Developing cost-effective, high-performance nitrogen reduction reaction (NRR) electrocatalysts is required for the production of green and low-cost ammonia under ambient conditions. Here, a strategy is proposed to adjust the reaction preference of noble metals by tuning the size and local chemical environment of the active sites. This proof-of-concept model is realized by single ruthenium atoms distributed in a matrix of graphitic carbon nitride (Ru SAs/g-C3N4). This model is compared, in terms of the NRR activity, to bulk Ru. The as-synthesized Ru SAs/g-C3N4 exhibits excellent catalytic activity and selectivity with an NH3 yield rate of 23.0 µg mgcat⁻¹ h⁻¹ and a Faradaic efficiency as high as 8.3% at a low overpotential (0.05 V vs the reversible hydrogen electrode), which is far better than that of the bulk Ru counterpart. Moreover, the Ru SAs/g-C3N4 displays a high stability during five recycling tests and a 12 h potentiostatic test. Density functional theory calculations reveal that compared to bulk Ru surfaces, Ru SAs/g-C3N4 has more facile reaction thermodynamics, and the enhanced NRR performance of Ru SAs/g-C3N4 originates from a tuning of the d-electron energies from that of the bulk to a single-atom, causing an up-shift of the d-band center toward the Fermi level.

1. Introduction

Single-atom catalysts (SACs), where metal active sites are atomically dispersed in a host material, have emerged as a new frontier in the area of heterogeneous catalysis in the past few years.[1] SACs provide close to 100% metal dispersion and thus can maximize metal utilization. Since SACs have unique catalytic sites, they usually exhibit a distinct catalytic selectivity as compared to their nanoclusters or nanoparticle counterparts.[2] For example, single atomic Pt immobilized in the surface of Ni nanocrystals shows a higher activity and chemoselectivity toward the hydrogenation of 3-nitrostyrene.[3] Isolated Co single-site catalysts anchored on a N-doped porous carbon nanobelt exhibits an excellent catalytic performance for oxidation of ethylbenzene with 98% conversion and 99% selectivity, whereas the Co nanoparticles are essentially inert.[4] Moreover, atomic Ni-anchored covalent triazine framework has a remarkable selectivity for the conversion of CO2 to CO, with a Faradaic efficiency (FE) of > 90% over the range of −0.6 to −0.9 V versus the reversible hydrogen electrode (RHE).[5] In view of these reported works, it is evident that the size of metal particles is a key factor in determining their catalytic performance, and decreasing the size offers an intriguing opportunity to alter the activity and selectivity of these metal catalysts. SACs, as the limit of size reduction, hold great potential to achieve high activity and selectivity in catalytic reactions.

Recently, the electrocatalytic N2 reduction reaction (NRR) in aqueous electrolytes for synthesizing ammonia at ambient...
conditions has gained increasing attention.[6] At present, the industrial-scale production of ammonia still relies heavily on the Haber–Bosch process, which was developed in the early 1900s.[7] This process takes place under harsh conditions (about 450 °C and 300 bar), is energy intensive, and emits massive amounts of greenhouse gases.[8] There are several advantages in electrocatalytic NRR for ammonia synthesis: at first, the required electricity can be supplied by green energy sources, such as solar, tide, wind, etc. In addition, the utilization of aqueous electrolytes has the potential of achieving the simplicity and low cost of this process, because the solvent water can directly serve as the hydrogen source.[9] Moreover, it has added benefits, such as modularity, scalability, and on-site, on-demand generation, which enables ammonia production in remote areas.[10]

Dispersion of metal in the form of single or a few metal atoms as actives sites on a suitable substrate could be an effective strategy to achieve facile ammonia synthesis.[9,11] So far, a variety of single-atom electrocatalysts for NRR has been reported, including Ru single atoms distributed on nitrogen-doped carbon which shows a high and stable NH₃ production rate of 3.665 mg_{NH₃} h⁻¹ mg_{Ru}⁻¹ at −0.21 V versus RHE.[11a] single Mo atoms anchored to nitrogen-doped porous carbon which achieves an NH₃ yield rate (34.0 µg mg_{cat}⁻¹ h⁻¹) with the FE of 14.6% at −0.3 V versus RHE,[11b] and Au single sites stabilized on hierarchical nitrogen-doped porous noble carbon which affords a stable NH₃ yield of 2.32 µg h⁻¹ with the FE of 12.3% at −0.20 V versus RHE.[11c] Summary of recent reported SACs-based NRR at the mild conditions is given in Table 1. However, the synthesis of SACs remains challenging because the high surface free energy of individual metal atoms drives metal aggregation toward nanoclusters or nanoparticles.[11d] Therefore, a suitable substrate that can strongly interact with noble metal clusters is needed to avoid metal aggregation. In recent years, 2D graphitic carbon nitride (g-C₃N₄) has been found to be a superior substrate for supporting catalysts, because it contains a high content of pyridine-like nitrogen which can provide abundant electron lone pairs for anchoring metal ions within its ligands.[12] The application of g-C₃N₄ as a substrate to support noble-metal SACs can offer two obvious advantages: 1) noble-metal atoms are stabilized by g-C₃N₄ in their neutral state which can facilitate catalytic activity[12c] and 2) the outstanding chemical stability facilitates g-C₃N₄ acts as a robust substrate for noble-metal catalysts.[13] In addition, noble-metal catalysts atomically dispersed on the g-C₃N₄ not only maximize the efficiency of these noble metal atoms in terms of cost, but also they will have high electrocatalytic activity and selectivity due to the high ratio of low-coordinated metal atoms. For these reasons, we study g-C₃N₄-supported noble-metal SACs as candidate electrocatalysts for NRR under ambient conditions.

Herein, we developed a new type of NRR catalyst by incorporating Ru single atoms (Ru SAs) into g-C₃N₄, to form the hybrid material (Ru SAs/g-C₃N₄) which was then supported on a free-standing copper foam (CF) to make an electrode for electrocatalytic NRR in strong alkaline electrolytes under ambient conditions. In this electrocatalytic NRR system, the highly conductive CF was utilized to compensate for the semiconducting property of g-C₃N₄. Moreover, the competitive hydrogen evolution reaction (HER) is expected to be suppressed in the strong alkaline electrolyte. In this work, the Ru SAs/g-C₃N₄ exhibited high NRR activity, yielding an NH₃ production rate of 23.0 µg mg_{cat}⁻¹ h⁻¹ and an FE as high as 8.3% at 0.05 V versus RHE under room temperature and ambient pressure in 0.5 NaOH electrolyte. These results are superior to that of CF-Ru nanoparticles (Ru NPs). Our catalytic modeling and density functional theory (DFT) calculations indicate that the relatively high activity and selectivity of NRR at single-atom Ru is due to an up-shift of the d-electron energies from Ru bulk to a Ru single atom, which in turn tunes the reaction thermodynamics of NRR to be more favorable.

2. Results and Discussion

2.1. Materials Synthesis and Characterization

The synthesis of CF-Ru SAs/g-C₃N₄ can be divided into several steps. As shown in Figure 1a, the melamine and RuCl₃ was first well-mixed in a water solution via magnetic stirring and then dried overnight at 80 °C. Next, the sample was further heat-treated at 600 °C for 6 h under the N₂ atmosphere. Finally, the acid-etched CF was immersed in the Ru SAs/g-C₃N₄ ink with the aid of the Nafion binder to obtain CF-Ru SAs/g-C₃N₄.

The morphology and microstructure of as-prepared Ru SAs/g-C₃N₄ was examined by scanning electron microscopy (SEM). Figure 1b displays a representative SEM image of g-C₃N₄. For a clearer illustration of the morphology of the as-prepared Ru SAs/g-C₃N₄, we also synthesized the pure g-C₃N₄ using the same method described above for the Ru SAs/g-C₃N₄ synthesis without the addition of RuCl₃ for comparison. The successful synthesis of pure g-C₃N₄ was confirmed by X-ray diffraction (XRD; Figure S1, Supporting Information), which exhibited two broad peaks at 12.1° and 27.3°, and these two diffraction peaks were attributed to the (100) and (002) facets of g-C₃N₄, respectively.[12e] Considering that g-C₃N₄ is a semiconductor, its optical band gap can be estimated by a Tauc plot; details of this calculation can be found in the literature.[19] Figure S2 (Supporting Information)

---

Table 1. Summary of heterogenous SACs for NRR at mild conditions.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Electrolyte</th>
<th>NH₃ yield</th>
<th>FE [%]</th>
<th>Potential (V vs RHE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SA-Mo/NPC(14)</td>
<td>0.1 m KOH</td>
<td>34.0 µg h⁻¹ mg_{cat}⁻¹</td>
<td>14.6</td>
<td>−0.45</td>
</tr>
<tr>
<td>ISAS-Fe/NC(14)</td>
<td>0.1 m PBS</td>
<td>62.9 µg h⁻¹ mg_{cat}⁻¹</td>
<td>16.8</td>
<td>−0.40</td>
</tr>
<tr>
<td>Ru/NC(14)</td>
<td>0.1 m HCl</td>
<td>3.67 mg h⁻¹ mg_{Ru}⁻¹</td>
<td>&gt;7.5</td>
<td>−0.21</td>
</tr>
<tr>
<td>Ru SAs/N-C(9)</td>
<td>0.05 m H₂SO₄</td>
<td>120.9 µg h⁻¹ mg_{Ru}⁻¹</td>
<td>29.6</td>
<td>−0.20</td>
</tr>
<tr>
<td>Au SAs-NDC(12,1)</td>
<td>0.1 m HCl</td>
<td>2.32 µg h⁻¹ cm⁻²</td>
<td>12.3</td>
<td>−0.20</td>
</tr>
<tr>
<td>Au/C₃N₄(15)</td>
<td>0.005 m H₂SO₄</td>
<td>1.31 µg h⁻¹ mg_{Au}⁻¹</td>
<td>11.1</td>
<td>−0.10</td>
</tr>
<tr>
<td>Fe/N-CNT(17)</td>
<td>0.1 m Na₂SO₄</td>
<td>10.25 µg h⁻¹ mg_{cat}⁻¹</td>
<td>10.50</td>
<td>−0.30</td>
</tr>
<tr>
<td>FeSe-N-C(18)</td>
<td>0.1 m KOH</td>
<td>34.83 µg h⁻¹ mg_{cat}⁻¹</td>
<td>9.28</td>
<td>−0.20</td>
</tr>
</tbody>
</table>
shows the band gap energy of the as-prepared g-C₃N₄ was determined to be 2.75 eV, and the value determined here was in accordance with that of pure C₃N₄, which provides further evidence of the successful synthesis of g-C₃N₄. Furthermore, the observed morphology of pure g-C₃N₄ by SEM was consistent with that of the as-prepared Ru SAs/g-C₃N₄ (Figure S3, Supporting Information). The transmission electron microscopy (TEM) image of the as-prepared Ru SAs/g-C₃N₄ in Figure S4 (Supporting Information) exhibited the typical 2D lamellar structure of g-C₃N₄. Moreover, the C/N molar ratio of the as-prepared Ru SAs/g-C₃N₄ measured by X-ray photoelectron spectroscopy (XPS) was about 0.73, close to the theoretical value of 0.75 (Figure S5, Supporting Information). In addition, the XRD was employed to characterize the as-prepared Ru SAs/g-C₃N₄ (Figure S6, Supporting Information), and it was found that Ru SAs/g-C₃N₄ also exhibited two characteristic peaks of pure g-C₃N₄. Although the as-prepared Ru SAs/g-C₃N₄ had a lower crystallinity compared to the pure g-C₃N₄ due to the existence of Ru species, it was still crystalline based on its XRD pattern. These results confirm the formation of g-C₃N₄ within the as-prepared Ru SAs/g-C₃N₄. The high-resolution TEM (HRTEM) photograph of the as-prepared Ru SAs/g-C₃N₄ did not reveal the presence of Ru nanoparticles (Figure 1c), but the existence of Ru in the as-prepared Ru SAs/g-C₃N₄ was confirmed by energy-dispersive X-ray spectroscopy (EDS) analysis (Figure S7, Supporting Information). The high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) image of the as-prepared Ru SAs/g-C₃N₄ demonstrated that individual Ru atoms were atomically dispersed (Figure 1d), and the corresponding EDS mapping images showed the homogeneous distribution of C, N, and Ru over the entire structure (Figure 1e).
XRD was employed to understand the structure and composition of CF-Ru SAs/g-C3N4 and CF-Ru NPs. As shown in Figure 2a, the XRD pattern of CF-Ru NPs showed known diffraction peaks including (002), (102), (110), and (103), which can be indexed to a hexagonal-close-packed Ru crystals (JCPDS No. 06-0663).[21] However, these characteristic peaks of the Ru crystal structure were absent in the XRD pattern of CF-Ru SAs/g-C3N4, indicating that Ru nanoparticles were not formed in Ru SAs/g-C3N4. The XPS spectra of Ru SAs/g-C3N4 and pure g-C3N4 are shown in Figure S5 (Supporting Information), and it was observed that three peaks appeared at 288, 399, and 534 eV, corresponding to the C 1s, N 1s, and O 1s electrons, respectively. Moreover, the presence of Ru 3d electrons was confirmed by the XPS analysis of the Ru SAs/g-C3N4, with Ru atom percentage of 0.6%, indicating that some Ru metal was incorporated into the g-C3N4 matrix. Figure 2b shows the XPS spectra of the C 1s for Ru SAs/g-C3N4 and pure g-C3N4, and only one strong peak appeared at 287.4 eV in pure g-C3N4, which can be assigned to the sp²-hybridized carbon in N–C=N.[19] For Ru SAs/g-C3N4, a doublet at 280.9 and 285.1 eV was identified, which agreed well with the 3d_{5/2} and 3d_{3/2} electrons of Ru ions in Ru-N moieties, indicating that Ru ions were successfully incorporated into the g-C3N4 matrix via Ru-N coordination bonds.[22] In addition, for Ru SAs/g-C3N4, a doublet at 280.9 and 285.1 eV was identified, which corresponded to the metallic Ru in Ru NPs, and a peak was found at 463.0 eV corresponding to the oxidized Ru.[9] These results confirm the absence of crystalline Ru in Ru SAs/g-C3N4 and that Ru atoms in Ru SAs/g-C3N4 are atomically dispersed. In addition, the microstructures of the Ru SAs/g-C3N4 and pure g-C3N4 were investigated by Fourier-transform infrared spectroscopy (FT-IR). As shown in Figure S8 (Supporting Information), several strong peaks in the 1200–1650 cm⁻¹ region were assigned to the characteristic stretching modes of CN heterocycles within g-C3N4 molecules,[24] and a slight blue-shift of these peaks was observed for Ru SAs/g-C3N4. These results are also indicative of the successful incorporation of Ru into the g-C3N4 substrate. The X-ray absorption near-edge spectroscopy (XANES) was employed to further understand the electronic and coordination structures of Ru SAs/g-C3N4. Figure 2e shows the Ru L₃-edge XANES profiles for Ru SAs/g-C3N4 and Ru NPs. It was found that Ru SAs/g-C3N4 exhibited a distinct energy absorption edge profile in a range between 2830 and 2850 eV compared with Ru NPs. The position of the white line in the Ru L₃-edge of Ru NPs...
was located at 2839.6 eV, which was in line with that of reported Ru powder.\(^{[25]}\) In contrast, the position of the white line in the Ru L\(_3\)-edge of Ru SAs/g-C\(_3\)N\(_4\) was located at 2841.0 eV, which matched well with that of reported highly charged Ru species.\(^{[25]}\)

In addition, the intensity of the pre-edge feature of Ru L\(_3\)-edge spectra is indicative for the covalency of the ligand-metal bonds, and a larger intensity of the white line corresponds to a higher oxidation state of Ru. The Ru L\(_3\)-edge spectrum of Ru SAs/g-C\(_3\)N\(_4\) exhibited a more prominent pre-edge line than Ru NPs, originating from the highly covalent bonding of Ru-N in Ru SAs/g-C\(_3\)N\(_4\). To gain further insights into the accurate structure of Ru SAs/g-C\(_3\)N\(_4\), a least-squares XANES fitting result was performed, and the used structure parameters of Ru SAs/g-C\(_3\)N\(_4\) were obtained from our following DFT calculations. As shown in Figure 2f, it was found that the position of the white line in the fitting curve of Ru SAs/g-C\(_3\)N\(_4\) well matched with the measured XANES result, which further confirmed that the Ru atoms in Ru SAs/g-C\(_3\)N\(_4\) were coordinated by N donor atoms from g-C\(_3\)N\(_4\) and thereby isolated to form an atomic dispersion.

The results from the above material characterizations demonstrate that g-C\(_3\)N\(_4\) is an excellent substrate for the deposition and fixation of Ru single atom sites. The incorporation of Ru ions into the g-C\(_3\)N\(_4\) through Ru-N coordination bonds prevented the aggregation of Ru atoms and led to the formation of Ru single-atom sites. The structure of the single-atom Ru sites will be described in more detail through our calculations (Section 2.3).

### 2.2. Catalytic Nitrogen Reduction

To evaluate the electrocatalytic NRR activities of CF-Ru SAs/g-C\(_3\)N\(_4\) under ambient conditions, several electrochemical tests were performed in N\(_2\)-saturated 0.5 m NaOH electrolyte, such as linear sweep voltammetry (LSV) and chronoamperometry. All tests were performed in a two-compartment cell separated by a proton conductive cation exchange membrane (Nafion 115), in which the protons (H\(^+\)) can react with N\(_2\) to form ammonia over the catalyst. The experimental apparatus for the electrocatalytic NRR is shown in Figure S9 (Supporting Information). At first, the LSV curves for CF-Ru SAs/g-C\(_3\)N\(_4\) in Ar or N\(_2\)-saturated 0.5 M NaOH solutions were measured to verify the source of ammonia. (Figure 3a). When the applied potential was less negative than −0.3 V versus RHE, and a higher current density in N\(_2\)-saturated solution was observed compared with that under Ar-saturated solution, this indicates that the electrocatalytic N\(_2\) reduction can be realized by the as-prepared CF-Ru SAs/g-C\(_3\)N\(_4\). As the applied potential was set more negative than −0.3 V versus RHE, the current densities in N\(_2\)-saturated and Ar-saturated solutions were very close, likely because the HER becomes dominant as compared to the NRR in this system. The Nesliers's reagent and ammonia-sensitive selecting electrode methods were carried out independently for the quantitative analysis of ammonia in the electrolyte after 1h of electrolysis in the presence of continuous Ar bubbling, and a very small amount of ammonia (< 10 ppb) was detected in the electrolyte, which suggested that the contribution of ammonia yield from the catalyst itself, the Nafion-dispersed liquid, and the ambient environment in the lab was almost negligible. Given that N\(_2\)H\(_4\) is a possible by-product of the electrocatalytic N\(_2\) reduction, the colorimetric method was employed to examine if N\(_2\)H\(_4\) was produced in the current experiments. No N\(_2\)H\(_4\) was detected in the electrolyte after 1h of electrolysis in the presence of continuous N\(_2\) bubbling (Figure S10, Supporting Information), indicating that the as-prepared CF-Ru SAs/g-C\(_3\)N\(_4\) has a good selectivity for the NRR.

Figure 3b shows the LSV curves of CF, CF-g-C\(_3\)N\(_4\), CF-Ru NPs, and CF-Ru SAs/g-C\(_3\)N\(_4\) for electrocatalytic NRR. At all applied potentials, CF had a much lower current density onset potential than that of CF-g-C\(_3\)N\(_4\), CF-Ru NPs, and CF-Ru SAs/g-C\(_3\)N\(_4\), which can be attributed to the inert HER activity of CF compared to that of Ru. In addition, a low current density was observed for CF-Ru SAs/g-C\(_3\)N\(_4\) at a potential range between −0.3 and 0 V versus RHE, while CF and CF-g-C\(_3\)N\(_4\) exhibited no current density within this potential range. This was partially due to the HER activity of Ru and more importantly, due to the ignition of electrocatalytic NRR activity of Ru at low potentials compared to that of CF and CF-g-C\(_3\)N\(_4\). Figure 3a also confirmed that electrocatalytic N\(_2\) reduction was realized by this as-prepared CF-Ru SAs/g-C\(_3\)N\(_4\) at low potentials. Therefore, it can be inferred here that the Ru in CF-Ru SAs/g-C\(_3\)N\(_4\) played the decisive role in the electrocatalytic NRR, while CF and CF-g-C\(_3\)N\(_4\) possessed no activity toward the electrocatalytic NRR.

Figure 3c,d shows the FE and ammonia yield rates of CF, CF-g-C\(_3\)N\(_4\), CF-Ru NPs, and CF-Ru SAs/g-C\(_3\)N\(_4\) under various applied potentials ranging from 0.05 to −0.6 V versus RHE. The data in these two figures were obtained based on the method of the ion-selective electrode meter. To confirm the reliability of this method for ammonia detection, it was confirmed that a colorimetric method using Nesliers’s reagent gave consistent results (Figure 3e); and it was also found that the values determined by the colorimetric method were a bit higher than those determined by ion-selective electrode meter. To further confirm this trend, the measurement of several prepared standard ammonia solutions was performed, and the results indeed revealed the same trend as the above experimental results. In addition, the ion-selective electrode meter exhibited a higher accuracy than the colorimetric method in this electrocatalytic NRR system (Figure S11, Supporting Information). As for CF-Ru NPs, and CF-Ru SAs/g-C\(_3\)N\(_4\) studied in this work, both of their FEs experienced a gradual decreasing trend as the applied potential increased to a more negative value. In fact, a remarkable increase of the current density was observed with the increase of applied potentials (Figure 3f), which was caused by the predominance of HER at higher overpotentials and thus resulted in the decline of FEs. In addition, there was no ammonia yield for CF, which confirmed that CF has no catalytic activity toward the NRR. The result further confirmed the contribution of ammonia from CF can be negligible. Moreover, the control experiment using CF-g-C\(_3\)N\(_4\) was also performed and shown in Figure 3c,d, and it was also found that no ammonia was produced when subtracting the ammonia measured during the Ar control experiment. This indicated that g-C\(_3\)N\(_4\) had no catalytic activity toward NRR for the production of ammonia, and the contribution of ammonia yield from the impurities of g-C\(_3\)N\(_4\) was also negligible. Compared to CF-Ru NPs, CF-Ru SAs/g-C\(_3\)N\(_4\) exhibited higher FEs at all tested potentials, and the highest FE of CF-Ru SAs/g-C\(_3\)N\(_4\) was 8.3% at 0.05 V versus RHE.
Moreover, the ammonia yield rate was normalized based on the weight of the catalysts and the NH\textsubscript{3} yield rate of CF-Ru SAs/g-C\textsubscript{3}N\textsubscript{4} was 23.0 $\mu$g mg\textsubscript{cat}\(^{-1}\) h\(^{-1}\) at 0.05 V versus RHE (Figure 3d). As far as we know, the NH\textsubscript{3} yield rate and FE that the CF-Ru SAs/g-C\textsubscript{3}N\textsubscript{4} achieved at 0.05 V versus RHE are comparable to recently reported NRR electrocatalysts. For example, Kong et al. reported that WO\textsubscript{3} nanosheets rich in oxygen vacancies afforded an NH\textsubscript{3} yield of 17.28 $\mu$g h\(^{-1}\) mg\textsubscript{cat}\(^{-1}\) and an FE of 7.0% at $-0.3$ V versus RHE.\cite{26} Chu et al. reported that NiO nanodots supported on graphene exhibited an NH\textsubscript{3} yield of 18.6 $\mu$g h\(^{-1}\) mg\textsubscript{cat}\(^{-1}\) and an FE of 7.8% at $-0.7$ V versus RHE.\cite{27} Luo et al. found that the MXene nanosheets achieved a stable NH\textsubscript{3} yield rate of 4.72 $\mu$g h\(^{-1}\) and an FE of 4.62% at $-0.1$ V versus RHE.\cite{28} However, an ultralow applied potential (0.05 V vs RHE) was used for CF-Ru SAs/g-C\textsubscript{3}N\textsubscript{4} here that makes it one of the most active and selective electrocatalysts for NRR at ambient conditions. Although the highest ammonia yield rate as high as 67.5 $\mu$g mg\textsubscript{cat}\(^{-1}\) h\(^{-1}\) was achieved at $-0.6$ V versus RHE, the FE for CF-Ru SAs/g-C\textsubscript{3}N\textsubscript{4} at $-0.6$ V versus RHE was extremely low. A plausible explanation is that N\textsubscript{2} has a low solubility in water, and the electrocatalytic NRR in this system was in a N\textsubscript{2} diffusion-controlled mode. At higher negative potentials, the HER was dominant\cite{11a} so the surface of CF-Ru SAs/g-C\textsubscript{3}N\textsubscript{4} was mainly occupied by the evolving hydrogen molecules which would block the mass transfer of N\textsubscript{2} to the surface of CF-Ru SAs/g-C\textsubscript{3}N\textsubscript{4}, and thus limit the electrocatalytic NRR activity.

The stability of the CF- Ru SAs/g-C\textsubscript{3}N\textsubscript{4} for electrocatalytic N\textsubscript{2} reduction was evaluated by consecutive recycling electrolysis at 0.05 V versus RHE. The ammonia yield rate and the current efficiency remained stable during five consecutive cycles (Figure 3g), indicating the high stability of CF-Ru SAs/g-C\textsubscript{3}N\textsubscript{4} for electrochemical N\textsubscript{2} reduction. Additionally, the stability of CF-Ru SAs/g-C\textsubscript{3}N\textsubscript{4} was also assessed by scanning at a constant potential of 0.05 and $-0.4$ V versus RHE for 12 h. The current density presented no obvious change at these two potentials (Figure 3g), and CF-Ru SAs/g-C\textsubscript{3}N\textsubscript{4} exhibited unremarkable decay of NH\textsubscript{3} production yield rate and FE at 0.05 V versus RHE during the 12 h potentiostatic test (Figure 3i), indicating that CF-Ru SAs/g-C\textsubscript{3}N\textsubscript{4} can effectively produce ammonia over

---

**Figure 3.** a) LSV curves of CF-Ru SAs/g-C\textsubscript{3}N\textsubscript{4} electrode in a N\textsubscript{2} and Ar saturated aqueous solution of 0.5 m NaOH. b) LSV curves of CF, CF-g-C\textsubscript{3}N\textsubscript{4}, CF-Ru NPs, and CF-Ru SAs/g-C\textsubscript{3}N\textsubscript{4} electrodes in a N\textsubscript{2} saturated aqueous solution of 0.5 m NaOH. c) FE and d) ammonia yield rates at different potentials ranging from 0.05 to $-0.60$ V versus RHE. e) Comparison of the ammonia-sensitive selecting electrode and Nessler reagent-based colorimetric method for the quantitative analysis of ammonia yield rate. f) Chronoamperometry results at the corresponding potentials. g) FE and ammonia yield rates during five consecutive cycles. h) Chronoamperometry results at 0.05 and $-0.40$ V versus RHE. i) FE and ammonia yield rates within 1 and 12 h tests.
a long period of time. The characterization for Ru SAs/g-C3N4 after cycling by XRD, XPS, and HAADF-STEM has been performed (Figure S12, Supporting Information), and the results confirmed that Ru atoms were still atomically dispersed without the formation of Ru NPs after the stability test. Therefore, the as-prepared Cf-Ru SAs/g-C3N4 was demonstrated to be a highly stable catalyst for electrochemical N2 reduction.

To gain more insights to the intrinsic reasons for the high NRR activity of Ru SAs/g-C3N4, we performed N2 temperature-programmed desorption (N2-TPD) for Ru SAs/g-C3N4. As shown in Figure S13 (Supporting Information), Ru SAs/g-C3N4 exhibited a peak of N2-TPD at 650 °C, which was attributed to the chemical adsorption of N2 on Ru SAs/g-C3N4. In fact, the temperature for the N2-TPD peak of Ru SAs/g-C3N4 here was even higher than that of recently reported Ru SAs/N-C, which further suggested the strong binding of N2 on Ru SAs/g-C3N4 and thus facilutated its high NRR activity.

3.2. Theoretical Investigations

To theoretically evaluate the reactivity of the NRR at the single-atom Ru on g-C3N4, DFT calculations were performed on Ru SAs/g-C3N4 (Figure 4a). Similar to the mechanisms found by Back and Jung, five possible NRR pathways were evaluated here: N2 associative and dissociative pathways, as well as pathways through the dissociation of NNH2, HNNH2, and H2NNH2. It can be seen from Figure 4a that the dissociation of N2 is the least favorable pathway due to the rate-limiting N2 dissociation step (2.34 eV). For the other pathways, the potential-determining step is the formation of NNH* (0.62 eV). It should be noted that though the desorption of NNH* is endothermic, the protonation of NNH* would form NH4+ in solution, which is expected to be a favorable step. Therefore, except the N2 dissociative pathway, all other pathways are thermodynamically exothermic at an appropriate applied potential. To model the Ru bulk structure, as studied in our experiments, similar NRR pathways on Ru(0001) were evaluated with DFT (Figure 4b). It can be clearly seen that though the formation of NNH* and 2N* are exothermic, adsorption of N2 on Ru(0001) is the rate-determining step and this step is not electrochemically tuned with an applied potential. Therefore, as compared to Ru(0001), Ru SAs/g-C3N4 is predicted to be more active for the NRR. The significant adsorption geometries of the hydrogenated-N2 species can be found in Figure S14 in the Supporting Information.

To evaluate the efficiency of NRR, DFT was performed to evaluate the competing HER on bare g-C3N4, Ru SAs/g-C3N4, and Ru(0001) (Figure 4c). It can be seen from the hydrogen evolution step that a bare g-C3N4 has facile HER but is unfavorable for NRR since it cannot stabilize N2 adsorption in our calculations so that the NRR activity should come from the Ru sites. Figure 4c shows that HER on Ru(0001) is ~0.19 eV more facile than on Ru SAs/g-C3N4 for the hydrogen evolution, indicating that HER is relatively difficult on under-coordinated surface sites due to the strong binding of H. Also, the adsorption free energy of H is more exothermic than that of N2 at Ru(0001) (Figure 4b), while these two binding energies at Ru SAs/g-C3N4 are similar. Our calculations clearly indicate that H adsorption would significantly reduce the number of NRR active sites on Ru(0001), while this H poisoning effect is much less significant at Ru SAs/g-C3N4, leading to selectivity for the NRR. Since our experiments were under alkaline conditions, we also evaluated the kinetic barrier of the water dissociation step, as shown in the inset of Figure 4c. It was found that both Ru SAs/g-C3N4 and Ru(0001) have a high dissociation barrier (0.82 and 0.84 eV, respectively), while no stable dissociation configuration was found on the bare g-C3N4. This clearly indicates that in addition to the less significant H poisoning effect found on Ru SAs/g-C3N4, the slow kinetic of water dissociation also hinders HER on all these evaluated sites. It should be noted that the tunability of adsorbate bindings is particularly important for tuning the activity of a specific catalytic site. As discussed, both the H and N2 binding energies are tuned stronger for the systems with single-atom Ru. For bulk Ru, the activity is dominated by nondefected Ru sites (e.g., the energetically favorable (0001) surface) which promotes HER and inhibits NRR. It should be mentioned that HER on both Ru SAs/g-C3N4 and Ru(0001) (Figure 4c) should be more facile than NNR (Figure 4a,b), which is in good agreement with our experimental result that the HER selectivity is higher than NRR in all the catalysts evaluated (Figure 3c). To understand the strengthened bindings of H and N2 at Ru SAs/g-C3N4, the projected density of states (PDOS) of the d-electrons of a Ru site of Ru SAs/g-C3N4 and the Ru(0001) surface were calculated (Figure 4d). Interestingly, with different atomic environments, these two Ru sites show very different PDOS distributions. Their calculated d-band centers (average energy of the d-electrons) indicate that Ru SAs/g-C3N4 has a d-band center closer to the Fermi level, which in turn leads to stronger adsorbate binding energies than the Ru bulk surface. Furthermore, the calculated charge density difference of Ru doped on g-C3N4 shows that the doping of Ru leads to significant electronic rearrangement of both the single-atom Ru and g-C3N4 (Figure 4d, inset), suggesting that the Ru-N bonding tunes the electronic properties of the system.

3. Conclusions

In summary, we have developed a new g-C3N4-supported Ru single-atom electrocatalyst and demonstrated the catalyst to be highly active toward electrochemical NRR in strong alkaline electrolytes at ambient conditions. The as-synthesized Ru SAs/g-C3N4 afforded an NH3 yield rate of 23.0 μg mgcat−1 h−1 and an FE of 8.3% at 0.05 V versus RHE. As revealed by the spectroscopic studies and electrochemical NRR tests, the outstanding NRR activity of Ru SAs/g-C3N4 was attributed to the formation of Ru single sites supported on the g-C3N4. Furthermore, DFT calculations showed that a single-atom Ru supported on g-C3N4 possesses more facile NRR reaction activity due to its stronger N2 adsorption and reduced H poisoning at the reactive sites, in good agreement with the measured catalytic activity and selectivity.

4. Experimental Section

Chemicals: Ruthenium(III) chloride (RuCl3, Ru content 45–55%), hydrogen peroxide solution (H2O2, reagent grade, 30 wt%), sulfuric acid.
Figure 4. Reaction free energy pathways of NRR on a) Ru SAs/g-C\textsubscript{3}N\textsubscript{4} and b) Ru(0001). The NH\textsubscript{3}\textsuperscript{+} will then be protonated and form NH\textsubscript{4}\textsuperscript{+} in solution (not shown). Insets show the adsorption geometries of N\textsubscript{2}*\textsuperscript{+}, 2N\textsuperscript{*}, NH\textsubscript{2}\textsuperscript{+}, and NH\textsubscript{3}. Teal, blue, brown, and white spheres represent Ru, N, C, and H atoms, respectively. Other important adsorption geometries can be found in Figure S14 in the Supporting Information. c) Reaction free energy pathways of HER on Ru SAs/g-C\textsubscript{3}N\textsubscript{4}, g-C\textsubscript{3}N\textsubscript{4}, and Ru(0001). Insets show the reaction pathways of water dissociation and the adsorption geometries of H\textsuperscript{+}. Teal, blue, brown, and white spheres represent Ru, N, C, and H atoms, respectively. d) Calculated projected density of states (PDOS) of d-electrons of a Ru atom of the Ru SAs/g-C\textsubscript{3}N\textsubscript{4} and Ru(0001) surface. Black dashed line represents the Fermi level. Blue and red horizontal bars represent the d-band center of the Ru site at g-C\textsubscript{3}N\textsubscript{4} and Ru(0001) surface, respectively. Inset shows the calculated charge density difference of the doping of Ru SAs at a g-C\textsubscript{3}N\textsubscript{4}. 

(H₂SO₄, 99.999%), hydrochloric acid solution (HCl, 32 wt% in H₂O), sodium hydroxide solution (NaOH, reagent grade, 10 N in H₂O), Nafon perfluorinated membrane (Nafon 115, thickness 0.005 in.), melamine (C₃H₆N₆, 99%), hydrazine hydrate (N₂H₄, 50–60%), Nessler’s reagent, potassium sodium tartrate solution, 4-(dimethylamino)benzaldehyde (reagent grade, 99%), and sodium borohydride powder (NaBH₄, reagent grade, ≥98.0%) were purchased from Sigma-Aldrich. All chemicals were used without further purification. Argon gas (99.99%) and nitrogen gas (99.99%) were purchased from Coregas Australia, and all solutions were prepared with deionized water.

The synthesis of g-C₃N₄ was made up to be 10 g with the weight percentage of RuCl₃ of 7.5%. The mixture was added to water at 80 °C and stirred until the solvent had evaporated. The mixture was then dried overnight in an oven at 80 °C to remove any remaining water. The samples were then mixed via mortar and pestle to provide further homogeneity and placed in a tube furnace and heat treated using the same method previously discussed for the pure g-C₃N₄ synthesis. Subsequently, the acid-etched CF was immersed in the obtained RuSAs/g-C₃N₄ ink with the aid of the Nafion binder, and the resulting CF-RuSAs/g-C₃N₄ was dried at room temperature overnight, and the loading amount of RuSAs/g-C₃N₄ was determined by the weight difference between the acid-etched CF with and without the loading of the catalyst. The synthesis of the control material CF-g-C₃N₄ was the same as the CF-RuSAs/g-C₃N₄ except the used ink was pure g-C₃N₄. The CF-RuNPs was synthesized using a facile ultrasonication-assisted chemical reduction method. First, the acid-etched CF was inserted in 20 mL RuCl₃ solutions (20 mmol L⁻¹), which was placed in an ultrasonic bath with the temperature kept at 50 °C for 1 h and the excessive NaBH₄ was slowly added into the above mixture. The obtained CF-RuNPs was then taken out from the solution and dried at room temperature overnight.

**Material Characterization:** SEM images were obtained on a Zeiss Sigma VP FESEM instrument operating at 3 kV after sputtering with an alunina boat and covered in aluminium foil with small holes to allow for the passing of nitrogen gas at 50 mL min⁻¹. This was done in an effort to prevent excessive material loss through melamine vaporization and NH₃ condensation and to retain as much of the g-C₃N₄ as possible. The heating process was as follows: from room temperature the sample was heated to 600 °C over 6 h and held at 600 °C for 4 h then cooled back to room temperature over a further 4 h.

RuSAs/g-C₃N₄ was synthesized through several steps. The total melamine plus RuCl₃ was made up to be 10 g with the weight percentage of RuCl₃ of 7.5%. The mixture was added to water at 80 °C and stirred and continuously heated to maintain the temperature until the water had evaporated. The mixture was then dried overnight in an oven at 80 °C to remove any remaining water. The samples were then mixed via mortar and pestle to provide further homogeneity and placed in a tube furnace and heat treated using the same method previously discussed for the pure g-C₃N₄ synthesis. Subsequently, the acid-etched CF was immersed in the obtained RuSAs/g-C₃N₄ ink with the aid of the Nafion binder, and the resulting CF-RuSAs/g-C₃N₄ was dried at room temperature overnight, and the loading amount of RuSAs/g-C₃N₄ was determined by the weight difference between the acid-etched CF with and without the loading of the catalyst. The synthesis of the control material CF-g-C₃N₄ was the same as the CF-RuSAs/g-C₃N₄ except the used ink was pure g-C₃N₄. The CF-RuNPs was synthesized using a facile ultrasonication-assisted chemical reduction method. First, the acid-etched CF was inserted in 20 mL RuCl₃ solutions (20 mmol L⁻¹), which was placed in an ultrasonic bath with the temperature kept at 50 °C for 1 h and the excessive NaBH₄ was slowly added into the above mixture. The obtained CF-RuNPs was then taken out from the solution and dried at room temperature overnight.

**Electrochemical Measurements:** Prior to N₂ reduction tests, Nafon 115 membranes were heat-treated in 5% H₂O₂, 0.5 M H₂SO₄, and deionized water for 1 h, respectively. After being rinsed with water thoroughly, the membranes were immersed in deionized water for future use. Electrochemical measurements were performed using an Autolab/PGSTAT302 Potentiostat–Galvanostat (Metrohm Autolab BV, Netherlands), with a gas-tight two-compartment electrochemical cell separated by a piece of Nafon 115 membrane at room temperature. A piece of Pt gauze was used as counter electrode, and a Ag/AgCl/NaCl sat. KC (4 M) electrode was employed as reference electrode. In all measurements, the Ag/AgCl reference electrode was calibrated with respect to RHE. The calibration was performed in the high-purity hydrogen-saturated electrolyte with a Pt foil as the working electrode. Cyclic voltammetry was run at a scan rate of 1 mV s⁻¹, and the average of the two potentials at which the current crossed 0 was taken to be the thermodynamic potential for the hydrogen electrode reaction. In 0.5 M NaOH solution, E_RHE = E_Ag/AgCl + 1.008. The calibration result agreed very well with the result obtained from the theoretical calculation based on the following Nernst equation

\[
E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \times \log \left( \frac{\text{pH}}{0.205} \right)
\]

(0.205 would be different if another KCl concentration was selected)

LSV tests were performed in N₂- and Ar-saturated solution at a scan rate of 5 mV s⁻¹. All LSV curves were steady-state ones after the working electrodes were scanned several times. The current density was normalized to the geometrical area. Potentiostatic tests were carried out at different potentials ranging from +0.05 to at −0.6 V versus RHE for 1 h at room temperature (∼293 K). Prior to each electrolysis, the work electrode was reduced at a low applied potential (−0.1 V vs RHE) for 30 min. 0.5 M NaOH solution was used as electrolyte, and it was presaturated with N₂ by introducing a pure N₂ gas stream for 1 h. The electrolyte was continuously bubbled with N₂ and was agitation solution with stirring by a magnetic stirrer at ∼150 rpm during each electrolysis experiment.

**Quantification of Ammonia:** The quantity of the produced NH₃ in the electrolyte was measured by an ion-selective electrode meter (Orion Star A214 Benchtop pH/ISE Meter; Thermo Scientific), and the method could be used to measure the ammonia in aqueous solution that had a concentration of 10 ppm as nitrogen or lower. Four standard ammonia solutions (10, 100, 1000, and 10 000 ppb) were prepared from a stock solution (1000 ppm ammonia as nitrogen standard) for the calibration with the slope in the range of −56 to −60 mV when the standards were between 20 and 25 °C. To minimize the impact of the background of the N₂-saturated electrolyte (0.5 M NaOH) on the quantitative analysis of the produced NH₃, each standard ammonia solution was prepared by the dilution of the stock NH₄Cl solution using the N₂-saturated 0.5 M NaOH solution. Ionic strength adjuster (ISA) was used to provide a constant background ionic strength and adjust the solution pH. ISA must be added to all samples and standards immediately before measurement to prevent ammonia loss, and 80 mL of standard or sample required the addition of 1.6 mL ISA with the stirring thoroughly.

In addition, to test if ammonia escaped from the electrolyte solution, the outlet gas was introduced to an acid bottle for wet scrubbing to collect the possible escaping ammonia. The ion-selective electrode meter was employed to measure the ammonia concentration in the acid wet scrubbing bottle, and the experimental results revealed that no ammonia was detected, suggesting that the ammonia escaping from the electrolyte solution could be negligible.

A colorimetric method using Nessler’s reagent for NH₃ detection was also performed to further examine the reliability of the former method, and the test solutions were measured as the absorbance at 420 nm by an UV-vis spectrometer (PerkinElmer Lambda 950). A standard curve of the Nessler’s reagent-based colorimetric method for the quantitative analysis of produced ammonia is shown in Figure S15 (Supporting Information). A series of standard ammonia solutions with different concentrations was prepared, and the values determined by Nessler’s reagent were almost identical to that of determined by the ion-selective electrode meter within experimental error, suggesting that it was reliable to use the selective electrode meter for the quantitative analysis of the produced NH₃ (Figure S11, Supporting Information).
Quantification of Hydrazine: In addition, the yield of hydrazine in the electrolyte was examined by Watt and Christop method. The color reagent was prepared by a mixture of para-(dimethylamino) benzaldehyde (5.99 g), HCl (concentrated, 30 mL), and ethanol (300 mL). The yields of hydrazine in the resulting electrolytes were detected after mixing with the color reagent by measuring the absorbance at 455 nm.

The Calculation of FE and NH₃ Yield: The calculation of FE of NH₃ based on Equation (2)

\[ FE = \frac{3 \times F \times c \times V}{17 \times Q} \]  

where \( F \) is Faraday constant, \( V \) is the total volume of electrolyte in cathodic compartment, \( Q \) is the total charge passed through the electrochemical system, and \( c \) is the calculated concentration of NH₃.

\[ \text{NH}_3 \text{ yield} = \frac{c \times V}{17 \times A} \]  

where \( t \) is the reaction time, \( A \) is the surface area of working electrode, \( V \) is the total electrolyte volume in cathodic compartment, and \( c \) is the concentration of NH₃.

Calculation of the Equilibrium Potential: A strong alkaline solution was employed as the electrolyte in this work with its pH value as high as 13.69, which was much greater than the pKa value for \( \text{NH}_4^+ \) (9.24). In this case, the newly produced ammonia gas formed a type of coordination with water, as shown in Equation (4)

\[ \text{N}_2(g) + 2\text{H}_2\text{O}(l) + 6\text{H}^+(aq) + 6e^- = 2\text{NH}_3 + \text{H}_2\text{O}(aq) \]  

In this half-reaction of \( \text{N}_2 \) reduction, the charge transfer of six electrons was required for the activation of one \( \text{N}_2 \) molecule, and the standard potential for this half reaction of NRR was 0.092 V. The Nernst equation was used to calculate the equilibrium potential of this reaction under these experimental conditions, assuming 1 atm of \( \text{N}_2 \). In addition, since the concentration of newly produced \( \text{NH}_3 \) in the electrolyte varied from 0.001 \( \times \) 10\(^{-3} \) to 0.01 \( \times \) 10\(^{-3} \) M, the \( \text{NH}_3 \) concentration was assumed as 0.005 \( \times \) 10\(^{-3} \) M for calculating the equilibrium potential of this NRR half-reaction

\[ E = E^\circ - RT/6F \ln \left[ \frac{[\text{NH}_3\text{OH}^+]}{[\text{H}^+][\text{NH}_4^+]^{1/3}} \right] + 0.059 V \times pH = 0.196 V \text{ versus RHE} \]  

Computational and Modeling Methods: In this study, the DFT calculations were conducted with Vienna Ab initio Simulation Package. Projector augmented-wave method and expanded Kohn–Sham (KS) wave functions in plane wave basis were, respectively, employed to describe the core[34] and valence[35] electrons. Electronic exchange was described by generalized gradient approximation and the correlation was described with the Perdew–Burke–Ernzerhof functional.[36] The Brillouin zone was sampled via a \( 3 \times 3 \times 1 \) Monkhorst-Pack \( k \)-point mesh.[37] An energy cutoff for all the calculations was set at 400 eV, and the force convergence criteria were set lower than 0.05 eV Å\(^{-1} \). The energy barriers were calculated using the climbing image nudged elastic band method (CI–NEB).[38] Since spin-polarization had negligible influence on this study, it was not included in these results. Entropic corrections were applied to the gas phase \( \text{N}_2 \) (0.59 eV) and \( \text{NH}_3 \) (0.60 eV) at a temperature of 298 K.

The Ru SAs/g-C\(_3\)N\(_4\) was modeled as one Ru atom bound with the three pyridinic N on a \( 8 \times 8 \) g-C\(_3\)N\(_4\) surface. To simulate the close-packed surface of the large Ru clusters, a \( 4 \times 4 \), four-layer, Ru(0001) slab was modeled. The bottom two layers were held fixed while the two topmost layers were allowed to relax. The reaction free energy profile of the NRR was calculated according to the computational hydrogen electrode method with the energy of proton–electron pair equaled to half of the total energy of \( \text{H}_2 \) in the gas phase.[39] The H binding energy \( E_{H} \) was calculated using Equation (6)

\[ E_{H} = E_{\text{tot}} - E_{\text{sys}} - \frac{1}{2}E_{H_{2}} \]  

where \( E_{\text{tot}} \) is the total energy of the adsorption system, \( E_{\text{sys}} \) is the total energy of the bare system without adsorbed H, and \( E_{H_{2}} \) is the total energy of a H\(_2\) molecule in vacuum. The free energy of HER (\( G_H \)) was calculated by Equation (7) with zero-point energy and entropic corrections[12]

\[ G_H = E_{H} + 0.24 \text{ eV} \]  

Supporting Information

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

Acknowledgements

B.Y. and H.L. contributed equally to this work. This work was financially supported by Australian Research Council (ARC) through Discovery Early Career Researcher Award (DE150101306) and Linkage Project (LP160109927), Faculty of Science Strategic Investment Funding 2019 of University of Newcastle, Liaoning Revitalization Talents Program—Pan Deng Scholars (XLYC1802005), Liaoning BaiQianWan Talents Program, the National Science Fund of Liaoning Province for Excellent Young Scholars, and Science and Technology Innovative Talents Support Program of Shenyang (RC180166). The authors also wish to acknowledge financial assistance provided through CSIRO Energy, Australia, and “Shuang Chuang” Fellowship, Fujian, China. H.L. acknowledges the 2017 Hamilton/Schoch Fellowship, 2018 Department Excellence Fellowship, and 2019–2020 University Graduate Continuing Fellowship. The computational work was supported by the Welch Foundation (F-1841) and the Texas Advanced Computing Center.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

ammonia synthesis, g-C\(_3\)N\(_4\), hydrogen evolution, single atoms

Received: July 13, 2019
Revised: October 13, 2019
Published online:
