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# Glycerine-based synthesis of a highly efficient Fe<sub>2</sub>O<sub>3</sub> electrocatalyst for N<sub>2</sub> fixation†

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The electrochemical nitrogen reduction reaction (NRR) is a promising approach to convert N<sub>2</sub> into high value-added NH<sub>3</sub>. However, it is still a challenge to achieve an efficient electrocatalyst for the NRR. Herein, it is demonstrated that the Fe<sub>2</sub>O<sub>3</sub> nanoparticles (NPs) generated from a glycerine-based synthesis can be applied as highly efficient catalysts for the NRR. The Fe<sub>2</sub>O<sub>3</sub> NPs show good performance with a high NH<sub>3</sub> yield (22 μg mg<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>) and a favorable Faradaic efficiency (FE) (3.5%) at -0.5 V vs. reversible hydrogen electrode (RHE). The facile synthesis strategy and satisfactory electrochemical properties demonstrate the potential application of the as-synthesized Fe<sub>2</sub>O<sub>3</sub> NPs for NRR.

## 1. Introduction

Ammonia (NH<sub>3</sub>) is a highly important chemical in many aspects of industrial production and daily life.<sup>1,2</sup> Fixation of N<sub>2</sub> to NH<sub>3</sub> is an important step for the natural N<sub>2</sub> cycle.<sup>3-5</sup> The current synthesis of NH<sub>3</sub> mainly depends on the industrial Haber-Bosch process, which involves serious energy consumption and leads to large amounts of greenhouse gas emissions.<sup>6,7</sup> To realize a green and sustainable strategy for N<sub>2</sub> fixation, electrochemical reduction of N<sub>2</sub> has recently attracted much attention, being an environmentally friendly route involving mild conditions.<sup>8-10</sup>

To date, a number of catalysts have been developed for the NRR, including noble metals,<sup>11-13</sup> transition metals,<sup>14,15</sup> metal-free materials,<sup>16-18</sup> metal-C composite materials<sup>19-21</sup> and Au-Fe<sub>3</sub>O<sub>4</sub>.<sup>22</sup> These catalysts have demonstrated potential applications in the NRR with improved FE and NH<sub>3</sub> yield. Most of the catalysts were synthesized with the assistance of surfactants (structure-directing agents) through solution methods.<sup>23</sup> However, the surfactants could passivate the catalyst surface, which decreases the activity of the catalyst since the reactions take place on the catalyst surface. Therefore, the catalyst with a clean surface could be very important for achieving the high activity.

Herein, we successfully synthesized the clean-surface Fe<sub>2</sub>O<sub>3</sub> electrocatalyst for NRR by using glycerine as solvent with a subsequent calcination process. There was no need of surfactants in the synthesis process and the particles were further calcinated, guaranteeing the clean nature of the Fe<sub>2</sub>O<sub>3</sub> surface. The as-prepared Fe<sub>2</sub>O<sub>3</sub> NPs demonstrated a good

electrocatalytic performance for NRR, with a high NH<sub>3</sub> yield (22 μg mg<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>) and a favorable FE (3.5%) at -0.5 V vs. reversible hydrogen electrode (RHE).

## 2. Materials and reagents

Glycerine (C<sub>3</sub>H<sub>8</sub>O<sub>3</sub>) (purity, 99.5%), iron(III) nitrate nonahydrate (Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O) (purity, 98.5%) and ethanol (CH<sub>3</sub>CH<sub>2</sub>OH) (purity ≥ 98.5%) were purchased from Sinopharm Chemical Reagent Co. Ltd.

### 2.1. Synthesis of Fe<sub>2</sub>O<sub>3</sub> nanoparticles (NPs)

121.2 mg of iron(III) nitrate nonahydrate was added into 5 mL glycerin. Then the solution was ultrasonicated for 10 min. The uniform solution was transferred into the Teflon-lined stainless-steel autoclave and heated at 180 °C for 20 h. The obtained product washed with ethanol and water for three times and dried at room temperature for 12 h. Then the product was put into a tubular furnace, heated to 450 °C for 2 h at the heating rate of 10 °C min<sup>-1</sup> under air. Finally, Fe<sub>2</sub>O<sub>3</sub> NPs was obtained.

### 2.2. Characterization

A Rigaku Dmax-rc X-ray diffractometer was used to perform X-ray diffraction (XRD) characterization. The transmission electron microscopy (TEM) images were obtained on a JEM 1400 TEM instrument. The X-ray photoelectron spectroscopy (XPS) characterization was conducted with ESCALAB 250.

### 2.3. Electrode preparation

5 mg as-obtained Fe<sub>2</sub>O<sub>3</sub>, 40 μL Nafion (5% wt) and 960 μL ethanol were mixed by ultrasound for forming suspension. 50 μL suspension was modified on 1 × 1 cm carbon cloth (CC). The Fe<sub>2</sub>O<sub>3</sub>-CC was used as working electrode.

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#### 2.4. Electrochemical reduction of N<sub>2</sub>

Electrochemical reduction of N<sub>2</sub> was carried out in a typical three-electrode gastight two-compartment reaction vessel separated by an anion exchange membrane (Nafion 211) on a CHI760 electrochemical workstation (Chenhua, Shanghai). The experiment was performed in 0.1 M Na<sub>2</sub>SO<sub>4</sub> solution (50 mL each compartment). A Pt wire was used as the counter electrode and an Ag/AgCl (4.0 M KCl) was used as reference. All potentials were converted to RHE. The electrolyte was then purged with N<sub>2</sub> for at least 30 min. N<sub>2</sub> was delivered into the cathodic compartment at a constant rate of 20 mL min<sup>-1</sup>. The potentiostatic tests were performed in 0.1 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution at different potentials such as -0.3, -0.4, -0.5, -0.6, and -0.7 V vs. RHE. The NH<sub>3</sub> yields and FEs of products were calculated as follows:

$$\text{NH}_3 \text{ yields } (\mu\text{g mg}_{\text{cat}}^{-1} \text{h}^{-1}) = m/(t \times m_{\text{cat}}) \quad (1)$$

$$\text{FE } (\%) = \alpha m F / M Q \quad (2)$$

where  $m$  is the mass of NH<sub>3</sub>,  $m_{\text{cat}}$  is the mass of catalyst,  $\alpha$  is the quantity of transferred electrons for producing NH<sub>3</sub>,  $M$  is the relative molecular mass, and  $Q$  is the total quantity of the electric charge.

#### 2.5. Determination of NH<sub>3</sub> and N<sub>2</sub>H<sub>2</sub>

The detections of NH<sub>3</sub> and N<sub>2</sub>H<sub>2</sub> were made by indophenol blue and Watt–Chrisp methods, respectively, according to the reported literature.<sup>24</sup>

### 3. Results and discussion

The Fe<sub>2</sub>O<sub>3</sub> electrocatalysts were synthesized by using glycerine as the solvent with a subsequent calcination process. In the synthesis system, there was no surfactant and the particles were further calcinated. Therefore, the Fe<sub>2</sub>O<sub>3</sub> particles with clean surface could be obtained by our present synthetic route. Fig. 1(a) shows the X-ray diffraction (XRD) pattern of the as-synthesized Fe<sub>2</sub>O<sub>3</sub>, which agrees well with the JCPDS No. 33-0664. This demonstrates the successful formation of Fe<sub>2</sub>O<sub>3</sub>. Low peak intensity may be caused by small size of Fe<sub>2</sub>O<sub>3</sub> particles. Transmission electron microscopy (TEM) images of the Fe<sub>2</sub>O<sub>3</sub>

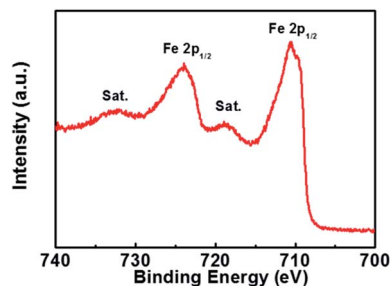


Fig. 2 High resolution XPS spectrum of Fe 2p.

suggests that the diameters of as-synthesized Fe<sub>2</sub>O<sub>3</sub> nanoparticles are in the range of 4–6 nm (Fig. 1(b) and (c)).

To investigate the surface elemental state of Fe<sub>2</sub>O<sub>3</sub> NPs, we analyzed the chemical states of the Fe<sub>2</sub>O<sub>3</sub> NPs by XPS analysis. There are two Fe<sup>3+</sup> peaks located at 711.8 eV and 725.3 eV, corresponding to Fe 2p<sub>1/2</sub> and Fe 2p<sub>3/2</sub>,<sup>25</sup> agreeing well with Fe<sub>2</sub>O<sub>3</sub> NPs (Fig. 2). The XPS spectrum result further demonstrated the successful synthesis of Fe<sub>2</sub>O<sub>3</sub> NPs.

The synthesized Fe<sub>2</sub>O<sub>3</sub> NPs were then used as the electrocatalysts for the electrochemical nitrogen reduction reaction (NRR). The produced ammonia was analyzed and quantified based on the indophenol blue method. Before NRR experiment, the corresponding calibration curve for ammonia by indophenol blue method was first determined and shown in Fig. 3.

The N<sub>2</sub>-fed electrolytes in 0.1 M Na<sub>2</sub>SO<sub>4</sub> electrolytes at different potentials for 2 h were mixed with the indophenol reagent, and their absorbance changed at 660 nm were depicted in Fig. 4(a). It indicated the substantial electroreduction of inert N<sub>2</sub> into valuable NH<sub>3</sub> was achieved using the as-synthesized Fe<sub>2</sub>O<sub>3</sub> electrocatalyst. Fig. 4(b) presented the chronoamperometric curves as a function of reaction time at varying applied potentials in 0.1 M Na<sub>2</sub>SO<sub>4</sub>, demonstrating the Fe<sub>2</sub>O<sub>3</sub> nanoparticles have good stability for NRR from -0.3 V to -0.6 V. The average NH<sub>3</sub> yield and the corresponding Faradaic efficiency (FE) was given in Fig. 4(c), in which the favorable NH<sub>3</sub> yield was 22.0 μg mg<sub>cat</sub><sup>-1</sup> h<sup>-1</sup> with FE value of 3.5% at -0.5 V. The NRR performance of the as-synthesized Fe<sub>2</sub>O<sub>3</sub> is comparable to lots of the NRR electrocatalysts (Table S1†). Therefore, the present synthesized Fe<sub>2</sub>O<sub>3</sub> with clean surface might be as a potential catalyst for electrochemical NRR in consideration that there are

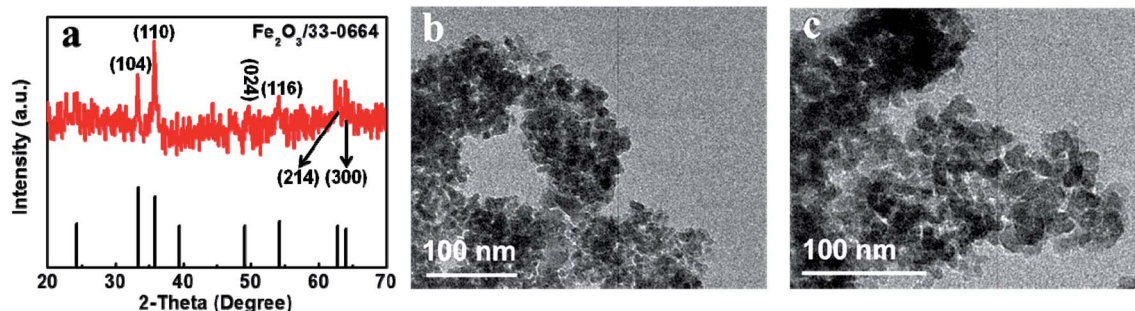


Fig. 1 (a) XRD pattern and (b and c) TEM images of the Fe<sub>2</sub>O<sub>3</sub> after calcination at 450 °C.



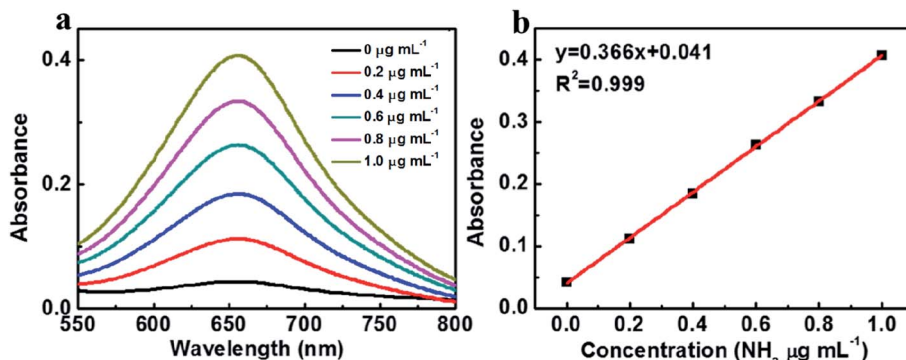


Fig. 3 (a) UV-vis absorption spectra of different concentration ammonia in 0.1 M  $\text{Na}_2\text{SO}_4$  solution, (b) standard curve of ammonia in 0.1 M  $\text{Na}_2\text{SO}_4$  solution.

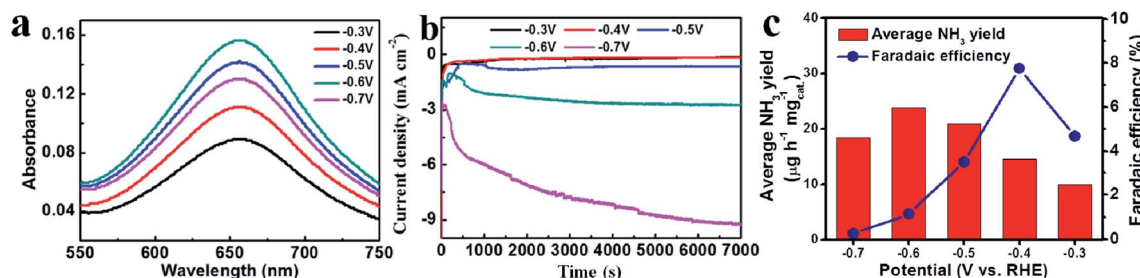


Fig. 4 UV-vis absorption spectra in (a) 0.1 M  $\text{Na}_2\text{SO}_4$  electrolytes stained with the indophenol indicator after NRR electrolysis at a series of potentials for 2 h, (b) time-dependent current density curves for  $\text{Fe}_2\text{O}_3$  at different potentials in 0.1 M  $\text{Na}_2\text{SO}_4$  solution, (c)  $\text{NH}_3$  yields and FEs for  $\text{Fe}_2\text{O}_3$  at a series of potentials in 0.1 M  $\text{Na}_2\text{SO}_4$ .

abundant Fe element in the earth. TEM image of catalyzed  $\text{Fe}_2\text{O}_3$  was tested after nitrogen fixation at  $-0.5$  V. It was found that the morphology did not change significantly, which indicated the good stability of the as-synthesized  $\text{Fe}_2\text{O}_3$  (Fig. S1†).

The NRR performance is highly related to the electrochemically active surface area (ECSA). Therefore, the ECSA of the as-prepared  $\text{Fe}_2\text{O}_3$  was further studied. Here, the ECSA was reflected by double layer capacitance ( $C_{dl}$ ) since there was a linear proportional relationship between ECSA and  $C_{dl}$ , which could be obtained by cyclic voltammetry curves in the range of 0.1–

0.2 V (Fig. 5(a)). Based on Fig. 5(b), the high  $C_{dl}$  of  $1.6 \text{ mF cm}^{-2}$  (Fig. 5(b)) further demonstrated that  $\text{Fe}_2\text{O}_3$  had high ECSA for NRR.

The hydrazine byproduct was further determined through a Watt–Chrip method. Fig. 6(a) showed the corresponding calibration curve based on UV-vis absorption at 455 nm. As shown in Fig. 6(b), the by-product of hydrazine was not detected, implying the high selectivity of  $\text{Fe}_2\text{O}_3$  for  $\text{NH}_3$  production (Fig. 6). Hence, the as-prepared  $\text{Fe}_2\text{O}_3$  catalyst could be used as a high-selective catalyst for producing  $\text{NH}_3$  by electrochemical NRR.

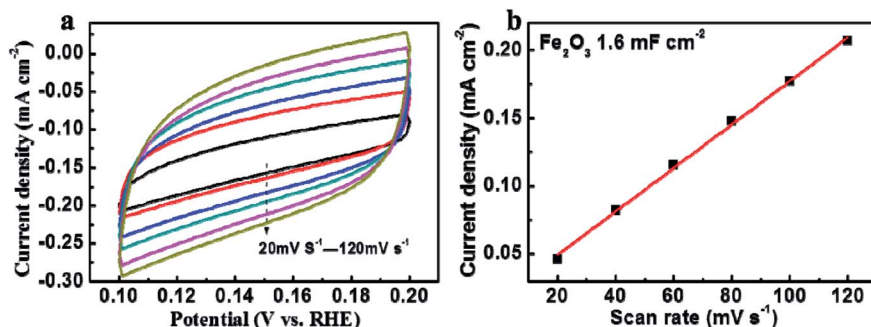


Fig. 5 (a) Cyclic voltammetry curves of  $\text{Fe}_2\text{O}_3$  at different scanning rate of potential in 0.1 M  $\text{Na}_2\text{SO}_4$  solution, (b) the double-layer capacitance of  $\text{Fe}_2\text{O}_3$ .



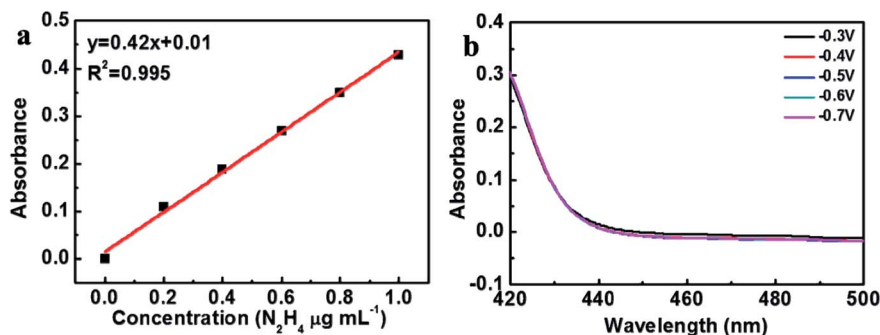


Fig. 6 (a) Standard curve of hydrazine in 0.1 M  $\text{Na}_2\text{SO}_4$  solution, (b) UV-vis absorption spectra of hydrazine in 0.1 M  $\text{Na}_2\text{SO}_4$  electrolytes after NRR electrolysis at a series of potentials for 2 h.

We also explored the NRR performance of  $\text{Fe}_2\text{O}_3$  in 0.1 M KOH. The selected potential was  $-0.5$  V. Unfortunately, the current density declined rapidly within 2 h (Fig. S2†).

## 4. Conclusions

In summary,  $\text{Fe}_2\text{O}_3$  synthesized by glycerine-based route with subsequent calcination process can be adopted as highly efficient NRR catalysts. Thanks to the clean surface of the catalyst, the  $\text{Fe}_2\text{O}_3$  NPs exhibited good performance with a  $22 \mu\text{g mg}_{\text{cat}}^{-1} \text{h}^{-1}$   $\text{NH}_3$  yield and a 3.5% Faraday efficiency at  $-0.5$  V for  $\text{NH}_3$  production, which outperformed lots of the previous catalysts. The flexible strategy and the good electrochemical performance endow  $\text{Fe}_2\text{O}_3$  with potential application in NRR.

## Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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