Three-Phase Electrolysis by Gold Nanoparticle on Hydrophobic Interface for Enhanced Electrochemical Nitrogen Reduction Reaction

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Electrochemical nitrogen reduction reaction (NRR) provides a facile and sustainable strategy to produce ammonia (NH₃) at ambient conditions. However, the low NH₃ yield and Faradaic efficiency (FE) are still the main challenges due to the competitive hydrogen evolution reaction (HER). Herein, a three-phase electrocatalyst through in situ fabrication of Au nanoparticles (NPs) located on hydrophobic carbon fiber paper (Au/o-CFP) is designed. The hydrophobic CFP surface facilitates efficient three-phase contact points (TPCPs) for N₂ (gas), electrolyte (liquid), and Au NPs (solid). Thus, concentrated N₂ molecules can contact the electrocatalyst surface directly, inhibiting the HER since the lowered proton concentration and overall enhancing NRR. The three-phase Au/o-CFP electrocatalyst presents an excellent NRR performance with high NH₃ yield rate of 40.6 µg h⁻¹ mg⁻¹ at −0.30 V and great FE of 31.3% at −0.10 V versus RHE (0.1 M Na₂SO₄). The N₂-bubble contact angle result and cyclic voltammetry analysis confirm that the hydrophobic interface has a relatively strong interaction with N₂ bubble for enhanced NRR and weak electrocatalytic activity for HER. Significantly, the three-phase Au/o-CFP exhibits excellent stability with a negligible fluctuation of NH₃ yield and FE in seven-cycle test. This work provides a new strategy for improving NRR and simultaneously inhibiting HER.

1. Introduction

Ammonia (NH₃) as one of the most important chemical products plays a key role in many areas, including agricultural fertilizer, textile industries, and medicaments.[1–4] Moreover, NH₃ is also drawing considerable attention due to its advantages of high-efficiency carbon-free energy carrier with high hydrogen density as well as convenient storage and transportation at room temperature.[5–7] Presently, the production of NH₃ is mainly relied on the industrial Haber-Bosch (H-B) process by coactivation of nitrogen (N₂) and hydrogen (H₂) over Fe-based catalysts under high temperature and high pressure (300–550 °C and 200–350 atm).[8–10] Unfortunately, over 1% of the global energy supply annually is consumed during the H–B process because of the high N≡N bond dissociation energy.[11–14] Meanwhile, large amounts of green-house gases are produced. Therefore, it is extremely urgent to explore a facile and sustainable approach for NH₃ production.

Encouragingly, the electrochemical ammonia synthesis provides an alternative method because of the merits of low cost...
and friendly to environment.\textsuperscript{15–17} It has been proved theoretically and experimentally that noble metal catalysts, such as Au,\textsuperscript{18} Pt,\textsuperscript{19,20} and Ru,\textsuperscript{21,22} represent better NRR activities superior to non-metal catalysts, owing to the stronger N–H bonding and higher electrical conductivity. Specially, Au is arguably one of the most promising catalysts for the electrochemical N\textsubscript{2} reduction reaction. Recently, researchers have improved the NH\textsubscript{3} yield and Faraday efficiency by modifying Au morphology\textsuperscript{23–25} crystalline structure\textsuperscript{26} and crystal facet.\textsuperscript{18,27} However, the low yield and Faradaic efficiency are still far from ideal performance of NRR due to competitive hydrogen evolution reaction (HER).\textsuperscript{13} Therefore, it is an urgent topic to develop an electrocatalytic system that can simultaneously promote the N–H reaction for NRR and suppress the reduction of proton for HER.

One fact cannot be ignored is extremely low solubility of N\textsubscript{2} in electrolyte, thus limiting the supply of N\textsubscript{2} molecules to the catalyst surface by their low concentration and slow diffusivity.\textsuperscript{28} Meanwhile, the protons (H\textsuperscript{+}) are readily available in aqueous solutions by water ionization, resulting in overwhelmingly competitive HER. Therefore, a promising strategy is the increase of N\textsubscript{2} concentration and the reduction of H\textsuperscript{+} concentration on the catalyst surface to improve NRR and suppress HER. Recently, the hydrophobic interface is highly appealing in gas-involved electrochemical reactions because it can provide abundant three-phase contact points (TPCPs) for gas, electrolyte (liquid) and catalyst (solid). Additionally, the hydrophobic interface affords a fast gas diffusion path, resulting in sufficient supply of gas to the catalyst surface.\textsuperscript{29–32} Thus, electrochemical gas evolution reactions prefer to operate on TPCPs located at the hydrophobic surface rather than wetted by the electrolyte.\textsuperscript{29} Moreover, the H\textsuperscript{+} concentration at the hydrophobic interface becomes lower than hydrophilic interface due to the insufficient contact between water and the hydrophobic interface.\textsuperscript{30,31} Therefore, designing a three-phase electrocatalyst at hydrophobic interface should be an effective method to reinforce NRR and suppress HER. So far, only Ling et al. and Du et al. just focused on the surface modification of electrocatalysts by the introduction of a hydrophobic zeolitic imidazolate frameworks to cover Au or Au–Ag forming a three-phase interface for suppressed HER and enhanced electrochemical NRR.\textsuperscript{3,4,5} However, the continuous hydrophobic shell prevented the available and sufficient contact of N\textsubscript{2}, electrolyte and catalyst. Moreover, the complicated synthesis and fabrication process largely hinders its practical applications and commercial viability. To the best of our knowledge, there are no reports on the forming of a three-phase electrocatalyst by the hydrophobic interface of the support electrode for NRR.

Herein, we report an artful strategy to design a three-phase electrocatalyst with abundant TPCPs by direct in situ fabrication of Au nanoparticles (NPs) on hydrophobic carbon fiber electrode. A superior ammonia yield of 40.6 µg h\textsuperscript{−1} mg\textsuperscript{−1} at −0.3 V versus reversible hydrogen electrode (RHE) and Faradaic efficiency of 31.3% at −0.1 V versus RHE were achieved, which are much higher than those of Au/i-CFP. Notably, the Au/o-CFP also showed outstanding stability with a negligible fluctuation of electrocatalytic activity after seven recycles. N\textsubscript{2}-bubble contact angle result analysis showed that Au/o-CFP possesses an aerophilic property with a relatively strong interaction toward N\textsubscript{2} bubble, leading to significant increased NRR. Additionally, the low H\textsuperscript{+} concentration at the hydrophobic interface resulted in suppressed HER, which is also confirmed by cyclic voltammetry (CV) analysis.

2. Results and Discussion

The three-phase electrocatalysts presented here is a hydrophobic carbon fiber paper with loading of Au NPs (Au/o-CFP), which was simply fabricated by in situ reduction of H\textsubscript{2}AuCl\textsubscript{4} on carbon fiber paper. As shown in Figure 1a, the HAuCl\textsubscript{4} solution firstly overspread the carbon fiber paper. After drying, the carbon fiber paper was immersed into NaBH\textsubscript{4} solution for 1 min. Then, well-dispersed Au NPs formed on the carbon fiber. Scanning electron microscopy (SEM) reveals that Au NPs display spherical morphology and are uniformly distributed on the surface of carbon fiber (Figure 1b). The average size of Au NPs is about 6.8 nm, which is counted based on transmission electron microscopy (TEM) images (Figure S1, Supporting Information). The size of the obtained Au NPs depends on the amount of H\textsubscript{2}AuCl\textsubscript{4}, where the higher volume of H\textsubscript{2}AuCl\textsubscript{4}, the larger size of Au (Figure S1, Supporting Information). A lattice spacing of 0.236 nm is observed from the high-resolution TEM (HRTEM) image, indicating the (111) interplanar distance of the face centered cubic (fcc) Au crystal (Figure 1c,d). X-ray photoelectron spectroscopy (XPS) was performed to study the chemical state of Au NPs. The result of Au 4f spectrum shows two peaks at 84 and 87.7 eV (Figure S2, Supporting Information), which can be ascribed to 4f\textsubscript{7/2} and 4f\textsubscript{5/2} electrons, respectively. Contact-angle measurement was carried out to study the surface property relating to water wetting. The average contact angle of Au/o-CFP surface is 128.6° (Figure 1e), indicating the electrode possesses a significant hydrophobicity.

The NRR performance was performed in an H-type cell with three-electrode system. The Au/o-CFP was directly used as a working electrode. All potentials in the test were converted into the potentials versus reversible hydrogen electrode (RHE). The sweep voltammetry (LSV) curves were conducted in Ar- and N\textsubscript{2}-saturated 0.1 m Na\textsubscript{2}SO\textsubscript{4} aqueous solution (pH = 7). As shown in Figure 2a, the curve between −0.1 and −0.6 V in N\textsubscript{2} shows an obvious difference with that in Ar, which suggests a significant response of Au/o-CFP to N\textsubscript{2}. Thus, it is proposed that the maximal NH\textsubscript{3} yield can be obtained in the voltage range. The chronoamperometry tests were further used to determine the NH\textsubscript{3} yield and Faraday efficiency of Au/o-CFP. The time-dependent current density curves in N\textsubscript{2}-saturated electrolyte are shown in Figure 2b and all the curves of Au/o-CFP holds stable at different potentials for 2 h, suggesting a good durability of Au/o-CFP. Concentrations of NH\textsubscript{3}, production and hydrazine (N\textsubscript{2}H\textsubscript{4}) were analyzed by UV–Vis spectroscopy (Section 4), and the corresponding standard curves were displayed in Figures S3 and S4, Supporting Information. The UV absorption spectra of the electrolyte after 2 h reaction are displayed in Figure 2c. Notably, the highest absorbance value (655 nm) at −0.30 V was achieved, indicating the maximal NH\textsubscript{3} yield at this potential on the Au/o-CFP. According to the standard curve, the average NH\textsubscript{3} yield and Faraday efficiency are further calculated as shown in Figure 2d. Significantly, the highest NH\textsubscript{3} yield rate of 40.6 µg h\textsuperscript{−1} mg\textsuperscript{−1} is obtained at −0.30 V versus RHE and the greatest Faradaic efficiency of 31.3% is achieved at −0.10 V versus RHE. More importantly, this efficiency is superior to most of recently reported NRR electrocatalysts, such as B doped Ag NPs (26.48 µg h\textsuperscript{−1} mg\textsuperscript{−1} cat., 8.86%),\textsuperscript{36} porous Au...
Figure 1. a) Schematic diagram for illustrating the fabrication of Au/o-CFP and electrocatalytic nitrogen reduction to ammonia; b) high resolution SEM image of Au NPs on carbon paper; c,d) HRTEM images of Au NPs; e) water contact angle measurement of Au/o-CFP.

The water contact angle of Au/o-CFP electrode changed from 128.6° to 0°, indicating the electrode possessing a remarkable hydrophilicity. The morphology of Au electrocatalysts was kept well (Figure S7, Supporting Information) after O2 plasma treatment. Figure 3a shows the LSV curves of Au/o-CFP and Au/i-CFP in Ar-saturated electrolyte. It is obvious that the current density of Au/o-CFP is much lower than that of Au/i-CFP at the same driven voltage, suggesting fewer protons involved in electrolysis, resulting in reduced HER. To verify the effect of hydrophobic interface on suppressed HER, we calculate the electrochemically active surface areas by extracting the double layer capacitance \(C_{dl}\) which is investigated by the cyclic voltammetry (CV) measurements in the range of \(-0.2\) and \(-0.4\) V under Ar condition (Figure S8, Supporting Information). The \(C_{dl}\) value of Au/o-CFP is calculated to be 0.085 mF cm\(^{-2}\), which is much lower than that of Au/i-CFP (1.15 mF cm\(^{-2}\)), demonstrating the lower electrocatalytic activity of Au/o-CFP for HER. This result can be ascribed to the insufficient contact area between water and hydrophobic surface. Furthermore, the average NH\(_3\) yield...
rate and Faradaic efficiency conducted at $-0.30\,\text{V}$ are detected. As shown in Figure 3b, the Au/i-CFP exhibits a much lower NRR performance (12.6 $\mu$g h$^{-1}$ mg$^{-1}$, 7.86%), which is below the half of that for Au/o-CFP NRR performance. These results demonstrate the hydrophobic interface play a key role for enhanced NRR activity and suppressed HER activity for Au/o-CFP. Based on above results, a proposed mechanism for enhanced NRR performance and suppressed HER activity of Au/o-CFP is shown in Figure 3c,d. Because of the extremely low solubility and slow diffusion rate of $N_2$ and easily available $H^+$, the supply of high concentrations of $N_2$ molecule to catalyst surface and limiting the concentration of $H^+$ becomes more important in aqueous solution. The hydrophilic interface provides sufficient contact between catalyst and water, resulting in more absorbed $H^+$ (Figure 3c). Moreover, the Au/i-CFP shows a high gas-bubble contact angle ($CA_g$) of 141.5° (Figure S9a, Supporting Information), implying a weak interaction with $N_2$ bubble. Consequently, the concentration of $N_2$ molecule is low and the concentration of $H^+$ is high near the surface of catalyst, resulting in enhanced HER and suppressed NRR. By contrast, the hydrophobic interface provides sufficient $N_2$ with a fast diffusion pathway and $H^+$ with relative low concentration due to the hydrophobic property.\[29-32\] Moreover, the surface of Au/o-CFP with a gas-bubble contact angle ($CA_g$) of 112° provided an aerophilic property with a relatively strong interaction toward $N_2$ bubble (Figure S9b, Supporting Information), resulting in sufficient supply of $N_2$ to catalyst. Therefore, abundant three-phase contacts for $N_2$, water and Au form (Figure 3d), resulting in enhanced NRR performance and suppressed HER performance.

To confirm the origin of $NH_3$, three controlled experiments were conducted: i) the working electrode in electrolyte with continual Ar flow at $-0.30\,\text{V}$ for 2 h electrolysis; ii) the working electrode in electrolyte with continual $N_2$ flow at open circuit potential for 2 h electrolysis; iii) bare carbon paper in electrolyte with continual $N_2$ flow at $-0.30\,\text{V}$ for 2 h electrolysis. Significantly, the corresponding UV–vis absorption spectra (Figure S10, Supporting Information) indicate that negligible product of $NH_3$ is generated for the three conditions. The $^{15}$N isotopic labeling experiment is further conducted to verify the original N source of the $NH_3$. As shown in Figure S11, Supporting Information, the spectra indicate a triplet coupling for $^{14}NH_4^+$ and a doublet coupling for $^{15}NH_4^+$ when using $^{14}N_2$ and $^{15}N_2$ as gas seed, which is consistent with that for $(^{14}NH_4)_2SO_4$ and $(^{15}NH_4)_2SO_4$. This result demonstrates the produced $NH_3$ resulted from the electrocatalytic NRR on Au/o-CFP. Furthermore, the particle size effect of Au NPs on NRR performance on Au NPs was also analyzed at $-0.30\,\text{V}$ versus RHE. As shown in Figure 4a, the $NH_3$ yield rate and Faradaic efficiency decreases with the size increases.
suggesting the size of Au may be another important factor for its high electrocatalytic activity for NRR.\[38,42,43\] Additionally, the durability of electrocatalyst is an important factor for the practical application. Figure S12, Supporting Information illustrates the long-term stability measured by chronoamperometry at \(-0.30\) V. There is only a slight decrease in current density after 24 h electrocatalysis. After the test, the Au/o-CFP exhibits a negligible decay of NH\(_3\) yield and Faradaic efficiency. Furthermore, the XPS spectra for Au in the 4f region is almost unchanged after 24 h electrocatalysis, demonstrating its remarkable stability (Figure S2, Supporting Information). More significantly, Au/o-CFP shows a minor change in NH\(_3\) yield rate and Faradaic efficiency during seven times recycling tests (Figure 4b), indicating an excellent durability of Au/o-CFP for NRR.

In this work, no N\(_2\)H\(_4\) is detected during the electrocatalytic NRR in 0.1 M Na\(_2\)SO\(_4\). Therefore, a proposed NRR mechanism of Au/o-CFP is described in Figure S13, Supporting Information. Owing to unsaturated coordination, N\(_2\) molecule is weakly

**Figure 3.** a) LSV curves of Au/o-CFP and Au/i-CFP in Ar-saturation electrolyte; b) ammonia yield rates and Faradaic efficiencies at \(-0.30\) V for Au/o-CFP and Au/i-CFP. The schematic illumination three-phase contact for N\(_2\) (gas), electrolyte (liquid), and catalyst (solid) at c) hydrophilic interface and d) hydrophobic interface.

**Figure 4.** a) Comparison of catalytic performances with the size of Au NPs increasing; b) Cycling tests of Au/o-CFP catalyst at \(-0.30\) V versus RHE.
chemisorbed on Au NPs surface to form Au–N\textsubscript{2} bond. Continuously, the nitrogen atom, which is far away from Au surface, is more likely to attract one proton, leading to the formation of H–N bond and the breaking of N\textsubscript{2}N bond. Then after binding with another two protons in sequence, one NH\textsubscript{3} molecule could be released. Finally, the remaining Au=N bond is further hydrogenated like the above process to generate the second NH\textsubscript{3} molecule. On basis of these results, the NRR mechanism in our case could be accepted and confirmed as a distal associative pathway\cite{37,44}.

3. Conclusion
In summary, we have demonstrated that Au/o-CFP can be adopted as highly efficient NRR electrocatalysts, which taking the advantage of hydrophobic CFP support, promoting the efficient three-phase contact of N\textsubscript{2} gas, H\textsubscript{2}O(liquid), and Au (solid). Thus, a high concentration of N\textsubscript{2} molecules and low concentration of H\textsuperscript{+} can achieve on the catalyst surface due to the fast diffusion gas pathway, which enhances the NRR and simultaneously inhibits the HER. As expected, the three-phase Au/o-CFP electrocatalyst shows a high NH\textsubscript{3} yield rate of 40.6 \mu g h\textsuperscript{-1} m\textsuperscript{-1} and great Faradaic efficiency of 31.3\%, much higher than those of Au/i-CFP. It also exhibits an excellent stability after seven consecutive cycles. N\textsubscript{2}-bubble contact angle analyses also demonstrate that Au/o-CFP possesses a relatively strong interaction with N\textsubscript{2} bubble, resulting in significantly enhanced NRR. Furthermore, the CV measurement result confirms that Au/o-CFP has a smaller double layer capacitance in Ar-saturated electrolyte, indicating a weak catalytic activity for HER. This work demonstrates a unique class of three-phase electrocatalysts with enhanced performance for NRR and suppressed performance for HER.

4. Experimental Section

Materials and Chemicals: Chlorauric acid (HAuCl\textsubscript{4}, 99.9\%) and sodium borohydride (NaBH\textsubscript{4}) were bought from Sigma-Aldrich. Ammonium chloride (NH\textsubscript{4}Cl), salicylic acid, sodium citrate dehydrate (Na\textsubscript{3}Cit), sodium hypochlorite solution (NaClO), anhydrous sodium sulfate (Na\textsubscript{2}SO\textsubscript{4}), and Na\textsubscript{3}Cit were purchased from Alfa-Aesar. Hydroxylamine hydrochloride (NH\textsubscript{2}O\textsubscript{H}Cl) and B were bought from Sigma-Aldrich.

Production Detection: The indophenol blue method\cite{46} was used for determining the concentration of generated ammonia. First, 2 mL electrolyte was mixed with three solutions (A, B, and C) for 2 h at ambient condition. In which, A is 2 mL NaOH (1 m) solution containing 5 wt\% salicylic acid and 5 wt\% sodium citrate, B is 1 mL NaClO (0.05 m) and C is 0.2 mL C\textsubscript{2}FeN\textsubscript{2}Na\textsubscript{2}O (1 wt\%). Then, an UV–vis spectrophotometer was used to detect the absorption spectra of mixed electrolyte. The absorbance of indophenol blue was detected at 655 nm. To obtain the ammonia yield, the concentration-absorbance curve was getting by using NH\textsubscript{4}Cl with a range concentration (0–1 \mu g mL\textsuperscript{-1}) as standards. The equation: $\text{NH}_3 = C_{\text{NH}_3} \times V/(t \times m)$ was used to calculate the ammonia yield. In which $C_{\text{NH}_3}$ (\mu g mL\textsuperscript{-1}), V (mL), t (h), and m (mg) are the mass concentration of NH\textsubscript{3}, the volume of Na\textsubscript{2}SO\textsubscript{4} electrolyte, the electrolysis time and the mass of catalysts, respectively.

The method of Watt and Chirip was used to determine the concentration of hydrazine in 0.1 m Na\textsubscript{2}SO\textsubscript{4} electrolyte.\cite{41} In brief, the color reagent was a mixture of 5.99 g p-(dimethylamino) benzaldehyde, 300 mL ethanol and 30 mL concentrated HCl. Following that 5 mL electrolyte was added into 5 mL color reagent and stir for 10 min at ambient condition. The absorbance of the mixture solution was determined at 455 nm. The yields of hydrazine were calculated from a concentration-absorbance standard curve, which is obtained by detecting hydrazine monohydrate with a concentration range (0–1 \mu g mL\textsuperscript{-1}).

The $^{15}$N and $^{13}$N isotopic experiments were conducted using $^{14}$N\textsubscript{2} and $^{15}$N\textsubscript{2} as feeding gases for nitrogen reduction reaction. Before test, $^{15}$N\textsubscript{2} and $^{13}$N\textsubscript{2} gases were purged through 1 mm H\textsubscript{2}SO\textsubscript{4} solution and water to eliminate the potential contaminants. After 6-h electrochemical NRR in 0.1 m Na\textsubscript{2}SO\textsubscript{4} solution at ~0.3 V versus RHE, the total electrolyte solution for four reactions was left concentrated to 2.0 mL. Then, this solution was mixed with H\textsubscript{2}SO\textsubscript{4} and DMSO-d\textsubscript{4} solutions and used for $^{15}$N NMR measurement (Agilent DD2-600).

Faradaic Efficiency Determination: The Faradaic efficiency was calculated by the following equation: $\text{FE} = 3F \times \text{NH}_3/Q$, in which (F = 96 500 C mol\textsuperscript{-1}), $\text{NH}_3$ and Q represents the Faradaic constant, the mole of generated NH\textsubscript{3} and the total electric quantity during the NRR test, respectively.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

electrochemical nitrogen reduction, gold nanoparticles, hydrophobic interfaces, three-phase contact points

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