Glycerine-based synthesis of a highly efficient Fe$_2$O$_3$ electrocatalyst for N$_2$ fixation

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The electrochemical nitrogen reduction reaction (NRR) is a promising approach to convert N$_2$ into high value-added NH$_3$. However, it is still a challenge to achieve an efficient electrocatalyst for the NRR. Herein, it is demonstrated that the Fe$_2$O$_3$ nanoparticles (NPs) generated from a glycerine-based synthesis can be applied as highly efficient catalysts for the NRR. The Fe$_2$O$_3$ NPs show good performance with a high NH$_3$ yield (22 $\mu$g mg$_{\text{cat}}$ $^{-1}$ h$^{-1}$) 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$_2$O$_3$ NPs for NRR.

1. Introduction

Ammonia (NH$_3$) is a highly important chemical in many aspects of industrial production and daily life.\textsuperscript{1,2} Fixation of N$_2$ to NH$_3$ is an important step for the natural N$_2$ cycle.\textsuperscript{3-5} The current synthesis of NH$_3$ mainly depends on the industrial Haber-Bosch process, which involves serious energy consumption and leads to large amounts of greenhouse gas emissions.\textsuperscript{6,7} To realize a green and sustainable strategy for N$_2$ fixation, electrochemical reduction of N$_2$ has recently attracted much attention, being an environmentally friendly route involving mild conditions.\textsuperscript{8-10}

To date, a number of catalysts have been developed for the NRR, including noble metals,\textsuperscript{11-13} transition metals,\textsuperscript{14,15} metal-free materials,\textsuperscript{16-18} metal–C composite materials\textsuperscript{19-21} and Au–Fe$_2$O$_3$.\textsuperscript{22} These catalysts have demonstrated potential applications in the NRR with improved FE and NH$_3$ yield. Most of the catalysts were synthesized with the assistance of surfactants (structure-directing agents) through solution methods.\textsuperscript{23} 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$_2$O$_3$ 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$_2$O$_3$ surface. The as-prepared Fe$_2$O$_3$ NPs demonstrated a good electrocatalytic performance for NRR, with a high NH$_3$ yield (22 $\mu$g mg$_{\text{cat}}$ $^{-1}$ h$^{-1}$) and a favorable FE (3.5%) at $-0.5$ V vs. reversible hydrogen electrode (RHE).

2. Materials and reagents

Glycerine (C$_3$H$_8$O$_3$) (purity, 99.5%), iron(m) nitrate nonahydrate (Fe(NO$_3$)$_3$·9H$_2$O) (purity, 98.5%) and ethanol (CH$_3$CH$_2$OH) (purity $\geq$ 98.5%) were purchased from Sinopharm Chemical Reagent Co. Ltd.

2.1. Synthesis of Fe$_2$O$_3$ nanoparticles (NPs)

121.2 mg of iron(m) 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 $^\circ$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 $^\circ$C for 2 h at the heating rate of 10 $^\circ$C min$^{-1}$ under air. Finally, Fe$_2$O$_3$ 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$_2$O$_3$, 40 $\mu$L Nafion (5% wt) and 960 $\mu$L ethanol were mixed by ultrasound for forming suspension. 50 $\mu$L suspension was modified on 1 $\times$ 1 cm carbon cloth (CC). The Fe$_2$O$_3$–CC was used as working electrode.
2.4. Electrochemical reduction of N2

Electrochemical reduction of N2 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 Na2SO4 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 N2 for at least 30 min. N2 was delivered into the cathodic compartment at a constant rate of 20 mL min⁻¹. The potentiostatic tests were performed in 0.1 M Na2SO4 aqueous solution at different potentials such as −0.3, −0.4, −0.5, −0.6, and −0.7 V vs. RHE. The NH3 yields and FEs of products were calculated as follows:

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

\[
\text{FE (\%)} = \frac{a m F}{M Q} \quad (2)
\]

where \(m\) is the mass of NH3, \(m_{\text{cat}}\) is the mass of catalyst, \(a\) is the quantity of transferred electrons for producing NH3, \(M\) is the relative molecular mass, and \(Q\) is the total quantity of the electric charge.

2.5. Determination of NH3 and N2H2

The detections of NH3 and N2H2 were made by indophenol blue and Watt–Chrisp methods, respectively, according to the reported literature. 24

3. Results and discussion

The Fe2O3 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 Fe2O3 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 Fe2O3, which agrees well with the JCPDS No. 33-0664. This demonstrates the successful formation of Fe2O3. Low peak intensity may be caused by small size of Fe2O3 particles. Transmission electron microscopy (TEM) images of the Fe2O3 suggests that the diameters of as-synthesized Fe2O3 nanoparticles are in the range of 4–6 nm (Fig. 1(b) and (c)).

To investigate the surface elemental state of Fe2O3 NPs, we analyzed the chemical states of the Fe2O3 NPs by XPS analysis. There are two Fe³⁺ peaks located at 711.8 eV and 725.3 eV, corresponding to Fe 2p₁/₂ and Fe 2p₃/₂, agreeing well with Fe2O3 NPs (Fig. 2). The XPS spectrum result further demonstrated the successful synthesis of Fe2O3 NPs.

The synthesized Fe2O3 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 N2-fed electrolytes in 0.1 M Na2SO4 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 N2 into valuable NH3 was achieved using the as-synthesized Fe2O3 electrocatalyst. Fig. 4(b) presented the chronoamperometric curves as a function of reaction time at varying applied potentials in 0.1 M Na2SO4, demonstrating the Fe2O3 nanoparticles have good stability for NRR from −0.3 V to −0.6 V. The average NH3 yield and the corresponding Faradaic efficiency (FE) was given in Fig. 4(c), in which the favorable NH3 yield was 22.0 μg mg⁻¹ cat⁻¹ h⁻¹ with FE value of 3.5% at −0.5 V. The NRR performance of the as-synthesized Fe2O3 is comparable to lots of the NRR electrocatalysts (Table S1†). Therefore, the present synthesized Fe2O3 with clean surface might be as a potential catalyst for electrochemical NRR in consideration that there are.
abundant Fe element in the earth. TEM image of catalyzed Fe$_2$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 Fe$_2$O$_3$ (Fig. S1†).

The NNR performance is highly related to the electrochemically active surface area (ECSA). Therefore, the ECSA of the as-prepared Fe$_2$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 mF cm$^{-2}$ (Fig. 5(b)) further demonstrated that Fe$_2$O$_3$ had high ECSA for NNR.

The hydrazine byproduct was further determined through a Watt–Chrisp 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 Fe$_2$O$_3$ for NH$_3$ production (Fig. 6). Hence, the as-prepared Fe$_2$O$_3$ catalyst could be used as a high-selective catalyst for producing NH$_3$ by electrochemical NNR.

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

**Fig. 4** UV-vis absorption spectra in (a) 0.1 M Na$_2$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 Fe$_2$O$_3$ at different potentials in 0.1 M Na$_2$SO$_4$ solution, (c) NH$_3$ yields and FEs for Fe$_2$O$_3$ at a series of potentials in 0.1 M Na$_2$SO$_4$.

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

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We also explored the NRR performance of Fe$_2$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, Fe$_2$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 Fe$_2$O$_3$ NPs exhibited good performance with a 22 $\mu$g mg$_{cat}^{-1}$ h$^{-1}$ NH$_3$ yield and a 3.5% Faraday efficiency at $-0.5$ V for NH$_3$ production, which outperformed lots of the previous catalysts. The flexible strategy and the good electrochemical performance endow Fe$_2$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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Fig. 6 (a) Standard curve of hydrazine in 0.1 M Na$_2$SO$_4$ solution, (b) UV-vis absorption spectra of hydrazine in 0.1 M Na$_2$SO$_4$ electrolytes after NRR electrolysis at a series of potentials for 2 h.
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