View Article Online

## Journal of Materials Chemistry A

Materials for energy and sustainability

## Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: W. Xiong, Z. Guo, S. Zhao, Q. Wang, Q. Xu and X. Wang, *J. Mater. Chem. A*, 2019, DOI: 10.1039/C9TA07790A.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the <u>Ethical guidelines</u> still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



rsc.li/materials-a

### ARTICLE

Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

# Facile, Cost-Effective Plasma Synthesis of Self-Supportive FeS<sub>x</sub> on Fe Foam for Efficient Electrochemical Reduction of N<sub>2</sub> under Ambient Conditions

Wei Xiong<sup>[a]</sup>, Zheng Guo<sup>[a]</sup>, Shijun Zhao<sup>\*[b]</sup>, Qian Wang<sup>[c]</sup>, Qiyong Xu<sup>[c]</sup>, and Xinwei Wang<sup>\*[a]</sup>

Electrochemical N<sub>2</sub> reduction reaction (NRR) in an aqueous medium has recently aroused great attention for the synthesis of NH<sub>3</sub> under ambient conditions. However, this process generally suffers from low NH<sub>3</sub> production rate and often requires a noble-metal based electrocatalyst with some sophisticated nanosynthesis method. This work reports a new non-precious, self-supportive iron sulfide (FeS<sub>x</sub>) NRR electrocatalyst, synthesized by a simple H<sub>2</sub>S-plasma treatment on low-cost Fe foam. The H<sub>2</sub>S-plasma treatment sulfurizes the Fe surface to afford a self-supportive FeS<sub>x</sub> thin layer on the Fe foam (FeS<sub>x</sub>/Fe). The synthesized FeS<sub>x</sub>/Fe foam can be directly used as the electrode for the NRR, and it is demonstrated to show a remarkable NH<sub>3</sub> production rate of  $4.13 \times 10^{-10}$  mol s<sup>-1</sup> cm<sup>-2</sup> and a high Faradaic efficiency of 17.6%, which significantly outperformed many other reported non-precious electrocatalysts. Further material characterizations show that the surface FeS<sub>x</sub> converts to the mackinawite FeS after the NRR; the mackinawite FeS is possibly the actual high-activity NRR electrocatalyst, and density functional theory calculation is further employed to elucidate the NRR mechanism. Given the high performance and low cost, we envision that the plasma-synthesized FeS<sub>x</sub>/Fe will be of great promise for the electrochemical NH<sub>3</sub> synthesis under ambient conditions.

#### Introduction

Published on 02 August 2019. Downloaded by UNIVERSITE PARIS SUD on 8/5/2019 7:47:23 AM

Ammonia (NH<sub>3</sub>) is the largest chemical product in the world, with an annual production of 150 million metric tons globally.<sup>1</sup> Currently, over 90% of the synthetic NH<sub>3</sub> is produced by the industrial Haber-Bosch process using N<sub>2</sub> and H<sub>2</sub> gases over Fe-based catalysts at high temperature (400-500 °C) and high pressure (150-200 atm), which demands 1% of the world energy supply and generates a huge amount of CO2.2-4 In stark contrast, many natural plants and bacteria carry metalloenzyme nitrogenase which can activate the highly stable N=N triple bond (941 kJ/mol) and enable the NH<sub>3</sub> generation from N<sub>2</sub> under ambient conditions.<sup>5</sup> Inspired by this biological process, significant effects have been devoted to seeking the synthesis methods of  $NH_3$  from  $N_2$  under mild conditions. Recently, the electrochemical N<sub>2</sub> reduction reaction (NRR) in an aqueous medium has aroused great attention for the ambient synthesis of NH<sub>3</sub>.<sup>6-12</sup> This electrochemical approach directly utilizes abundant water as the hydrogen source, and it can be readily coupled with an intermittent renewable energy source, such as wind, solar, or marine, to support the needed electricity, therefore also allowing for the use in the areas with limited transportation accessibility and unsuited for building large chemical plants.<sup>4, 6</sup> Nevertheless, the activation of the N=N bond under mild conditions is a significant challenge, for not only its very high bond energy but also its lack of dipole moment,<sup>13</sup> and therefore an electrocatalyst is extremely required for the NRR. Moreover, the NRR in an aqueous medium is always accompanied with a fierce competition with the hydrogen evolution reaction (HER), because of their close redox potentials, which therefore renders an even more severe challenge on the selectivity of the electrocatalyst toward the NRR.<sup>6-7, 14-15</sup>

Very recently, the electrocatalysts based single-atom Ru<sup>16</sup> and Au nanoparticles<sup>9</sup> were reported to show high rates and Faradaic efficiencies for NH<sub>3</sub> production. However, the use of the noble metals of Ru and Au, along with the required sophisticated synthesis for single atoms and nanoparticles, could cause a serious cost issue for large-scale applications. Other electrocatalysts based on non-precious metal compounds (e.g. Fe<sub>2</sub>O<sub>3</sub>,<sup>17-18</sup> Bi<sub>4</sub>V<sub>2</sub>O<sub>11</sub>,<sup>19</sup>  $MoS_{2}$ ,<sup>20-21</sup>  $Mo_2C$ ,<sup>22</sup> Fe<sub>3</sub>S<sub>4</sub><sup>23</sup>), black-P,<sup>24</sup> and carbon materials<sup>15, 25-28</sup> were also intensively studied, but the reported NH<sub>3</sub> production rates and Faradaic efficiencies were still comparatively low. Therefore, there is still a great and urgent need to develop highlyefficient non-precious NRR electrocatalysts, desirably with a simple and cost-effective synthesis approach.

Herein, we report a new self-supportive iron sulfide (FeS<sub>x</sub>) NRR electrocatalyst, which was synthesized by a simple H<sub>2</sub>S-plasma treatment on low-cost Fe foam. Upon the H<sub>2</sub>S-plasma treatment, the surface of the Fe foam was sulfurized to afford a self-supportive thin layer of FeS<sub>x</sub>, which exhibited a remarkable electrocatalytic activity toward NRR. Using the Fe foam supported FeS<sub>x</sub> (FeS<sub>x</sub>/Fe)

<sup>&</sup>lt;sup>a.</sup> School of Advanced Materials, Shenzhen Graduate School, Peking University, Shenzhen, 518055 (China) \*E-mail: wangxw@pkusz.edu.cn

<sup>&</sup>lt;sup>b.</sup> Department of Mechanical Engineering, City University of Hong Kong, Hong Kong, China \*E-mail: shijzhao@cityu.edu.hk

<sup>&</sup>lt;sup>c</sup> School of Environment and Energy, Shenzhen Graduate School, Peking University, Shenzhen, 518055, China

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

Journal Name

#### ARTICLE

directly as the working electrode, at -0.30 V versus reversible hydrogen electrode (RHE), the FeS<sub>x</sub>/Fe electrode exhibited a remarkable NH<sub>3</sub> production rate of 4.13×10<sup>-10</sup> mol s<sup>-1</sup> cm<sup>-2</sup> with a fairly high Faradaic efficiency of 17.6%, and these numbers significantly outperformed those reported for other non-precious electrocatalysts. Notably, the active N<sub>2</sub> fixation sites in biological nitrogenase are featured for the Fe–S clusters,<sup>29</sup> and their resemblance with respect to the herein reported pure-inorganic FeS<sub>x</sub> catalyst certainly deserves additional attention, as it may provide significant insights on the mimicking of the natural N<sub>2</sub> fixation process.

#### **Experimental Procedures**

H<sub>2</sub>S plasma treatment of Fe foam (preparation of the FeS<sub>x</sub>/Fe foam): The H<sub>2</sub>S plasma treatment was carried out in a home-built system consisting of a quartz tube inside a tubular furnace.<sup>30</sup> Commercial Fe foam was cut into 1 cm × 2 cm sized pieces, and the sample pieces were placed at the center zone inside the quartz tube. The tube was heated to 160 °C during the plasma treatment. 50 sccm H<sub>2</sub>S (3% diluted in Ar) gas was continuously flowed through the tube, and the pressure inside the tube was maintained at 600 mTorr by vacuum pumping. The upstream part of the quartz tube was wrapped with copper coil, through which a radiofrequency (13.56 MHz) power of 60 W was supplied to generate the H<sub>2</sub>S plasma inside the upstream zone of the tube. The plasma power was supplied in a pulsed mode, to avoid overheating of the tube. Each plasma pulse was 15 s long, and the entire sulfurization process consisted of 200 H<sub>2</sub>S plasma pulses in total.

**Preparation of the Fe\_2O\_3/Fe foam:** The aforementioned commercial Fe foam was heated in air at 600 °C for 1 h to afford the  $Fe_2O_3$  surface layer on Fe.

Material Characterizations: The surface morphology of the plasmatreated FeS<sub>x</sub>/Fe foam was examined by SEM (Zeiss, SUPRA55), which was equipped with EDS (Oxford Instruments, X-max<sup>N</sup> 20) for the elemental mapping analysis. The surface FeS<sub>x</sub> layer was examined by cross-sectional STEM (Jeol, JEM-3200F), XPS (Thermo Scientific, Escalab 250Xi), XRD (Bruker, D8 Advance), and Raman spectroscopy (Horiba, LabRAM HR800). For STEM measurements, the cross-sectional sample was prepared by using the focused ion beam (FIB) (FEI, Scios) technique to cut a thin lamella from the FeS<sub>x</sub>/Fe foam. To protect the surface FeS<sub>x</sub> layer, a 400 nm Pt film was first deposited on the FeS<sub>x</sub>/Fe before using the FIB to cut the sample. The HAADF-STEM images were taken with an electron acceleration voltage of 300 kV, and the elemental maps were obtained by EDS (Thermo Scientific, UltraDry). For XPS experiments, a monochromatic Al Ka X-ray source was used, and the binding energy was referenced to Au  $4f_{7/2}$  (83.96 eV). The high-resolution XPS spectra were acquired using a pass energy of 20 eV. For Raman experiments, the excitation wavelength was 532 nm.

#### Figure 2a, the electrochemical NRR measurements were Carried Sut in a two-compartment cell, where the two compartments were covered with lids and separated by a Nafion 211 membrane. Prior to the measurements, the Nafion membrane was pretreated by sequentially immersing in 5% $H_2O_2$ aqueous solution and ultrapure water (both at 80 °C) for 1 h each. The electrochemical data were collected on a CHI604E electrochemical workstation using standard

Electrochemical NRR measurements: As schematically illustrated in

three-electrode configuration. Pt foil and Hg/HgO electrodes were used as the counter and reference electrodes, respectively, and 0.1 M KOH aqueous solution was used as the electrolyte. The reported potentials were all *iR*-compensated and converted to the RHE scale. The electrochemical polarization curves were obtained by the potentiostatic chronoamperometry method, where the applied potential was stepwise increased and held constant in each step for 120 s to allow the current to reach a steady state. To characterize the NRR activity, pure N<sub>2</sub> gas (99.999%, 1 atm) was continuously bubbled into the electrolyte toward the working electrode, and before the measurement, 30 min of  $N_2$  bubbling was first conducted to saturate the electrolyte and the compartments. For the control experiments, pure Ar gas (99.999%, 1 atm) was used (instead of N<sub>2</sub>) for the bubbling, and all the other experimental procedures were the same as those for N2. The Ar control experiments were performed in parallel to the NRR experiments, in order to exclude any potential interference from the ambient atmosphere (e.g. trace ambient ammonia<sup>12</sup>). All the NRR experiments were performed for at least three times to confirm the data reproducibility.

#### **Results and Discussion**



**Scheme 1.** Scheme and photographs showing the  $H_2S$  plasma treatment on Fe foam to afford a surface layer of FeS<sub>x</sub> on Fe.

Scheme 1 schematically shows the straightforward plasma approach to obtain the FeS<sub>x</sub> electrocatalyst. A piece of commercial porous Fe foam was treated by  $H_2S$  plasma at 160 °C for an accumulated time of 50 min, and a thin uniform layer of FeS<sub>x</sub> was formed on the Fe surface (i.e. FeS<sub>x</sub>/Fe). The temperature of the plasma treatment was particularly chosen so as to limit the sulfur diffusion in Fe and therefore limit the sulfurization within the top tens of nm. The photographs in Scheme 1 show that the entire piece of the Fe foam changed the color uniformly after the  $H_2S$  plasma treatment, which indicates a full uniform coverage of the FeS<sub>x</sub> on Fe and implies that this plasma process could be readily scaled up. The microstructure of the obtained FeS<sub>x</sub>/Fe foam was

Published on 02 August 2019. Downloaded by UNIVERSITE PARIS SUD on 8/5/2019 7:47:23 AM

#### Journal Name

examined by scanning electron microscopy (SEM), and a typical SEM image and the corresponding energy-dispersive X-ray spectrum (EDS) are shown in Figure 1a,b. After the plasma treatment, the integrity of the mesoporous foam structure was well retained, and the surface  $FeS_x$  layer was fairly uniform and smooth. The good mesoporosity and uniform surface conversion to  $FeS_x$  were both important for electrocatalysis, because they can enable fast diffusion of reactive species, efficient penetration of electrolyte, and significantly enlarged surface area for electrochemical reaction.



**Figure 1.** (a) SEM and (b) the corresponding EDS spectrum of the  $FeS_x/Fe$  foam. (c) Cross-sectional STEM HAADF image and (d-g) the associated EDS elemental maps of (e) Fe, (f) S, (g) Pt, and (d) their composite, showing the surface  $FeS_x$  layer of the  $FeS_x/Fe$  foam. (h) XPS survey spectrum and the high-resolution spectra of (i) the Fe 2p and (j) S 2p core-level emissions.

The surface FeS<sub>x</sub> layer was further examined by crosssectional scanning transmission electron microscopy (STEM). To prepare the STEM sample, a protective platinum layer was first deposited on the FeS<sub>x</sub>/Fe. Figure 1c shows the high-angle annular dark field (HAADF) STEM image of the FeS<sub>x</sub> layer on Fe, and Figure 1d-g show the corresponding elemental distributions, as obtained by EDS mapping. These results show that a uniform ~70 nm  $\text{FeS}_{x}$ layer was formed on the Fe surface. X-ray photoelectron spectroscopy (XPS) was further used to analyze the composition of the FeS<sub>x</sub> layer. Figure 1h shows the XPS survey spectrum, and Figure 1i,j show the high-resolution spectra for the Fe 2p and S 2p corelevel emissions. The Fe spectrum shows a paired spin-orbit peaks at 707.3  $(2p_{3/2})$  and 720.0 eV  $(2p_{1/2})$ , and the S spectrum shows a paired spin-orbit peaks at 162.5  $(2p_{3/2})$  and 163.7 eV  $(2p_{1/2})$ . These numbers of binding energies agree well with those for FeS2,30 suggesting that the surface FeS<sub>x</sub> was FeS<sub>2</sub>. Also, from the areal intensities of the Fe and S 2p peaks, the atomic ratio of S/Fe was determined to be 2.03±0.03, which again suggests the formation of FeS<sub>2</sub>. The crystal structure of the formed FeS<sub>2</sub> was examined by X-

ray diffraction (XRD) and high-resolution TEM with is fast in Equation transform (FFT) image analysis (Figure S1), and both the techniques showed that the formed FeS<sub>2</sub> was a mixed pyrite- and marcasite-type FeS<sub>2</sub>, resembling the case of using the H<sub>2</sub>S plasma for the atomic layer deposition of FeS<sub>2</sub>.<sup>30</sup> The mixed phase of FeS<sub>2</sub> was further confirmed by Raman spectroscopy (Figure S12), and in addition, no Raman signals for elemental S were observed.



**Figure 2.** Characterizations of electrocatalytic NRR performance. (a) Electrochemical polarization curves of the FeS<sub>x</sub>/Fe electrode in N<sub>2</sub>and Ar-saturated solutions. Inset schematically illustrates the measurement setup. (b) Chronoamperograms for potentiostatic measurements. (c) Ion chromatograms of the post-NRR electrolytes for quantifying the production of NH<sub>3</sub> by NRR. Same line colors were used in (b) and (c), and the curve for the initial electrolyte (before NRR) was also shown for comparison. (d) NH<sub>3</sub> production rates at various potentials. (e) Faradaic efficiency of NH<sub>3</sub> production and  $\Delta j/jN_2$  ratio with respect to the applied potential. The blue-color bin in (d) and blue-color dot in (e) represent the numbers obtained by NMR using isotopic <sup>15</sup>N<sub>2</sub> labeling. (f) Comparison of Fe, Fe<sub>2</sub>O<sub>3</sub>, and FeS<sub>x</sub> for their NH<sub>3</sub> production rates and Faradaic efficiencies.

The electrocatalytic NRR performance of FeS<sub>x</sub> was characterized in 0.1 M KOH aqueous electrolyte at room temperature (21 °C) using a two-compartment cell with threeelectrode configuration as schematically illustrated in Figure 2a (inset). Each of the cell compartments was covered with a lid, in order to avoid any potential interference from the ambient atmosphere (e.g. trace ambient ammonia<sup>31</sup>). The FeS<sub>x</sub>/Fe foam was directly used as the working electrode. To characterize the NRR performance, pure N<sub>2</sub> gas (99.999%, 1 atm) was continuously bubbled into the electrolyte, and an additional 30 min of N<sub>2</sub> bubbling was conducted prior to the measurement. For the control experiments, pure Ar gas (99.999%, 1 atm) was instead used for the bubbling. More experimental details are provided in Supporting Information. The electrochemical polarization curves were obtained by stepwise increasing the potential from -0.14 to -0.42 V (vs. RHE) and holding the potential constant for 120 s in each step to allow the current to reach a steady state (Figure S2). The values of the steady-state currents were used to generate the polarization curves as shown in Figure 2a for the measurements taken under  $N_2$  or Ar gas bubbling. The current density (j) was found to be considerably greater under N<sub>2</sub> bubbling  $(i_{N2})$  than that under Ar bubbling  $(i_{Ar})$ , especially in the potential range from -0.22 to -0.38 V (vs. RHE).

ARTICLE

Journal Name

#### ARTICLE

Presumably, the current under Ar bubbling should correspond to the HER, and assuming that the HER and NRR are two separate competing processes, the difference between the above two curves  $(\Delta j = j_{\rm N2} - j_{\rm Ar})$  should correspond to the NRR. Our results showed that this difference of current density ( $\Delta j$ ) reached its maximum of  $-138 \ \mu A/cm^2 \ at -0.30 \ V$  (vs. RHE), and this number accounted for as high as 19.7% of the total current density under N<sub>2</sub> bubbling ( $j_{\rm N2}$ ). The high  $\Delta j/j_{\rm N2}$  ratio implied that a fairly large portion of the cathodic current was used to reduce N<sub>2</sub>.

The reduction products of  $N_2$  (e.g.  $NH_3$  and  $N_2H_4$ ) were quantified by the following procedures. To obtain sufficient amounts of the products for quantitative assessment, we first biased the FeS<sub>x</sub> electrode at a certain constant potential for 20 h, and then collected the electrolyte at the  $FeS_x$  electrode side to analyze the quantities of the accumulated products. This procedure was repeatedly conducted at various constant potentials of -0.14, -0.22, -0.30, -0.38, and -0.42 V (vs. RHE), and the trace of the current density variation over each 20 h period was also recorded for each potential. As shown in Figure 2b, the current densities remained fairly constant over time, suggesting a good stability of the electrocatalyst. The negligible variation of the current density also suggests a constant generation rate of the reaction product, and therefore the product generation rate could be calculated by dividing the total product amount by the total reaction time. As the major product of the NRR, the amount of NH<sub>3</sub> was guantified by the ion chromatography, indophenol blue, and Nessler's reagent methods. As shown in the following, all the three methods gave out quite similar results, owing to the reasonably high concentration of  $NH_3$  in the post-NRR electrolyte (up to ~2 mM), which was significantly higher than the detection limits of these methods.<sup>31</sup> Figure 2c shows the ion chromatograms of the post-NRR electrolytes, and using the absolute calibration curve shown in Figure S3, the concentration of NH<sub>3</sub> in the reaction product solution could be obtained. Similarly, for the indophenol blue and Nessler's reagent methods, the photographs and absorption spectra are shown in Figures S4 and S5, and the calibration curves are shown in Figure S6. The obtained concentrations of NH<sub>3</sub> were used to calculate the production rates of NH<sub>3</sub> at various potentials on the FeS<sub>x</sub> electrocatalyst. As shown in Table S1, the numbers obtained from the three methods were guite similar, and therefore we simply used the numbers from the ion chromatography to plot Figure 2d,e. Control experiment was carried out in parallel, using the same setup but instead using Ar for the bubbling for 20 h (potential = 0 V vs. RHE). The resultant electrolyte was also analyzed for NH<sub>3</sub> using the same methods as above, and the obtained curves are included in Figures 2c, S4, and S5 for comparison. Clearly, the NH<sub>3</sub> production from the control experiment was negligible, which confirmed that the previously obtained  $\mathsf{NH}_3$  production was exclusively from the electrochemical NRR process. Figure 2d plots the NH<sub>3</sub> production rate with respect to the applied potential (see also Table S2), and a maximum rate of 4.45×10<sup>-10</sup> mol s<sup>-1</sup> cm<sup>-2</sup> was observed at -0.30 V (vs. RHE). The Faradaic efficiency (FE) of NH<sub>3</sub> production was also calculated (Figure 2e), and its maximum number was able to reach 18.9% at -0.30 V (vs. RHE). Both of these numbers were fairly high, and they were among the best values reported recently (Table S3).<sup>15, 32</sup> To confirm the high performance

#### of NH<sub>3</sub> production, we adopted a recently published protocol of using isotopic <sup>15</sup>N labelling.<sup>33</sup> With the use of 1the 39 N<sub>2</sub>9gas 799% isotopic purity) as the nitrogen source, the NRR experiment was performed again at -0.30 V (vs. RHE), and the production of the <sup>15</sup>N-labelled ammonia (i.e. <sup>15</sup>NH<sub>3</sub>) was quantified by nuclear magnetic resonance (NMR).<sup>33</sup> More experimental details are provided in Supporting Information. The obtained results (Figure S8) show that at –0.30 V (vs. RHE) the $^{15}\mathrm{NH}_3$ production rate and Faradaic efficiency were 4.13 mol $s^{-1}$ cm<sup>-2</sup> and 17.6%, respectively. These numbers (included in Figure 2d,e) are quite close to those previously obtained by ion chromatography, indophenol blue, and Nessler's reagent methods, which therefore confirms the high performance of the NH<sub>3</sub> production by our FeS<sub>x</sub> catalyst. Given that the <sup>15</sup>N labelling results are more convincing, we report these numbers for our catalyst in the following (Figure 2f) and to benchmark with other reports (Table S3). Besides, in Figure 2e is also plotted the $\Delta j/j_{N2}$ ratio for comparison, and the $\Delta j/j_{N2}$ ratio was found to be only slightly higher (0.3 $\sim$ 1.7%) than the FE of NH<sub>3</sub>, suggesting a high selectivity of NH<sub>3</sub> over other reduction products. In fact, we also quantified the production of N<sub>2</sub>H<sub>4</sub> using the Watt-Chrisp spectrophotometric method (Figures S6 and S7), and found out that N<sub>2</sub>H<sub>4</sub> was the major byproduct to account for the minor discrepancy shown in Figure 2e (see also Table S2). To sum up, the plasma-prepared FeS<sub>x</sub> showed very good electrocatalytic



performance toward the production of NH<sub>3</sub> from N<sub>2</sub> in ambient

condition, with high NH<sub>3</sub> production rate, high Faradaic efficiency,

and excellent stability.

**Figure 3.** (a) Nyquist and (b) Bode plots of the EIS data measured at -0.30 V (vs. RHE) in N<sub>2</sub>- and Ar-saturated solutions. (c) Plot of  $R_{\text{NRR}}^{-1}/(R_{\text{NRR}}^{-1}+R_{\text{HER}}^{-1})$  with respect to the applied potential. The inset shows the equivalent circuit used to fit the EIS data.

To gain insights on the electrocatalytic mechanism, electrochemical impedance spectroscopy (EIS) measurements were carried out on the  $FeS_x/Fe$  electrode in Ar- and N<sub>2</sub>-saturated solutions. Figure 3a,b show the Nyquist and Bode plots for the EIS data measured at -0.30 V (vs. RHE). The Nyquist plot shows single semicircles for both the cases, and the semicircle diameter was smaller for the N2-saturated case than the Ar-saturated case; the Bode plot shows single peaks in the frequency range of 0.1 Hz – 10 kHz, and the peak frequency was larger for the N<sub>2</sub>-saturated case than the Ar-saturated case. Similar measurements were also taken for other potentials and the results exhibited the same trend (Figure S9). The single Nyquist semicircle and Bode peak refer to a single equivalent charge-transfer process in the assessed frequency range (0.1 Hz - 10 kHz), which therefore suggests that the electrochemical HER and NRR herein were comparable in their reaction rates<sup>34-36</sup> and they might be viewed as two parallel processes. Therefore, the EIS data taken in the N2-saturated solution were fitted using a slightly modified equivalent circuit as

Published on 02 August 2019. Downloaded by UNIVERSITE PARIS SUD on 8/5/2019 7:47:23 AM

#### Journal Name

shown in the Figure 3c inset, where the charge-transfer resistance ( $R_{ct}$ ) was separated into  $R_{HER}$  and  $R_{NRR}$  to account for the two reaction channels in parallel, and the values of  $R_{HER}$  were simply adopted from the fittings of the EIS data measured in the Arsaturated solution where no NRR occurred. Details of the fitting results are listed in Table S4. We further calculated the value of  $R_{NRR}^{-1}/(R_{NRR}^{-1}+R_{HER}^{-1})$  at each potential, which corresponds to the percentage of the NRR current. As shown in Figure 3c, the data of  $R_{NRR}^{-1}/(R_{NRR}^{-1}+R_{HER}^{-1})$  exhibited the same trend as that of the  $\Delta j/j_{N2}$  ratios (Figure 2e), which indicates a good agreement between the ac and dc measurements.



**Figure 4.** (a) XPS Fe 2p and (b) S 2p spectra of the post-NRR FeS<sub>x</sub>. (c) Raman spectra of the initial and post-NRR FeS<sub>x</sub>. The spectrum for the mackinawite FeS is also included for comparison. (d) Freeenergy diagram for the NRR on the mackinawite FeS(011) surface, obtained from DFT calculation (U = 0 V). (e) Charge density difference of the N<sub>2</sub>-adsorbed surface; the red and green isosurfaces (0.002 e/Å<sup>3</sup>) denote electron accumulation and depletion in the space, respectively.

We further conducted the material characterizations of the surface  $FeS_x$  after the NRR. Although the mesoscopic surface morphology of the FeS<sub>x</sub>/Fe electrode remained almost the same after the NRR (Figure S10), considerable differences were found in the XPS results as shown in Figure 4a,b. Based on the areal intensities of the XPS peaks, the S/Fe atomic ratio was found to be much reduced to 0.94±0.04 after the NRR, suggesting a 1:1 stoichiometry for the post-NRR  $FeS_x$  (i.e.  $x \approx 1$ ); the peak positions also shifted to 706.9  $(2p_{3/2})$  and 720.3 eV  $(2p_{1/2})$  for Fe 2p and 161.8  $(2p_{3/2})$  and 162.7 eV  $(2p_{1/2})$  for S 2p, and these binding energy values match well with those for mackinawite FeS.37-38 Raman measurement was further taken, and as shown in Figure 4c the results clearly indicate a phase transition to the mackinawite FeS after the NRR (see also Figure S12). The formation of the mackinawite FeS was also evidenced in XRD and high-resolution TEM results (Figure S11). The transition from FeS<sub>2</sub> to FeS was probably accompanied by the leaching of S and Fe (S leached more) into the electrolyte solution, because the FeS<sub>x</sub> surface layer became appreciably thinner (~10 nm) after the NRR (Figure S11). It is worth noting that apparently the surface of the post-NRR  $FeS_x$  was partially oxidized as observed by XPS (Figures 4a and S13), however

#### it is currently not sure whether the oxidation occurred during the NRR or during the air break just before the XPS<sup>O</sup> measurement, because the mackinawite FeS itself can be readily oxidized upon air exposure.<sup>38</sup> Some future works on in-situ characterizations are needed to clarify this issue. Nevertheless, the mackinawite FeS is for sure of critical importance for the NRR, because the iron oxide itself was not able to afford such a high performance (vide infra, Figure 2f). To further show the critical importance of the mackinawite FeS, we employed a vapour-phase atomic layer deposition (ALD) technique<sup>37-38</sup> to directly deposit a thin layer (~13 nm) of mackinawite FeS on the Fe foam. As shown in Figure S14, the NRR performance of the ALD FeS was almost identical to that of the above plasma-synthesized FeS<sub>x</sub>. Therefore, we speculate that the mackinawite FeS was possibly the actual electrocatalyst for the NRR.

To further elucidate the NRR mechanism, theoretical density functional theory (DFT) calculation was carried out. In light of the above characterizations and discussion, the DFT calculation was performed on the mackinawite FeS(011) surface, which exposes the electrocatalytic centers of the transition-metal Fe atoms. Figure 4d displays the calculated free energy diagram of the lowest energy pathway for the NRR, and the corresponding elementary reaction steps are illustrated in Figure S15. The NRR process prefers an alternating protonation pathway,<sup>39-40</sup> and the potential-determining step is suggested to be the first protonation step of the adsorbed  $N_2$ molecule ( $\Delta G = 0.46 \text{ eV}$ ). Interestingly, for this protonation step, the thermodynamically favoured configuration of the adsorbed dinitrogen moiety changes from an end-on configuration (\*NN), coordinating to one surface Fe atom, to a bridged configuration (\*NNH\*), where the two N atoms are coordinated to two neighbouring Fe atoms on the surface. This observation suggests that the protonation may go through an intermediate step, where the adsorbed end-on N<sub>2</sub> first lies down on the surface, forming a bridged \*NN\* configuration and then being protonated. This process is realizable ( $\Delta G = 0.22 \text{ eV}$ ) probably because of the wellsuited Fe-Fe distance on the surface of the mackinawite FeS host structure.

The charge density differences for the two N<sub>2</sub>-adsorbed configurations (\*NN and \*NN\*) were further calculated to uncover the electron transfer behaviors between the N<sub>2</sub> and Fe atoms. As shown in Figure 4e, for the end-on \*NN configuration, the lone-pair electrons on N<sub>2</sub> are donated to the Fe cation ( $\sigma$  donation) forming a weak Fe-N bond, while some Fe d-orbital electrons are donated back into the N<sub>2</sub>  $\pi^*$  antibonding orbital ( $\pi$  back-donation), weakening the N=N triple bond, and as a result, the N<sub>2</sub> bond length is appreciably increased to 1.140 Å in the \*NN configuration, as compared to 1.0976 Å in free N2. As for the bridged \*NN\* configuration, the  $\pi$  back-donation is considerably enhanced, because of the spatial match of the electron orbitals in the bridged Fe–N–N–Fe configuration. The insensitive  $\pi$  back-donation significantly weakens the N≡N triple bond and strengthens the Fe–N bonds (Figure 4e), and as a result, the N<sub>2</sub> bond length is significantly increased to 1.190 Å, approaching to the bond length of the N=N double bond in diazene (1.201 Å).<sup>41-42</sup> Apparently, the N<sub>2</sub> bond is highly activated in the bridged \*NN\* configuration, and this high activation is benefited from the well-suited Fe-Fe distance on the

ARTICLE

2

З

4

5 6

7

8

9

A Accepted

mistry

Materials

#### Journal Name

mackinawite FeS surface, which therefore highlights the importance of the mackinawite-structure FeS electrocatalyst for the NRR.

In the last, we also compared the NRR performance of FeS<sub>x</sub> with Fe<sub>2</sub>O<sub>3</sub>, which was recently reported as a good NRR electrocatalyst.<sup>17-18</sup> The Fe<sub>2</sub>O<sub>3</sub> catalyst was prepared by surface oxidation of the same-type Fe foam (Fe<sub>2</sub>O<sub>3</sub>/Fe), and thus the surface areas of the FeS<sub>x</sub>/Fe and Fe<sub>2</sub>O<sub>3</sub>/Fe electrodes were approximately the same (Figure S16). Using the same measurement procedure, the resultant maximum N<sub>2</sub> production rate and Faradaic efficiency of the Fe<sub>2</sub>O<sub>3</sub> electrocatalyst were obtained and plotted in Figure 2f. Note that the bare Fe foam did not show any measurable NH<sub>3</sub> production. Indeed, the Fe<sub>2</sub>O<sub>3</sub> catalyst showed a decent NH<sub>3</sub> production rate of 2.71×10<sup>-11</sup> mol s<sup>-1</sup> cm<sup>-2</sup> (at –0.3 V vs. RHE) with a Faradaic efficiency of 2.2%, which were both consistent with previous reports;<sup>18, 43</sup> however these numbers were apparently much lower than those of the FeS<sub>x</sub> electrocatalyst.

#### Conclusions

Published on 02 August 2019. Downloaded by UNIVERSITE PARIS SUD on 8/5/2019 7:47:23 AM

In summary, we reported a simple, cost-effective plasma sulfurization method to prepare self-supportive FeS<sub>x</sub> on Fe foam for the efficient NRR under ambient conditions. The prepared FeS<sub>x</sub>/Fe electrode was demonstrated to show a remarkable NH<sub>3</sub> production rate of 4.13×10<sup>-10</sup> mol s<sup>-1</sup> cm<sup>-2</sup> and a high Faradaic efficiency of 17.6%, which significantly outperformed many other non-precious electrocatalysts. Further material characterizations showed that the surface  $\mbox{FeS}_{x}$  converted to the mackinawite FeS after the NRR, and the mackinawite FeS was possibly the actual high-activity NRR electrocatalyst. DFT calculation was further employed to elucidate the NRR mechanism on FeS, and the well-suited Fe-Fe distance on the mackinawite FeS(011) surface was suggested to be the crucial factor for the high NRR activity. Given the high performance and low cost, we envision that the plasma-synthesized FeS<sub>x</sub>/Fe will be of high promise for the electrochemical NH<sub>3</sub> synthesis under ambient conditions. In addition, the structure of the FeS catalyst resembles, to some extent, the Fe-S clusters in biological nitrogenase, which may provide important insights on the mimicking of the natural N<sub>2</sub> fixation process.

#### **Conflicts of interest**

There are no conflicts to declare.

#### Acknowledgements

This work was financially supported by NSFC (Grant No. 51672011), Guangdong Natural Science Funds for Distinguished Young Scholar (Grant No. 2015A030306036), and Shenzhen Science and Technology Innovation Committee (Grant Nos. JCYJ20170303140959031 and JCYJ20180302150402760).

#### Notes and references

1 U. S. B. Ofcensus, Cybercemetery 2011.

- V. Kyriakou, I. Garagounis, E. Vasileiou, Aviewardices, nine Stoukides, Catal. Today 2016, 286, 201: 10.1039/C9TA07790A
- X. Guo, Y. Zhu, T. Ma, *J. Energy Chem.* **2017**, *26*, 1107.
- J. G. Chen, R. M. Crooks, L. C. Seefeldt, K. L. Bren, R. M. Bullock, M. Y. Darensbourg, P. L. Holland, B. Hoffman, M. J. Janik, A. K. Jones, *Science* **2018**, *360*, eaar6611.
- J. B. Howard, D. C. Rees, Chem. Rev. **1996**, 96, 2965.
- J. Deng, J. A. Iñiguez, C. Liu, *Joule* **2018**, *2*, 846.
- C. Guo, J. Ran, A. Vasileff, S. Z. Qiao, *Energy Environ. Sci.* **2018**, *11*, 45.
- G. F. Chen, X. Cao, S. Wu, X. Zeng, L. X. Ding, M. Zhu, H. Wang, *J. Am. Chem. Soc.* **2017**, *139*, 9771.
- L. SJ, B. D, S. MM, W. BR, Y. JM, J. Q, *Adv. Mater.* **2017**, *29,* 1700001.
- 10 V. Rosca, M. Duca, M. T. D. Groot, M. T. M. Koper, *Chem. Rev.* **2009**, *109*, 2209.
- 11 J. Wang, L. Yu, L. Hu, G. Chen, H. Xin, X. Feng, *Nat. Commun.* **2018**, *9*, 1975.
- S. L. Foster, S. I. P. Bakovic, R. D. Duda, S. Maheshwari, R. D. Milton, S. D. Minteer, M. J. Janik, J. N. Renner, L. F. Greenlee, *Nat.Catal.* 2018, 1, 490.
- K. Honkala, A. Hellman, I. N. Remediakis, A. Logadottir, A. Carlsson, S. Dahl, C. H. Christensen, J. K. Noerskov, *Science* 2005, *36*, 555.
- 14 A. R. Singh, B. A. Rohr, J. A. Schwalbe, M. Cargnello, K. Chan, T. F. Jaramillo, I. Chorkendorff, J. K. Nørskov, *Acs Catal.* **2017**, *7*, 706.
- S. Mukherjee, D. A. Cullen, S. Karakalos, K. Liu, H. Zhang,
  S. Zhao, H. Xu, K. L. More, G. Wang, G. Wu, Nano Energy
  2018, 48, 217.
- 16 Z. Geng, Y. Liu, X. Kong, P. Li, K. Li, Z. Liu, J. Du, M. Shu, R. Si, J. Zeng, *Adv. Mater.* **2018**, *30*, 1803498.
- 17 S. Chen, S. Perathoner, C. Ampelli, C. Mebrahtu, D. Su, G. Centi, *ACS Sustainable Chem. Eng.* **2017**, *5*, 7393.
- 18 J. Kong, A. Lim, C. Yoon, J. H. Jang, H. C. Ham, J. Han, S. Nam, D. Kim, Y.-E. Sung, J. Choi, H. S. Park, ACS Sustainable Chem. Eng. 2017, 5, 10986.
- 19 C. Lv, C. Yan, G. Chen, Y. Ding, J. Sun, Y. Zhou, G. Yu, Angew. Chem., Int. Ed. **2018**, *57*, 6073.
- 20 L. Zhang, X. Ji, X. Ren, Y. Ma, X. Shi, Z. Tian, A. M. Asiri, L. Chen, B. Tang, X. Sun, *Adv. Mater.* **2018**, 1800191.
- X. Li, T. Li, Y. Ma, Q. Wei, W. Qiu, H. Guo, X. Shi, P. Zhang,
  A. M. Asiri, L. Chen, B. Tang, X. Sun, *Adv. Energy Mater.* 2018, 8, 1801357.
- 22 H. Cheng, L.-X. Ding, G.-F. Chen, L. Zhang, J. Xue, H. Wang, Adv. Mater. 2018, 30, 1803694.
- X. Zhao, X. Lan, D. Yu, H. Fu, Z. Liu, T. Mu, Chem. Commun.
  2018, 54, 13010.
- 24 L. Zhang, L.-X. Ding, G.-F. Chen, X. Yang, H. Wang, *Angew. Chem., Int. Ed.* **2019**, *58*, 2612.
- 25 S. Zhao, X. Lu, L. Wang, J. Gale, R. Amal, Adv. Mater. 2019, 31, 1805367.
- C. Tang, H.-F. Wang, J.-Q. Huang, W. Qian, F. Wei, S.-Z. Qiao, Q. Zhang, *Electrochem. Energy Rev.* 2019, 10.1007/s41918.
- Y. Song, D. Johnson, R. Peng, D. K. Hensley, P. V. Bonnesen, L. Liang, J. Huang, F. Yang, F. Zhang, R. Qiao, A. P. Baddorf, T. J. Tschaplinski, N. L. Engle, M. C. Hatzell, Z. Wu, D. A. Cullen, H. M. Meyer, B. G. Sumpter, A. J. Rondinone, *Sci. Adv.* 2018, *4*, e1700336.
   Y. Liu, Y. Su, X. Ouan, X. Fan, S. Chen, H. Yu, H. Zhao, Y.
  - Y. Liu, Y. Su, X. Quan, X. Fan, S. Chen, H. Yu, H. Zhao, Y. Zhang, J. Zhao, ACS Catal. **2018**, *8*, 1186.

Journal Name

- D. F. Harris, D. A. Lukoyanov, S. Shaw, P. Compton, M. TokminaLukaszewska, B. Bothner, N. Kelleher, D. R. Dean, B. M. Hoffman, L. C. Seefeldt, *Biochemistry* 2018, 57, 701.
- 30 Z. Guo, X. Wang, Angew. Chem. **2018**, *57*, 5898.
- 31 L. F. Greenlee, J. N. Renner, S. L. Foster, ACS Catalysis 2018, 8, 7820.
- 32 D. Bao, Q. Zhang, F. L. Meng, H. X. Zhong, M. M. Shi, Y. Zhang, J. M. Yan, Q. Jiang, X. B. Zhang, *Adv. Mater.* 2017, 29, 1604799.
- S. Z. Andersen, V. Čolić, S. Yang, J. A. Schwalbe, A. C. Nielander, J. M. McEnaney, K. Enemark-Rasmussen, J. G. Baker, A. R. Singh, B. A. Rohr, M. J. Statt, S. J. Blair, S. Mezzavilla, J. Kibsgaard, P. C. K. Vesborg, M. Cargnello, S. F. Bent, T. F. Jaramillo, I. E. L. Stephens, J. K. Nørskov, I. Chorkendorff, *Nature* 2019, *570*, 504.
- L. Liao, S. Wang, J. Xiao, X. Bian, Y. Zhang, M. D. Scanlon, X. Hu, Y. Tang, B. Liu, H. H. Girault, *Energy Environ. Sci.* 2013, 7, 387.
- 35 J. Kubisztal, A. Budniok, A. Lasia, Int. J. Hydrogen Energy 2007, 32, 1211.
- 36 M. Jafarian, O. Azizi, F. Gobal, M. G. Mahjani, *Int. J. Hydrogen Energy* **2007**, *32*, 1686.
- W. Xiong, Z. Guo, H. Li, R. Zhao, X. Wang, ACS Energy Lett.
  2017, 2, 2778.
- 38 Y. Shao, Z. Guo, H. Li, Y. Su, X. Wang, Angew. Chem. 2017, 56, 3226.
- 39 S. Back, Y. Jung, Phys. Chem. Chem. Phys. 2016, 18, 9161.
- 40 C. J. M. van der Ham, M. T. M. Koper, D. G. H. Hetterscheid, *Chem. Soc. Rev.* **2014**, *43*, 5183.
- 41 C. Lv, Y. Qian, C. Yan, Y. Ding, Y. Liu, G. Chen, G. Yu, Angew. Chem., Int. Ed. **2018**, *57*, 10246.
- 42 H. Li, J. Shang, Z. Ai, L. Zhang, *J. Am. Chem. Soc.* **2015**, *137*, 6393.
- 43 X. Cui, C. Tang, X.-M. Liu, C. Wang, W. Ma, Q. Zhang, Chemistry 2018, 24, 18494.

#### ARTICLE

View Article Online DOI: 10.1039/C9TA07790A