Bismuth-Based Free-Standing Electrodes for Ambient-Condition Ammonia Production in Neutral Media

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HIGHLIGHTS

- The Bi2O3 nanoplates homogeneously decorated free-standing exfoliated graphene (Bi2O3/FEG) was prepared by a facile electrochemical deposition method.
- The Bi2O3/FEG first used as nitrogen reduction electrocatalyst exhibits excellent electrocatalysis performance and stability for nitrogen reduction reaction in neutral media.
- The superior electrocatalytic nitrogen reduction activity is attributed to the strong interaction of the Bi 6p band with the N 2p orbitals, binder-free nature of the electrodes, and facile electron transfer through the graphene nanosheets.

ABSTRACT Electrocatalytic nitrogen reduction reaction is a carbon-free and energy-saving strategy for efficient synthesis of ammonia under ambient conditions. Here, we report the synthesis of nanosized Bi2O3 particles grown on functionalized exfoliated graphene (Bi2O3/FEG) via a facile electrochemical deposition method. The obtained free-standing Bi2O3/FEG achieves a high Faradaic efficiency of 11.2% and a large NH3 yield of 4.21 ± 0.14 μgNH3 h⁻¹ cm⁻² at −0.5 V versus reversible hydrogen electrode in 0.1 M Na2SO4, better than that in the strong acidic and basic media. Benefiting from its strong interaction of Bi 6p band with the N 2p orbitals, binder-free characteristic, and facile electron transfer, Bi2O3/FEG achieves superior catalytic performance and excellent long-term stability as compared with most of the previous reported catalysts. This study is significant to design low-cost, high-efficient Bi-based electrocatalysts for electrochemical ammonia synthesis.

KEYWORDS N2 reduction; Bi2O3 nanoplate; Electrocatalysis; Free-standing
1 Introduction

Ammonia (NH₃) is considered to be a promising hydrogen energy carrier to alleviate the fossil fuel shortage and global climate change, as its high energy density, high hydrogen content, no carbon footprint and being easy to liquefy [1–3]. To date, the dominant method for industrial-scale NH₃ synthesis still depends on the traditional Haber–Bosch process [4–6]. However, this energy-intensive and environmentally hazardous process consumes 2% of the global annual energy and leads to 1% of the world’s CO₂ emission [7]. It is thus imperative to develop a sustainable and economical technique for NH₃ synthesis at mild conditions.

The electrochemical nitrogen reduction reaction (ENRR) is regarded as an energy-saving and carbon-free process, which can synthesize NH₃ at ambient conditions by utilizing renewable energy such as those from wind and solar [8–12]. Unfortunately, the scaled-up application of the ENRR process is seriously hampered by the low ammonia yields and Faraday efficiency due to the extremely weak N₂ adsorption, the low solubility of N₂ in aqueous electrolytes, and the sluggish cleavage of the N≡N bond [13]. Over the past 5 years, numerous metal-based materials, including metal [7, 14–18], metal oxides [19–21], metal sulfides [22, 23], metal nitrides [24], etc., have been developed as electrocatalysts for ENRR. Most of the above metal-based catalysts involving the metallic centers of Au [7], Ru [17], Ni [20], Mo [18, 22], etc., exhibited favorable activity for ENRR by elaborately designing the particle size, crystallinity, heteroatom doping, and/or vacancies. Despite the substantial progress, the ENRR still suffers from the major competitive hydrogen evolution reaction (HER). Therefore, the rational design of the active catalytic centers of efficient ENRR electrocatalysts that can efficiently reduce the large activation barrier of N≡N, accelerate its dissociation and most importantly suppress HER, is still a highly challenging but vitally important issue [25].

Bismuth-based catalysts are considered to be promising candidates for efficient ENRR in recent years [26–30]. Bi as a main group element with tunable p-electron density and intrinsic less reactive nature can selectively promote the reductive adsorption of N₂ to form NH⁺* without influencing the binding energy of the later intermediates, and also restrict the surface electron accessibility for effectively suppressing the competitive HER process [26–28]. Yan et al. demonstrated that overlapping of the Bi 6p bands and the 2p orbitals of the N atom both below and above the Fermi level can offer a lower free-energy change for the potential-determining step and better ENRR activity than typical transition metal catalysts [29]. Most of the Bi-based electrocatalysts for ENRR reported previously are mainly focused on the metallic bismuth (Bi⁰) [27–29]. It was reported that both the defect-rich Bi and 2D mosaic Bi nanosheets have been used for ENRR, and offered excellent selectivity in 0.2 M Na₂SO₄ (Faradaic efficiency (FE): 11.68% at −0.6 V vs. RHE) [28] and 0.1 M in Na₂SO₄ (FE: 10.46 ± 1.45% at −0.8 V vs. RHE) [31], respectively. As an abundant Bi-based material, Bi₂O₃ has received much attention in photocatalysis due to its unique electrical and optical properties [32–34]. It was also used as a precursor for the synthesis of other Bi-based materials [28]. However, bismuth oxide has hardly been reported for ENRR, with part of reason being that the semiconducting Bi₂O₃ shows poor charge transport, while the easy aggregation of Bi₂O₃ instead of nanosized status largely impairs the adsorption and reactivity to N₂. Therefore, a robust support is necessary to enhance the conductivity, at the same time offer well dispersion of the Bi₂O₃ nanoparticles.

Functionalized exfoliated graphene (FEG) acts as an ideal 3D-conductive scaffold for supporting catalysts, which is constructed by ultrathin partially oxidized graphene nanosheets anchoring on the graphite substrate [35–37]. The FEG modified by oxygen-containing groups (–OH, –COOH) that provide active defect sites, can act as an excellent substrate for metal oxides deposition when using the metal ions as the precursor [38]. It is the high surface area and excellent electron conductivity of graphene nanosheets that can accelerate the charge transport and keep credible electric contact, resulting in the enormously improved catalytic efficiency [39–42]. In addition, polymer binder (e.g., Nafion) is widely used for attaching the electrocatalysts to the collectors, which seriously hampers the mass transport and obstructs the charge transmission, and therefore reduces the overall catalytic performance of the electrocatalysts [43, 44]. Therefore, the in situ growth of metal oxides on FEG with highly exposed active sites, superior electron conductivity, and large surface area is vitally important to improve the electrocatalytic performance. Based on the above analysis results, it is reasonable to assume that the composite electrocatalysts composed of well-coupled Bi₂O₃ and FEG can act as a promising candidate to promote the electrochemical reduction of N₂ to NH₃.
Herein, we developed a new type of ENRR catalyst by immobilizing Bi$_2$O$_3$ nanoplates onto the surface of FEG, to form the free-standing hybrid material (Bi$_2$O$_3$/FEG), which was then directly used as an electrode for ENRR in different electrolytes under ambient conditions. In this ENRR system, the competitive hydrogen evolution reaction (HER) is expected to be suppressed by the better intrinsic ENRR activity of Bi. Moreover, the highly conductive FEG was utilized to compensate for the semiconducting property of Bi$_2$O$_3$ and eliminate its aggregation. The as-prepared Bi$_2$O$_3$/FEG catalyst exhibits high ENRR activity with a high NH$_3$ yield rate of $4.21 \pm 0.14 \mu$g NH$_3$ h$^{-1}$ cm$^{-2}$, and a favorable FE as high as 11.2% at $-0.5$ V versus RHE in 0.1 M Na$_2$SO$_4$ electrolyte, out-performing most reported ENRR catalysts.

2 Experimental

2.1 Synthesis of the Functionalized Exfoliated Graphene (FEG)

The FEG substrate was prepared through an electrochemical exfoliation method according to our previous work with slight modification [45]. The exfoliation process was performed in a typical three-electrode cell using the graphite foil [GF, the exposed surface area is $1 \times 1$ cm$^2$ (length x width)] as the working electrode, a platinum plate and a saturated calomel electrode (SCE) as the counter and reference electrodes, respectively. First, the GF was scanned between 0.5 and 1.7 V (vs. SCE) using cyclic voltammetry at 15 mV s$^{-1}$ in 0.5 M K$_2$CO$_3$ electrolyte for ten cycles. Subsequently, the electrode was further treated at a constant potential of 1.8 V (vs. SCE) for 2 h in 0.5 M KNO$_3$ aqueous solution to generate functional groups. Then, the electrode was potential dynamically scanned between $-1.0$ and 0.9 V (vs. SCE) at 50 mV s$^{-1}$ for 50 cycles in 3 M KCl electrolyte to recover the electrical conductivity. Finally, the FEG substrate was rinsed with deionized water and ethanol to remove the residuals.

2.2 Synthesis of the nanosized Bi$_2$O$_3$ Modified FEG (Bi$_2$O$_3$/FEG)

Bi$_2$O$_3$/FEG was synthesized through an electrochemical deposition process. 0.3 g of bismuth chloride (BiCl$_3$) was dissolved into 25 mL ethylene glycol (EG) and stirred at 25 °C for 1 h forming the electrolyte. The electrodeposition process was conducted in a two-electrode cell with a platinum plate as the counter electrode and a piece of FEG ($1 \times 1$ cm$^2$) as the working electrode. Bi$_2$O$_3$ nanoparticles were electrodeposited on FEG at a constant current density of 1 mA cm$^{-2}$ at ambient temperature for 5 min. The as-synthesized product was washed with tetrahydrofuran and ethanol and subsequently dried in a vacuum oven at 70 °C for 12 h, finally obtaining free-standing Bi$_2$O$_3$/FEG.

2.3 Electrocatalytic ENRR Measurements

Before ENRR tests, the Nafion 117 membrane was cut into small pieces and then treated with 3 wt% H$_2$O$_2$ water solution, deionized water, 1 mol L$^{-1}$ H$_2$SO$_4$ and deionized water for 1 h at 80 °C, respectively. Finally, the obtained membrane was repeatedly rinsed until neutral pH was obtained and then was preserved in deionized water. Electrochemical measurements were performed in an airtight two-compartment cell at ambient conditions using an electrochemical workstation (CHI 760E), with Bi$_2$O$_3$/FEG or FEG as the working electrode, Pt foil as the counter electrode, and Ag/AgCl (filled with 3.5 M KCl solution) as the reference electrode. The potentials were converted to reversible hydrogen electrode (RHE) scale via calibration with the Nernst equation ($E_{RHE} = E_{Ag/AgCl} + 0.059 \text{pH} + 0.205$ V). The linear sweep voltammetry (LSV) curves were collected in 0.1 M Na$_2$SO$_4$ electrolyte saturated with ultrahigh Ar or N$_2$ for 30 min at a sweep rate of 5 mV s$^{-1}$, respectively.

2.4 Determination of Ammonia

The concentrations of the synthesized NH$_3$ in the electrolyte were measured by a colorimetric method using Nessler’s reagent as the color reagent. For this method, 10 mL electrolyte was mixed with 0.2 mL 50% seignette salt solution. Then 0.2 mL Nessler’s reagent was added and the mixture was allowed still for 10 min. Then the mixture was detected as the absorbance at 420 nm by a UV–Vis spectrometer (Shimadzu UV-2600). A standard curve of the Nessler’s reagent-based colorimetric method is constructed by measuring a series of absorbances for the reference solution with different NH$_4$Cl concentrations (0.00, 0.10, 0.20, 0.30, 0.40, and 0.50 μg mL$^{-1}$). The background is corrected with a blank solution (as shown in Fig. S1).
An ion-selective electrode meter (Orion Star A214 Benchtop pH/ISE Meter; Thermo Scientific) for NH₃ detection was also performed to further verify the reliability of the colorimetric method. The details were according to our previous work [46] (as shown in Supporting Information).

### 2.5 Determination of Hydrazine

The yield of hydrazine in the electrolyte was evaluated via Watt and Chrisp method. The hydrazine chromogenic reagent is a mixture of para-(dimethylamino) benzaldehyde (0.599 g), ethanol (300 mL) and concentrated HCl (30 mL). After 2 h ENRR reaction, 2 mL of the above reagent was added into 2 mL of the electrolyte and then the mixture was detected at 460 nm. The concentration-absorbance curve was calibrated using standard hydrazine hydrate solution with a series of concentrations ($Y = 2.225 X + 0.03, R^2 = 0.99913$) (as shown in Fig. S2).

### 2.6 Calculation of Faradaic Efficiency (FE) and NH₃ Yield Rate

The FE for NH₃ production and NH₃ yield rate were calculated at an applied potential as follow (Eqs. 1 and 2):

$$FE_{NH₃} = C_{NH₃} \times V \times 3F/Q$$  

(1)

$$NH₃ \text{ yield rate} = \frac{C_{NH₃} \times V}{(t \times m)}$$  

(2)

where $C_{NH₃}$ is the concentration of NH₃, $V$ is the volume of the electrolyte, $F$ is the Faraday constant of 96,485 C mol⁻¹, $Q$ is the total charge passed through the electrochemical system, $t$ is the reaction time of ENRR process, and $m$ is the mass of the catalytic active site, i.e., the Bi atoms of Bi₂O₃ molecule on the surface of the Bi₂O₃/FEG electrode.

### 2.7 Calculation of Equilibrium Potential

At the very beginning of the ENRR, the newly produced ammonia formed a type of coordination with water, as shown in Eq. 3:

$$N₂(g) + 2H₂O(l) + 6H^+(aq.) + 6e^- \rightleftharpoons 2 \text{NH}_₃ \cdot \text{H}_₂\text{O (aq.)}$$

(3)

The equilibrium potential for ENRR under our experimental conditions is calculated using the Nernst equation as shown in Eq. 4, assuming 1 atm of N₂ and an NH₃·H₂O concentration of 0.5 × 10⁻⁵ M in the solution [46].

$$E = E^o - \frac{RT}{nF} \ln \left( \frac{[\text{NH}_₃ \cdot \text{H}_₂\text{O} ]^2}{[H^+]^6} \right) + 0.059 V \times pH = 0.196 V (\text{vs. RHE})$$

(4)

where $E^o = 0.092 V$ is the standard potential for the above half reaction of ENRR, $R = 8.314 J \text{ mol}^{-1} \text{ K}^{-1}$ is the molar gas constant, $n = 6$ is the number of electrons transferred in Eq. 3, $F = 96.485 C \text{ mol}^{-1}$ is the Faraday constant, $T = 298.15 K$ is the reaction temperature in this experimental condition.

### 3 Results and Discussion

#### 3.1 Materials Characterization

Scheme 1 illustrates the synthesis procedure to obtain the free-standing Bi₂O₃/FEG hybrid. Typically, the FEG substrate was prepared through electrochemical exfoliating the graphite foil into functionalized exfoliated graphene nanosheets with abundant oxygen functional groups. Sequentially, the Bi₂O₃ nanoplates were uniformly immobilized onto the FEG with BiCl₃ as the precursor through a facile electrochemical deposition method, during which

![Scheme 1](image-url)
the mass loading and the morphology of the Bi$_2$O$_3$ can be easily controlled by adjusting the electrolyte concentration and deposition duration. The actual weight of Bi in Bi$_2$O$_3$/FEG electrodes was determined to be approximately 0.74 mg cm$^{-2}$ by measuring the weight before and after the electrodeposition process, followed by ICP-AES confirmation.

The morphology and microstructure of as-prepared Bi$_2$O$_3$/FEG were investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Figure 1a shows the SEM images of the as-prepared Bi$_2$O$_3$/FEG hybrid. It can be clearly observed that, after electrochemical deposition, Bi$_2$O$_3$ nanoplates are uniformly grown on the surface of the loosely packed FEG layers. This is due to the fact that oxygen functional groups in graphene nanosheets play a structure-directing role in the electrochemical deposition. The Bi$^{3+}$ precursors can be captured through coordination bonding with the hydroxyl and carboxyl groups in graphene nanosheets, which were introduced in the electrochemical exfoliation process [38]. Then this uniform deposition of Bi$_2$O$_3$ in the nanosheets of FEG can be achieved by the following electrochemical process. The SEM and corresponding elemental (Bi, C, and O) mapping images of Bi$_2$O$_3$/FEG are shown in Fig. 1b. Uniform distribution of bismuth (from Bi$_2$O$_3$ nanoplates) combined with the carbon and oxygen can be detected over the whole area of the Bi$_2$O$_3$/FEG nanosheet, further demonstrating the presence of homogeneous Bi$_2$O$_3$ nanoplates on the graphene sheet of FEG. The transmission electron microscopy (TEM) of the as-prepared Bi$_2$O$_3$/FEG hybrid is shown in Fig. 1c, which further confirms the Bi$_2$O$_3$ nanoplates with a particle size of about 5 nm evenly decorated on the graphene nanosheets of FEG. The TEM image of Bi$_2$O$_3$/FEG in Fig. 1c (inset) further displays that numerous Bi$_2$O$_3$ nanoplates are homogeneously dispersed on the surface of FEG. As shown in Fig. 1c, the high-resolution TEM (HRTEM) image of Bi$_2$O$_3$/FEG hybrid reveals the uniform distributed Bi$_2$O$_3$ on the surface of FEG with well-defined nanocrystalline nature. The magnification corresponding HRTEM images in the circle area of Fig. 1c reveal the lattice fringes of 0.25 nm (Fig. 1d), which could be well indexed to the (102) plane of Bi$_2$O$_3$. The selected area electron diffraction (SAED) pattern indicates the monocrystalline nature of Bi$_2$O$_3$ nanoplates and reveals the (102), (100), and (002) planes of Bi$_2$O$_3$ (inset of Fig. 1d), further confirming the existence of Bi$_2$O$_3$ in FEG.

X-ray diffraction (XRD) patterns of pure FEG and the as-prepared Bi$_2$O$_3$/FEG hybrid are displayed in Fig. S3. The strong peak at 26.3° of FEG is indexed to the (002) plane of graphene [36] that confirms the successful synthesis of pure FEG. It is found that Bi$_2$O$_3$/FEG hybrid also exhibited a characteristic peak of graphene at 26.6°. This intense and sharp peak indicates highly crystalline graphene nature of Bi$_2$O$_3$/FEG, which is beneficial to the electron transfer. No characteristic diffraction peaks of Bi$_2$O$_3$ are observed because of its lower loading content. This also implies the good dispersion of the very small Bi$_2$O$_3$ particles on the FEG.

The full-range X-ray photoelectron spectroscopy (XPS) spectra of FEG and the as-prepared Bi$_2$O$_3$/FEG hybrid are shown in Fig. 1e, and it was observed that two peaks appeared at 285.6 and 532.0 eV, corresponding to the C 1$s$ and O 1$s$ core level spectrum, respectively. Moreover, the presence of Bi electrons was confirmed by the XPS analysis of Bi$_2$O$_3$/FEG, the three doublet peaks at around 690.0, 455.0, and 162.0 eV, corresponding to the Bi 4$p$, Bi 4$d$, and Bi 4$f$ electrons, indicating that some Bi$_2$O$_3$ was immobilized on the FEG. In the high-resolution Bi 4$f$ XPS spectrum (Fig. 1f), two main peaks centered at 159.8 and 165.1 eV can be identified as Bi 4$f_{7/2}$ and Bi 4$f_{5/2}$ signals of Bi$^{3+}$, respectively, in accordance with previous reports [47]. And the 0.8 eV blueshift of Bi 4$f_{7/2}$ and Bi 4$f_{5/2}$ peaks due to charge transfer from Bi$^{3+}$ center to the FEG. The results from the above characterizations demonstrate that FEG is an excellent substrate for the deposition and fixation of Bi$_2$O$_3$ nanoparticles. The incorporation of Bi$_2$O$_3$ nanoparticles into the FEG prevented the aggregation of Bi$_2$O$_3$ nanoparticles and provided more reactive sites, that may improve its performance of ENRR.

The contact angle measurement was then performed to investigate the hydrophilicity of FEG and Bi$_2$O$_3$/FEG. It can be seen from Fig. S4a, the surface of FEG whose contact angle is approximately $83^\circ$ exhibits strong hydrophilicity, which is mainly due to the oxygen functional groups (–OOH and –OH) of FEG. After decorated with Bi$_2$O$_3$, the contact angle of the as-prepared Bi$_2$O$_3$/FEG increases to around $110^\circ$ (Fig. S4b), indicating a hydrophobic property. This hydrophobicity is expected to be helpful in promoting the ENRR performance by providing strong interaction with N$_2$ gas [48].
3.2 Electrochemical Nitrogen Reduction

The ENRR performance of the prepared Bi₂O₃/FEG catalyst was evaluated in N₂-saturated 0.1 M Na₂SO₄ electrolyte under ambient conditions using a two-compartment electrochemical cell, separated by a Nafion 117 membrane. The free-standing Bi₂O₃/FEG hybrid material was directly used as the working electrode, with a platinum plate as the...
counter electrode and Ag/AgCl as the reference electrode (configuration shown in Fig. 2a). The feeding gas (ultra-high purity N₂, 99.999%) was continuously bubbled into the cathode via a bubbler during the experiment at the flow rate of 10 mL min⁻¹. All potentials were reported on a reversible hydrogen electrode (RHE) scale. First, we studied the potential dependence of ENRR activity of Bi₂O₃/FEG by LSV in Ar- and N₂-saturated 0.1 M Na₂SO₄ electrolytes at a scan rate of 5 mV s⁻¹. As shown in Fig. S5, the LSV curves of Bi₂O₃/FEG in Ar and N₂-saturated electrolytes exhibit the same shape, but a higher current density is achieved in the N₂-saturated electrolyte when potential is more negative than −0.4 V, implying that Bi₂O₃/FEG possesses catalytic activity for ENRR reaction.

Further, chronoamperometry tests at a series of potentials were carried out to explore the catalytic activity and identify the optimal potential of the Bi₂O₃/FEG electrode for the ENRR (Fig. 2b). The concentration of the produced ammonia in solution after the 2 h electrolysis was determined independently by a spectrophotometry method with Nessler’s reagent as a color reagent, while the possible N₂H₄ by-product was detected by a spectrophotometry method with p-C₆H₄NO as an indicator.

The average ammonia yields and the corresponding FE of Bi₂O₃/FEG at potentials from −0.4 to −0.8 V (vs. RHE) in 0.1 M Na₂SO₄ are plotted in Fig. 2b. The FE value at −0.4 V (vs. RHE) is 7.1%, and then the ENRR rate and FE rise with the negative potential increasing until −0.5 V (vs. RHE), where the relatively high NH₃ yield and the maximum FE value can reach 4.21 ± 0.14 μg NH₃ h⁻¹ cm⁻² (i.e., 5.68 μg NH₃ mg²⁻¹ h⁻¹) and 11.2%, respectively. No N₂H₄ by-product has been detected, indicating the good selectivity of the Bi₂O₃/FEG catalyst for ENRR. Meanwhile, ENRR was also conducted on FEG in N₂-saturated 0.1 M Na₂SO₄ solution at −0.5 V (vs. RHE) to verify the source of NH₃. No NH₃ was detected, indicating that FEG had no catalytic

![Fig. 2](https://example.com/fig2.png)

**Fig. 2**  
(a) Schematic reaction cell for ENRR.  
(b) Faradic efficiency and NH₃ yield rate at various potentials in 0.1 M Na₂SO₄ electrolyte (determined by the Nessler’s reagent).  
(c) Chronoamperometry results at the corresponding potentials.  
(d) FE and NH₃ yield rate at various potentials in 0.1 M Na₂SO₄ electrolyte (determined by ion-selective electrode meter)
activity toward ENRR for the production of NH₃, and the contribution of NH₃ yield from the impurities of FEG was also negligible. Therefore, it can be inferred here that the Bi₂O₃ in Bi₂O₃/FEG played a decisive role in the ENRR, while FEG possessed no activity toward the ENRR.

This ENRR catalytic performance of the as-prepared Bi₂O₃/FEG hybrid material can even comparable to the yields and efficiencies catalyzed by metal-based nanocatalysts as shown in Table S1. For example, Bi nanosheets (FE of 10.46% with an NH₃ yield rate of 2.54 μg h⁻¹ cm⁻² at −0.8 V (vs. RHE) in 0.1 M Na₂SO₄ electrolyte) [31] and Au nanorod (FE of 4.02% with an NH₃ yield rate of 1.648 μg h⁻¹ cm⁻² at −0.2 V vs. RHE in 0.1 M KOH electrolyte) [49]. The excellent ENRR performance of the as-prepared Bi₂O₃/FEG hybrid material is mainly due to the following reasons. On the one hand, this high ENRR activity is primarily attributed to the Bi center from Bi₂O₃, which can effectively inhibit the side reaction of HER during ENRR process by binding *N₂H more strongly without affecting the binding energy of ‘NH₂ or ‘NH [26, 31], and offer a lower free-energy change than traditional transition mental for a better ENRR activity [29]. On the other hand, the nanosized Bi₂O₃ and the large surface of FEG, which provide abundant active sites, may insure the efficient ENRR reaction. Besides, the facile electron and mass transfer process from the graphene nanosheets of Bi₂O₃/FEG accelerate the ENRR process through promoting the electron transport, and the hydrophobic property of Bi₂O₃/FEG provides strong interaction with N₂ gas further accelerate the ENRR.

In addition, as shown in Fig. 2c, the current density at different potentials behaves good stability, which can be attributed to the well dispersion and anchoring of the nanosized Bi₂O₃ nanoplates on the graphene nanosheets. Unexpectedly, though the NH₃ yield reaches the highest average value of 5.8 ± 0.15 μgNH₃ h⁻¹ cm⁻² at −0.8 V (vs. RHE), the FE values decrease obviously when the applied potentials are more negative than −0.5 V (vs. RHE). A plausible explanation is that the ENRR in this system was in a N₂ diffusion-controlled mode, and the feeding gas N₂ has extremely low solubility in aqueous electrolyte. At higher negative potentials, the competing reaction (HER) was dominant [46], so the surface of Bi₂O₃/FEG was mainly occupied by the hydrogen molecules which would impede the mass transfer of N₂ to the surface of Bi₂O₃/FEG, and thus strongly reduce the ENRR selectivity.

The concentrations of the NH₃ synthesized by Bi₂O₃/FEG at potentials from −0.4 to −0.8 V (vs. RHE) in 0.1 M Na₂SO₄ were also determined by ion-selective electrode to confirm the reliability of this colorimetric method for ammonia detection. As shown in Fig. 2d, the corresponding average NH₃ yields and FE were almost identical to that of determined by the Nessler’s reagent (Fig. 2b) within experimental error, suggesting that it was reliable to use the Nessler’s reagent for the quantitative analysis of the produced NH₃.

Subsequently, chronoamperometry tests in N₂-saturated 0.1 M KOH or 0.05 M H₂SO₄ electrolyte under the same experimental conditions as that of in Na₂SO₄ electrolyte were carried out to explore the catalytic activity of the Bi₂O₃/FEG in strong basic and acidic media. As shown in Fig. 3a, the optimum average NH₃ yield rate 3.07 ± 0.11 μgNH₃ h⁻¹ cm⁻² in the strong basic electrolyte occurred at −0.5 V (vs. RHE), indicating a wide pH response of Bi₂O₃/FEG. However, the relatively low FE of 0.59% may be caused by the high current density implying dominant HER (Fig. S7). Furthermore, the robust current stability of Bi₂O₃/FEG in 0.1 M KOH has been confirmed for 2 h electrolysis, as shown in Fig. 3b, indicating ideal stability of Bi₂O₃/FEG in the strong basic electrolyte. The NH₃ yields and the corresponding FE of Bi₂O₃/FEG at potentials from -0.2 to -0.6 V (vs. RHE) in 0.05 M H₂SO₄ are plotted in Fig. 3c. The NH₃ yield at −0.2 V (vs. RHE) is 2.8 μgNH₃ h⁻¹ cm⁻² with the FE of 1.36%, then the NRR rate and FE decrease sharply with the potential shifted negatively. The dissatisfaction catalytic performance in 0.05 M Na₂SO₄ electrolyte should attribute to the instability of Bi₂O₃ and the drastic HER competing reaction in acid medium. Comparing the optimum FE and NH₃ yield rates of Bi₂O₃/FEG in different electrolytes as shown in Fig. 3d, Bi₂O₃/FEG exhibits excellent electrocatalysis performance and stability for ENRR in neutral media even better than that in strong basic and acidic media under the same ambient conditions. It is highly desired to develop electrocatalysts for efficient and durable ENRR catalysis at neutral conditions, which is beneficial for alleviating the serious environment sufferings, reducing equipment and catalyst corrosions, lower the cost of the whole ENRR process, and further accelerating the practical applications of ENRR.

The stability of the Bi₂O₃/FEG was evaluated by consecutive recycling electrolysis and long-term
chronoamperometry test at −0.5 V (vs. RHE) in 0.1 M Na₂SO₄. As shown in Fig. 4a, no obvious change in the NH₃ yield and Faradaic efficiency could be observed during five consecutive recycling electrolysis, which suggests the excellent stability of Bi₂O₃/FEG for NH₃ synthesis at ambient conditions. In addition, slight degradation of current density in the process of long-term chronoamperometry test is detected for 12 h at −0.5 V (vs. RHE) (Fig. 4b). Moreover, no obvious variation of the NH₃ yield rate and FE could be observed after 12 h long-term chronoamperometry test, indicating the high robustness of Bi₂O₃/FEG toward ambient NH₃ synthesis. Furthermore, both the compositions and Bi₂O₃ nature of the Bi₂O₃/FEG could be well maintained after the long-term electrocatalysis reaction when comparing TEM images (Fig. 4c) and XPS (Fig. 4d) before and after the reaction. All these observations demonstrate the excellent electrochemical durability of the Bi₂O₃/FEG for the ENRR, which is another crucial factor for the enhancement of ENRR performances.

4 Conclusions

In summary, a highly efficient hybrid ENRR electrocatalyst composed of nanosized Bi₂O₃ supported on FEG was developed. Due to the synergistic effect between the nanosized Bi₂O₃ and the large surface area of FEG, the Bi₂O₃/FEG hybrid exhibited the superb electrocatalytic performance toward ENRR at a low overpotential of −0.5 V (vs. RHE) in the neutral electrolyte and under ambient temperature and pressure. The FE of Bi₂O₃/FEG in 0.1 M Na₂SO₄ electrolyte is 11.2% with the NH₃ yields of 5.68 μgₐm₁h⁻¹, which is superior to that of most state-of-the-art ENRR electrocatalysts reported up to date. The high ENRR activity is attributed to the Bi center from Bi₂O₃ during the ENRR process with the help of the facile electron transfer process from the graphene nanosheets of FEG. This work opens an avenue to rational designing of Bi-based carbon hybrid electrocatalysts and highlights the catalytic center engineering strategy to effectively manipulate the catalytic performance of electrocatalysts.
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