV was first measured to evaluate the electrochemical activity. As shown in Fig. 4(a), the activity is enhanced obviously when using  $CO_2$ -saturated KHCO3 solution instead of Ar-saturated KHCO3 solution, indicating CO<sub>2</sub> reduction has made a great contribution for the total activity. The Faradaic efficiency for each sample was measured to evaluate the product selectivity for electrocatalytic CO<sub>2</sub>RR. The analysis exhibits that no liquid reduction product in the electrolyte can be detected by using <sup>1</sup>H NMR (Fig. S11 in the ESM). Meanwhile, H<sub>2</sub> and CO are the gaseous reduction products analyzed by GC. CO is the main product from electrocatalytic CO<sub>2</sub>RR, and H<sub>2</sub> is the vice product from the hydrogen evolution reaction (HER). The similar Tafel slope result (Fig. S12 in the ESM) exhibits all the three Fe-N<sub>4</sub>/CF samples have the similar kinetic processes for CO production. Figures 4(b) and 4(c) show the Faradaic efficiency for  $H_2$  and CO from -0.4 to -0.8 V vs. RHE, respectively. The sums of Faradaic efficiency for H<sub>2</sub> and CO are approximately 100% at the whole potential range, further demonstrating the main reduction products are H<sub>2</sub> and CO. Fe-N<sub>4</sub>/CF-1,000 shows the best performance for electrocatalytic CO2RR to CO under all tested potentials, achieving the maximum Faradaic efficiency of 94.9% at -0.5 V vs. RHE. However, Fe-N<sub>4</sub>/CF-1,000 exhibits the lower total current density compared with Fe-N<sub>4</sub>/CF-800 and Fe-N<sub>4</sub>/CF-900 (Fig. 4(d)), which may be caused by the decrease of active sites for electrocatalytic CO<sub>2</sub>RR and HER when increasing the pyrolysis temperature during the preparation of catalysts. Previous investigations suggest that Fe-N<sub>4</sub> sites in carbon matrix is the active sites for electrocatalytic CO<sub>2</sub>RR [34, 35]. Since Fe-N<sub>4</sub>/CF-1,000 owns abundant single Fe-N<sub>4</sub> sites in the carbon foam, CO<sub>2</sub> can be absorbed on the iron atoms and further protonated to CO. Additionally, pyridinic N in graphene has been demonstrated to improve the electrocatalytic HER performance [36, 37]. According to the analysis of XPS N 1s spectra in Fig. 3(b), the content of pyridinic N decreased by the most from Fe-N<sub>4</sub>/CF-800 to Fe-N<sub>4</sub>/CF-1,000, indicating that a large amount of active sites for HER have been removed at high temperature. Furthermore, Fe-N<sub>4</sub>/CF-1,000 has the largest turnover frequency (TOF) for CO production at all applied potential (Fig. S13 in the ESM) [27]. Therefore, Fe-N<sub>4</sub>/CF-1,000 is the optimum catalyst for electrocatalytic CO<sub>2</sub>RR to CO. For the comparison, the performance of FeNC@1,000 was also evaluated. As shown in Fig. 4(d), the current density of FeNC@1,000 is extremely low, which may be led by the low activity and the unordered structure limiting the diffusion of reactants and products. The performance at lower potentials are not given because of the extremely low concentration of products. Obviously, the H<sub>2</sub> Faradaic efficiency of FeNC@1,000 (Fig. 4(b)) is much higher than Fe-N<sub>4</sub>/CF-1,000, owing to the Fe<sub>3</sub>C nanoparticles encased in carbon layers favoring the HER [38]. Therefore, the CO Faradaic efficiency of FeNC@1,000 (Fig. 4(c)) is much lower than Fe-N<sub>4</sub>/CF-1,000, and drops sharply due to the diffusion limitation without the porous environment. Furthermore, the durability of Fe-N<sub>4</sub>/CF-1,000 was evaluated at -0.5 V vs. RHE in CO<sub>2</sub>-saturated 0.5 M KHCO3 electrode. The current density and the Faradaic efficiency for H<sub>2</sub> and CO as a function of elapsed time show almost negligible change over 60 hours (Fig. 4(e)), demonstrating that Fe-N<sub>4</sub>/CF-1,000 owns the high stability for electrocatalytic CO<sub>2</sub>RR to CO. This stability of Fe-N<sub>4</sub>/CF-1,000 may be attributed to the



**Figure 4** Electrocatalytic CO<sub>2</sub>RR performance in 0.5 M KHCO<sub>3</sub> solution at 25 °C. (a) Linear sweep voltammetric curves for Fe-N<sub>4</sub>/CF-1,000. (b) Faradaic efficiency for H<sub>2</sub> formation. (c) Faradaic efficiency for CO formation. (d) Total current density at each potential. (e) Stability of Fe-N<sub>4</sub>/CF-1,000 at -0.5 V vs. RHE.

stable single iron atoms coordinated with four nitrogen atoms in the carbon matrix.

#### 4 Conclusions

In summary, we report a multiscale structural modulation from macro-scale to atomic-scale for the carbon foam confining single iron atoms to enhance the performance of electrocatalytic CO2RR to CO. Such catalyst possesses pore-enriched environment, efficient electrical conductivity and abundant active sites, which efficiently improves the diffusion, electron transfer and intrinsic catalytic activity, achieving a CO Faradaic efficiency of 94.9% at -0.5 V vs. RHE in CO<sub>2</sub>RR. Furthermore, the long-term test indicates that the performance can be maintained over 60 hours due to the stable single iron atoms cooperated with four nitrogen atoms in the carbon matrix. This study shows a strategy to modulate the structure and electronic properties of carbon foam confining single iron atoms to efficiently improve both the activity and stability for electrocatalytic CO<sub>2</sub> reduction to CO. This strategy can be expanded to the design of multiscale carbon foam confining other single atom catalysts (such as Co, Ni, Cu) with corresponding metal phthalocyanine as precursors.

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