Hydrogen radicals-induced electrocatalytic N_2 reduction at low potential

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Abstract

Realizing efficient hydrogenation of N_2 molecules in the electrocatalytic nitrogen reduction reaction (NRR) is crucial in achieving high activity at low potential because it theoretically requires a higher equilibrium potential than other steps. Analogous to metal hydride complexes for N_2 reduction, achieving this step by chemical hydrogenation can weaken the potential dependence of the initial hydrogenation process. However, this strategy is rarely reported in electrocatalytic NRR, and the catalytic mechanism remains ambiguous and lacks experimental evidence. Here we show a highly efficient electrocatalyst (ruthenium single atoms anchored on graphdiyne/graphene sandwich structures) with a hydrogen radicals-transferring mechanism, in which graphdiyne (GDY) generates hydrogen radicals (H•), which can effectively activate N_2 to generate NNH radicals (•NNH). A dual-active site is constructed to suppress competing hydrogen evolution, where hydrogen preferentially adsorbs on GDY and Ru single atoms serve as the adsorption site of •NNH to promote further hydrogenation of NH_3 synthesis. As a result, a high activity and selectivity are obtained simultaneously at -0.1 V versus a reversible hydrogen electrode. Our findings illustrate a novel hydrogen transfer mechanism that can greatly reduce the potential and maintain the high activity and selectivity in NRR, and provide powerful guidelines for design concept of electrocatalysts.

Introduction

Electrocatalytic NRR generally suffers from poor NH_3 selectivity and activity due to the competitive hydrogen evolution and high reaction barrier[1, 2]. From the thermodynamic perspective, it typically proceeds at a potential similar to that required for the hydrogen evolution reaction (HER), accounting for the extremely low Faradaic efficiency (FE) towards NH_3 synthesis[3-5]. Especially at large potential, HER is more likely to occur. From the kinetic view, the formation of *NNH (* represents the catalyst surface sites), which is widely considered as a rate-limiting step, limits the improvement of NRR activity due to its relatively large energy barrier[6-9]. Accordingly, it is imperative to construct an electrocatalyst that could balance the competition between H and N_2 on the active site and accelerate the reaction kinetics of hydrogenation process, thereby enhancing the NRR activity at low potential. As shown in Fig. 1a, an NRR electrocatalyst of Ru single atoms (Ru SAs) on graphdiyne/graphene sandwich structures (GDY/G) is designed. Ru, as a second-generation NH_3 catalyst, has shown high activity towards NRR due to the appropriate N_2 adsorption energy and required potential much lower than that of other precious metals[10, 11]. Recently, single-atom catalysts with atomically dispersed metal active centers have attracted extensive research interest due to their maximum atomic efficiency[12]. These catalysts have well-defined active sites, providing a unique opportunity to further understand the reaction mechanism on the active sites[13]. Due to the unique atomic structures and electronic properties, single-atom catalysts exhibit extremely excellent catalytic activity and selectivity in many electrocatalytic reactions[14, 15]. For example, Ru single-atom catalysts enable high FE due to the lower adsorption capacity of H than that on metal particles or clusters[16, 17]. Graphdiyne (GDY), a carbon allotrope composed of sp^2 and sp-hybrid carbon atoms, has high intrinsic activity for HER due to uneven surface charge distribution compared with several other carbon materials, such as graphene, carbon nanotubes, fullerenes[18, 19]. Thus, an electrocatalyst with dual-active sites is constructed, where H adsorption and N_2 hydrogenation process take place at spatially separated sites, respectively. Here, the H^+ preferentially attacks GDY rather than Ru single atoms, effectively inhibiting the coverage of H at the Ru active sites, thus improving the FE of NRR process (Fig. 1b). Furthermore, we show that the GDY can generate hydrogen radicals (H•), and a new mechanism via H• transfer pathway is proposed that expedites the reaction kinetics of hydrogenation process. In brief, the combined effect of both the dual-active sites and the H•-transferring mechanism leads to high activity and selectivity simultaneously on Ru SAs/GDY/G catalyst at low potential (-0.1 V versus a reversible hydrogen electrode).

The whole design concept of NRR on Ru SAs/GDY/G catalyst goes through the following steps (Fig. 1a). The GDY can generate H• (step i). H• can react with N_2 to form NNH radicals (•NNH) and then the •NNH adsorbs on Ru single atoms to form *NNH (step ii and iii in Fig. 1c). Subsequently, *NNH goes through a step-by-step hydrogenation to form $*NH_3$ and then desorbs to form NH_3 (step iv in Fig. 1d).

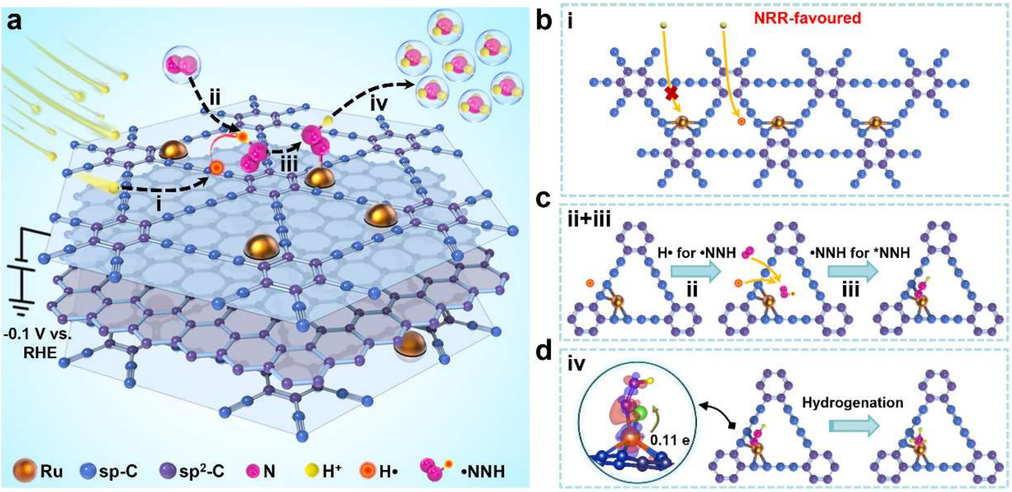


Fig. 1 Conceptual diagram of N_2 electroreduction to ammonia (NH_3) on Ru SAs/GDY/G. Ru SAs/GDY/G stands for ruthenium single atoms (Ru SAs) anchored on graphdiyne/graphene sandwich structures (GDY/G). **a** Proposed reaction scheme for N_2 electroreduction to NH_3 on Ru SAs/GDY/G. **b** Mass transfer of protons to the Ru SAs/GDY/G surface in electrolytes. **c** Schematic representation of the •NNH generation mechanism and *NNH adsorption configurations on Ru single atom. **d** The hydrogenation of NH_3 synthesis on Ru single atom and the charge density fluctuations of *NNH adsorption configurations (charge density accumulation and depletion depicted in orange and blue, respectively).

Results and Discussion

Synthesis and characterization of catalysts

The Ru SAs/GDY/G catalyst was synthesized through a simple impregnation method on the graphdiyne/graphene sandwich structures (Supplementary Fig. S1). Briefly, the GDY/G was fabricated via Eglinton coupling reaction using a fast, simple and efficient microwave synthesis[20]. This strategy involves mixing $Cu(OAc)_2 \cdot H_2O$ and graphene with monomer hexaethynylbenzene (HEB) at room temperature, followed by microwave radiation of the mixture for only 1 min in the household microwave oven.

The photograph of as-prepared GDY/G powder is shown in Supplementary Fig. S2a. X-ray photoelectron spectroscopy (XPS) and inductively coupled plasma mass spectrometry (ICP-MS) analysis confirm that only a very small amount of copper remains in the GDY/G, with a content of 0.16 wt% (Supplementary Fig. S2b). The residual copper has no effect on electrocatalytic performance, which will be discussed later in this work. The XPS C 1s spectrum of GDY/G is deconvoluted into four peaks at 284.4, 285.0, 286.4, and 288.5 eV, assigning to C-C (sp^2), C-C (sp), C-O, and C=O, respectively (Supplementary Fig. S3)[21]. From the GDY structural model, the theoretical ratio of sp to sp^2 carbon atoms should be 2. However, the experimentally obtained ratio is less than 2 due to the existence of graphene[20]. Transmission electron microscopy (TEM) image of GDY/G indicates a lamellar structure, in which the smooth surface of graphene is covered by GDY thin film (Fig. 2a and Supplementary Fig. S4a). The high-resolution TEM (HRTEM) in Supplementary Fig. S5 shows a well-defined interface between GDY and graphene, further elaborating that the GDY film grows in-plane on graphene. Due to the van der Waals interaction and lattice match between GDY and graphene, the GDY thin film uniformly distributed on both sides of the graphene[22]. In the absence of graphene, the GDY samples obtained by the same strategy are severely stacked (Supplementary Fig. S6a-c), confirming the importance of graphene as template in GDY growth. Additionally, the interlayer space of 0.367 nm and 0.366 nm are observed at the edges of the GDY/G and GDY, respectively, which is classified to the interlayer space of GDY (Fig. 2b and Supplementary Fig. S6d). Atomic force microscopy (AFM) image (Fig. 2c) suggests that the thickness of GDY/G is about 6.84

nm, in which the thickness of graphene is 2.74 nm (Supplementary Fig. S4b). Therefore, it can be calculated that the thickness of the GDY film on the graphene side is about 2.05 nm. Afterwards, the Ru SAs/GDY/G was obtained by impregnation method, and its morphology was first characterized by TEM in Supplementary Fig. S7. It shows a sandwiched-like structure originating from GDY/G, and no obvious Ru nanoparticles or clusters can be observed on the GDY/G scaffold. From the aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) (Fig. 2d), isolated Ru single atoms anchored on the GDY/G can be clearly assigned as bright dots. The content of Ru is estimated to be 1.8 wt% based on ICP-MS analysis, which is in agreement with the results of energy-dispersive X-ray spectroscopy (EDX) (1.5 wt%, Supplementary Fig. S8). EDX mapping analysis in Fig. 2e reveals the existence of Ru, C, and Cl elements throughout the Ru SAs/GDY/G and the uniform dispersion of Ru element in the GDY/G. The X-ray diffraction (XRD) patterns of Ru SAs/GDY/G in Fig. 2f indicate that there are no peaks related to Ru-based crystals, further demonstrating the single-atomic nature of Ru in Ru SAs/GDY/G. The XRD patterns of Ru SAs/GDY/G and GDY/G are similar. A broad peak over 23°corresponds to the interlayer distance of GDY[23], and two peaks at 26.2 and 54.0 are ascribed to the (002) and (004) planes of graphitic carbon[24]. For comparison, the Ru nanoparticles on graphene sheet (Ru NPs/G) control sample was prepared and characterized. ICP-MS analysis shows that the Ru content in the Ru NPs/G is 8.4 wt%. The Ru nanoparticles are distributed in the graphene matrix with a highly agglomerated distribution, and a clearly visible crystal structure of Ru nanoparticles is illustrated in Supplementary Fig.

S9. The corresponding fast-Fourier transform (FFT) exhibits that the lattice spacing of 0.214 nm is attributed to the (002) plane of hexagonal Ru. The specific surface area and pore volume of Ru SAs/GDY/G are 211.20 m^2 g^{-1} and 0.37 cm^3 g^{-1}, respectively, which is higher than that of Ru NPs/G (98.68 m^2 g^{-1} and 0.26 cm^3 g^{-1}, Supplementary Fig. S10).

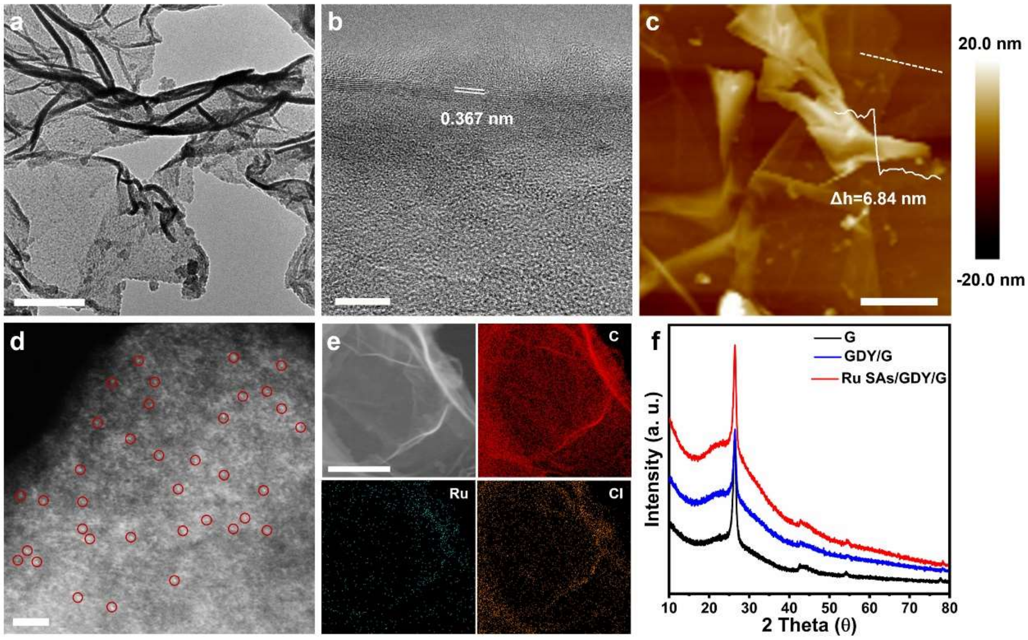


Fig. 2 Characterizations of GDY/G and Ru SAs/GDY/G. GDY/G stands for graphdiyne/graphene sandwich structures. **a** Transmission electron microscopy (TEM) image of GDY/G. Scale bar, 500 nm. **b** High-resolution TEM (HRTEM) image of GDY/G. Scale bar, 10 nm. **c** Atomic force microscopy (AFM) image of GDY/G. Scale bar, 500 nm. **d** Aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image of Ru SAs/GDY/G. Some of Ru single atoms are indicated by the red circles. Scale bar, 2 nm. **e** HAADF-STEM image and corresponding EDX elemental mapping images of Ru SAs/GDY/G, C (red), Ru (cyan), and Cl (orange). Scale bar, 300 nm. **f** X-ray diffraction (XRD) patterns of Ru SAs/GDY/G, GDY/G and G. G stands for graphene sheet.

The structure of catalysts was further investigated by Raman spectroscopy, XPS and X-ray absorption spectroscopy (XAS). Fig. 3a shows Raman spectra of Ru SAs/GDY/G, GDY/G and G. The distinct peaks at approximately 1353.1, 1583.2 and 2701.1 cm^{-1} are assigned as D band, G band and 2D band of graphene, respectively. The Y peak centered at 2158.6 and 2172.7 cm^{-1} in the Ru SAs/GDY/G and GDY/G is attributed to the triple bond vibration of the diacetylenic linkages (-C≡C-C≡C-) in GDY. The obvious red shift suggests the generation of coordination bonds between Ru and C of the diacetylenic linkages in GDY[25]. XPS analysis shows the presence of oxidized ruthenium on the surface of Ru SAs/GDY/G. In Fig. 3b, the binding energies of Ru $3p_{3/2}$ and Ru $3p_{1/2}$ peaks in the Ru SAs/GDY/G are 462.9 and 484.9 eV, respectively, which correspond to the oxidized ruthenium[26]. Correspondingly, the two peaks appeared at 461.5 and 483.6 eV in Ru NPs/G are attributed to the metallic ruthenium[27]. The binding energies of Ru SAs/GDY/G are higher than that of Ru NPs/G, and lower than that of Ru^{3+}, indicating that the valence states of Ru in the Ru SAs/GDY/G are between 0 and 3[26]. X-ray absorption fine structure (XAFS) was performed to further reveal the state of the Ru species in the Ru SAs/GDY/G at the atomic level, with Ru foil, $RuCl_3$ and RuO_2 as reference. In Fig. 3c, the near-edge absorption energy of Ru SAs/GDY/G is situated between Ru foil and $RuCl_3$ references, further implying that the oxidation state of Ru sits between Ru^0 and Ru^{3+}, and the results are consistent with XPS analysis. The comparison of the k^2-weighted EXAFS paths is shown in Supplementary Fig. S11. The Fourier transformed k^2-weighted extended XAFS (FT-EXAFS, without phase correction) spectrum of Ru SAs/GDY/G exhibits two distinct peaks at around 1.56 Å and 1.86 Å, assigning to the Ru-C and Ru-Cl superimposed contribution, respectively

(Fig. 3d)[28, 29]. No obvious Ru-Ru coordination peak at 2.42 Å and other peaks are observed, demonstrating the atomic dispersion of Ru atoms on GDY/G. Moreover, the Cl 2p XPS spectrum further indicates the existence of Cl in Ru SAs/GDY/G (Supplementary Fig. S12a). The atomic dispersed Ru sites of Ru SAs/GDY/G were further confirmed by the wavelet transform (WT)-EXAFS due to its high resolution in both R and k space[30]. The Ru K-edge WT-EXAFS oscillations in Fig. 3g show one intensity maximum at ~4.1 $Å^{-1}$, which corresponding to the first coordination shell of Ru element (Ru-C and Cl coordination). Compared with the WT plots of Ru foil, $RuCl_3$ and RuO_2 references, no intensity maximum arising from Ru-Ru contribution is observed. The above results directly confirm the dispersion of isolated Ru atom in Ru SAs/GDY/G. The EXAFS fitting results show that the Ru-C bond length and Ru-Cl bond length is 2.05 Å and 2.34 Å, respectively, revealing that the Ru atoms anchored on GDY/G are coordinated by four C atoms and a Cl atom (Fig. 3e and f, Supplementary Table S1). The corresponding structure model of Ru SAs/GDY/G is shown in Supplementary Fig. S12b.

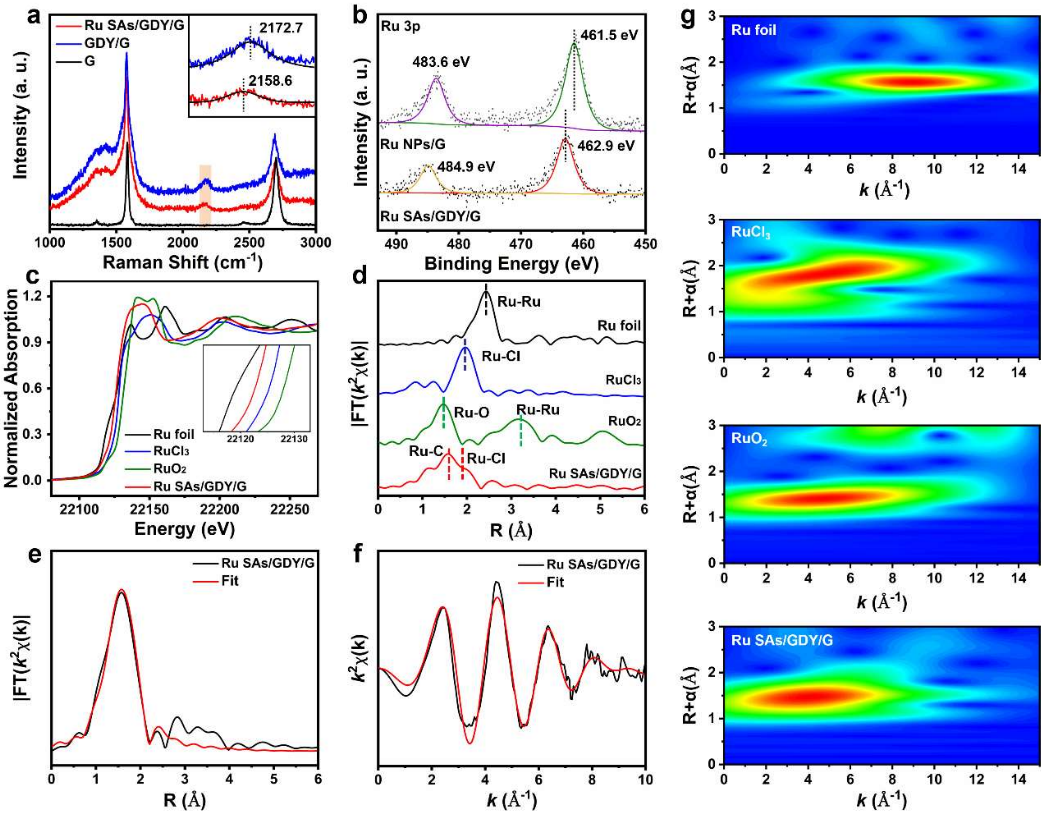
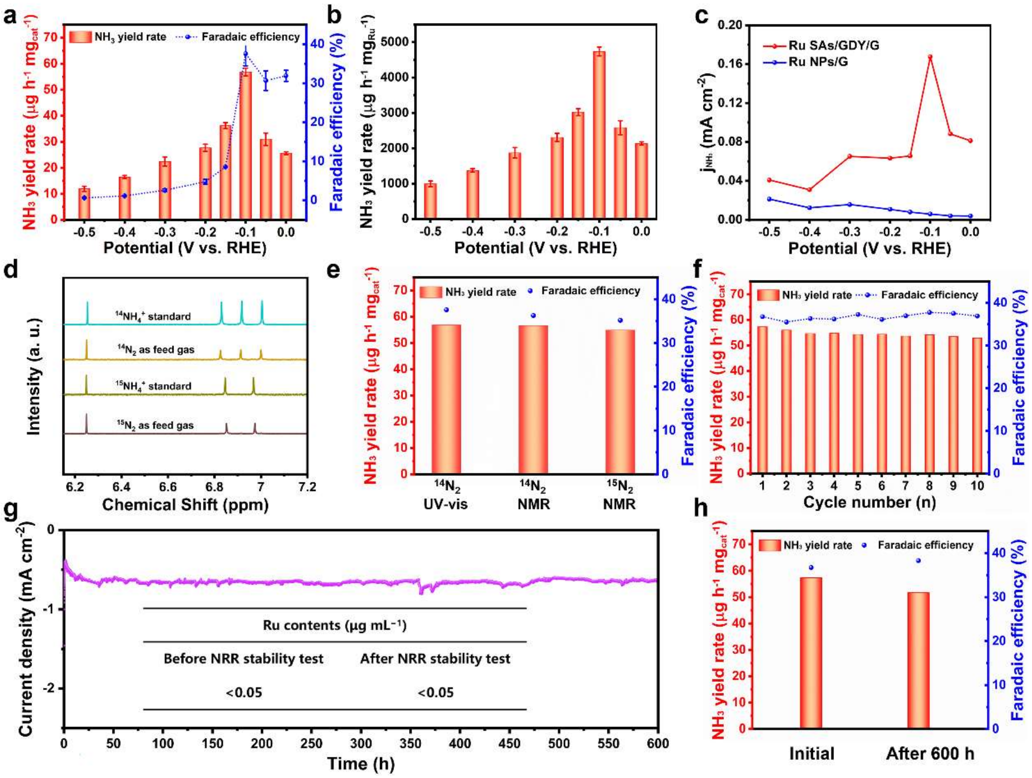


Fig. 3. Structural analysis of Ru SAs/GDY/G. **a** Raman spectra of Ru SAs/GDY/G, GDY/G and G. **b** The high-resolution Ru 3p XPS spectra of Ru SAs/GDY/G and Ru NPs/G. Ru NPs/G stands for ruthenium nanoparticles on graphene sheet. **c** X-ray absorption near-edge structure (XANES) spectra and **d** Fourier transformed (FT) k^2-weighted χ(k)-function of the EXAFS spectra at the Ru K-edge of Ru SAs/GDY/G, referenced Ru foil, $RuCl_3$ and RuO_2. **e** EXAFS fitting curves of Ru SAs/GDY/G at R-space. **f** EXAFS fitting curves of Ru SAs/GDY/G at *k*-space. **g** Wavelet transform (WT) for the k^2-weighted EXAFS signals of the Ru K-edge.

Electrocatalytic N_2 reduction performance

The electrochemical nitrogen reduction reaction (NRR) was conducted in a customized H-cell separated by a Nafion 117 membrane at room temperature (Supplementary Fig. S13). Based on the rigorous experimental protocol, a series of tests were carried out to obtain reliable evidence of NRR activity[31]. The produced ammonia was analyzed and quantified by spectrophotometric and NMR methods. As shown in Supplementary Fig. S14-19, no NH_3 and NO_x contaminants are observed in the fully purified gas ($^{14}N_2$ and $^{15}N_2$). Moreover, no NH_3 contaminant was detected in the electrolyte (1) bubbled by purified N_2 or Ar without applying potential for 1 h, (2) saturated by purified N_2 or Ar under open circuit potential (OCP) for 1 h, (3) saturated by purified Ar at different applied potentials for 1 h (Supplementary Fig. S20 and 21). To assess the NRR performance of catalysts, linear sweep voltammetry (LSV) was carried out in Ar versus N_2-saturated acidic sodium sulfate electrolytes (pH 2.2, 0.5 M Na_2SO_4), and all potentials were converted to reversible hydrogen electrode (RHE) by experimental calibration (Supplementary Fig. S22). Remarkably, the clear differences of current density for Ru SAs/GDY/G can be observed in Ar and N_2-saturated electrolytes (Supplementary Fig. S23a), indicating the electrochemical responses for NRR[32], which is larger than that of Ru NPs/G (Supplementary Fig. S23b). The NH_3 production and possible byproduct N_2H_4 in the electrolyte were quantified, and no byproduct N_2H_4 was detected during NRR test (Supplementary Fig. S24 and S25). Then, chronoamperometry measurements were conducted to further systematically study the NRR activity of Ru SAs/GDY/G with continuous N_2 bubbling (Supplementary Fig. S26a), and the corresponding UV-vis absorption spectra are shown in Supplementary Fig. S26b. The average NH_3 yield rate and FE of Ru SAs/GDY/G are exhibited in Fig. 4a. Strikingly, the highest NH_3 yield rate of 56.8 $\mu g\ h^{-1}\ mg_{cat.}^{-1}$ (4.7 $mg\ h^{-1}\ mg_{Ru}^{-1}$) with a FE of 37.6% was achieved at an applied potential of -0.1 V vs. RHE, nearly 6.1 and 5.0 times than that of Ru NPs/G, respectively (Fig. 4b and Supplementary Fig. S27).

Such NH_3 yield rate and selectivity achieved simultaneously at low potential outperforms most of previously reported work (Supplementary Table S2). Additionally, the NRR activity of Ru SAs/GDY/G was also evaluated in 0.5 M Na_2SO_4 and 0.1 M KOH. As shown in Supplementary Fig. S28, the Ru SAs/GDY/G catalyst exhibits a remarkable NH_3 yield rate of 57.6 μg h^{-1} $mg_{cat.}^{-1}$ at -0.15 V and FE of 31.5 % at -0.1 V in 0.5 M Na_2SO_4, and shows a maximum NH_3 yield rate of 60.1 μg h^{-1} $mg_{cat.}^{-1}$ at -0.2 V and FE of 32.4 % at 0 V in 0.1 M KOH. From the above results, it is found that the Ru SAs/GDY/G catalyst can effectively catalyze the NRR in acidic sodium sulfate electrolyte, 0.5 M Na_2SO_4 and 0.1 M KOH, and the required potential is the lowest in acidic sodium sulfate electrolyte. As shown in Fig. 4c, the highest partial current density of 0.17 mA cm^{-2} over the Ru SAs/GDY/G catalyst is almost eight times than that of the Ru NPs/G (0.02 mA cm^{-2}). Interestingly, sole GDY/G shows no detectable NH_3 production at different applied potentials (Supplementary Fig. S29a), whereas anchoring Ru single atoms on GDY/G enable the NRR significantly, indicating that GDY/G is inert for NRR process and the single-atom dispersed Ru is regarded as main active site for NRR. Additionally, we also evaluated the NRR performance of GDY/G at different pH values, showing almost no NH_3 formation (Supplementary Fig. S29b and c). Thus, we conclude that the residual copper in GDY/G has no effect on electrocatalytic NH_3 production. For further confirmation of N source and accurate quantification of the NH_3 product from Ru SAs/GDY/G during NRR, isotope labelling experiments were performed. The ^1H nuclear magnetic resonance (NMR) spectra show that a doublet signal corresponding to $^{15}NH_4^+$ and triple signal representing $^{14}NH_4^+$ are observed when using $^{15}N_2$ and $^{14}N_2$ as gas supply, respectively, revealing that the feeding gas is the only N source (Fig. 4d). The NH_3 yield rate and FE determined by NMR are 56.6 μg h^{-1} $mg_{cat.}^{-1}$ and 36.3 % using $^{14}N_2$ as gas, and 54.9 μg h^{-1} $mg_{cat.}^{-1}$ and 35.2% using $^{15}N_2$ as gas at -0.1 V for Ru SAs/GDY/G, revealing the reliability of quantitative tests (Fig. 4e and Supplementary Fig. S30-32). Moreover, amount of accumulated NH_3 quantified by spectrophotometric and NMR methods shows a good linear increase with the prolongation of reaction time when $^{14}N_2$ is used (Supplementary Fig. S33), suggesting the stability of NH_3 production rate. The enhanced NRR activity of Ru SAs/GDY/G was confirmed by electrochemically active surface area (ECSA) and electrochemical impedance spectroscopy (EIS) measurement. The ECSA assessed by the double layer capacitance (C_{dl})[33] are shown in Supplementary Fig. S34a-c. The determined C_{dl} of Ru SAs/GDY/G and Ru NPs/G are 6.32 and 2.26 mF cm^{-2}, respectively, revealing more exposed active sites for Ru SAs/GDY/G. The charge transfer resistance (R_{ct}) of the Ru SAs/GDY/G is much smaller than that of Ru NPs/G, which could favor charge transfer and thus enhance NRR kinetics (Supplementary Fig. S34d). The GDY/G possesses a faster charge transfer capacity than GDY, implying that the graphene can not only serve as a template for GDY growth, but also improve the conductivity of the catalyst. Furthermore, both NH_3 yield rate and FE of the Ru SAs/GDY/G exhibit no significant variation through ten consecutive tests (Fig. 4f and Supplementary Fig. S35). During the long-term electrocatalysis for 600 h at -0.1 V, the current density of the Ru SAs/GDY/G hardly attenuates (Fig. 4g). It just shows a trivial loss in NH_3 yield rate and slight increase in FE after 600 h stability test, confirming the superior electrochemical durability (Fig. 4h). Careful examination of TEM, aberration-corrected HAADF-STEM (Supplementary Fig. S36), EDX (Supplementary Fig. S37 and 38), Raman and XPS spectra (Supplementary Fig. S39) and XAS spectra (Supplementary Fig. S40) display that the morphology and structure of the Ru SAs/GDY/G remain unchanged after cycling test, confirming its robustness towards NH_3 synthesis. Importantly, no Ru species in the electrolyte solution are detected after 600 h stability test on the Ru SAs/GDY/G under -0.1 V, which reveal the excellent stability of Ru single atoms. The above results show that the Ru SAs/GDY/G simultaneously obtains high FE and NH_3 yield rate, as well as superior stability.



Ru contents (μg mL⁻¹)	
Before NRR stability test	After NRR stability test
<0.05	<0.05

Fig. 4. Electroreduction of N_2 to NH_3 under ambient conditions. a NH_3 yield rate and Faradaic efficiency (FE) of Ru SAs/GDY/G at selected potentials. **b** NH_3 yield rate normalized by the mass of Ru for Ru SAs/GDY/G at different potentials. **c** Partial

current densities (j_{NH3}) of NRR at different applied potentials of Ru SAs/GDY/G and Ru NPs/G. **d** ^{1}H NMR spectra of the NRR products using different feed gases. **e** Comparison of the calculated NH_3 yield rate and FE at -0.1 V by NMR and UV-vis methods. **f** Cycling test and **g** stability test of Ru SAs/GDY/G at -0.1 V. Inset: the Ru contents in electrolytes before and after 600 h stability. **h** NH_3 yield rate and FE of initial and after 600 h stability test.

The mechanism of electrocatalytic NRR

We performed density functional theory (DFT) calculations to further explain the mechanism of NRR on the Ru SAs/GDY/G. The NRR selectivity was also investigated. The predominance of H adsorption over N_2 adsorption is believed to be the main reason for the potential-dependent decrease in NRR activity[34, 35]. Notably, N_2 preferentially adsorbs on Ru active site compared to the other active sites (Supplementary Fig. S41 and 42). The H adsorption is significantly suppressed on Ru active site with high free-energy change of 0.69 eV, and thus effectively suppressing the competitive HER (Fig. 5a-b and Supplementary Fig. S43). To further unravel the mechanism of NRR on Ru SAs/GDY/G, kinetic isotope effect (KIE) experiments were carried out to describe the rate-determining step[36, 37]. Fig. 5c shows that the NH_3 yield rate of both Ru SAs/GDY/G and Ru NPs/G decrease when the H_2O/H_2SO_4 solvent is replaced by D_2O/D_2SO_4 solvent. The KIE values of both Ru SAs/GDY/G and Ru NPs/G are greater than 1, indicating that the hydrogenation step is a rate-determining step[38]. Furthermore, the lower KIE value (1.28) of Ru SAs/GDY/G shows excellent proton transfer kinetics compared to Ru NPs/G (1.92), which accelerates the hydrogenation step in NRR. Here, for the first time, we discovered that GDY could generate H• through *in situ* electron paramagnetic resonance (EPR) technology. 5,5-dimethyl-1-pyrrolidine-N-oxide (DMPO) as a radical trapping reagent was tested to rule out the possible interference, and no EPR peaks are observed before electrochemical test (Supplementary Fig. S44a). Nine characteristic peaks with an intensity ratio of 1:1:2:1:2:1:2:1:1 are clearly observed for both GDY/G and Ru SAs/GDY/G under Ar atmosphere at -0.1 V (Fig. 5d), which are consistent with the simulation results and are assigned to DMPO-•H (A_N = 22.8 G, A_H = 16.5 G)[39, 40]. In comparison, no EPR signal obtained for the graphene (Supplementary Fig. S44b) reveals that the formation of H• in GDY/G is attributed to GDY. In order to reveal the source of H•, isotope experiments of GDY/G were carried out with D_2O/D_2SO_4 electrolyte instead of H_2O/H_2SO_4 electrolyte. The captured signal was assigned to DMPO-•D, with the typical characteristic parameter of A_N = 16.7 G, A_H = 22.7 G, A_D = 3.5 G, and no EPR peaks corresponding to DMPO-•H are observed, indicating that the hydrogen source of the hydrogen radicals comes from the electrolyte (Supplementary Fig. S45). The Ru SAs/GDY/G possesses stronger DMPO-•H signal than that of the GDY/G, whereas Ru NPs/G does not generate H• (Supplementary Fig. S46a). When the electrocatalysis is operated under N_2 atmosphere, the DMPO-•H signal becomes undetectable and the new signal corresponding to •NNH_x (A_N = 13.9 G, A_H = 8.5 G, and A_N = 1.5 G) is presented for Ru SAs/GDY/G (Supplementary Fig. S46b), which suggests that the H• generated by GDY is rapidly consumed to participate NRR process. Taken together, the above results indicate that the hydrogenation process of NRR for Ru SAs/GDY/G involves a new mechanism via H• transfer pathway. DFT computational studies further confirm the proposed mechanism. As previously reported in the literature, the enzymatic, distal and alternating pathways are possible mechanisms of NRR[41]. Due to that the N_2 molecule cannot be stabilized as the side-on configuration on the Ru single atom of the Ru SAs/GDY/G, which is suggested by the DFT calculation, the enzymatic pathway is not considered in this work. It shows that the alternating pathway is more favorable than the distal pathway with the optimal end-on adsorption configuration of N_2 (Supplementary Fig. S42). As shown in Fig. 5e, the Ru SAs/GDY/G exhibits a particularly high free-energy change of 0.64 eV, revealing the difficult adsorption of N_2 on its surface. The corresponding first-hydrogenation energy is even higher ($\Delta G_r(*N_2 \rightarrow *NNH) = 0.96$ eV), indicating the whole activating process of N_2 is thermodynamically forbidden if only the Ru single atom is involved, which is nevertheless conflict with our experiments. With the assistance of H•, our calculation suggests the first-hydrogenation of the N_2 molecule becomes much easier ($\Delta G_r(H\bullet \rightarrow \bullet NNH) = 0.33$ eV). It is obvious that the H• can effectively activate N_2 to generate •NNH, which is consistent with the captured $\bullet NNH_x$ in the experimental results (Supplementary Fig. S46b). Thus, we speculate that the NRR process undergoes a H• transfer pathway with significantly decreased free-energy gap (Fig. 5f). The first step is the activation of the N_2 molecule by H•, giving rise to the •NNH, followed by the exothermic •NNH adsorption (*NNH) on Ru. Subsequently, the stepwise hydrogenation of *NNH occurs through the alternating pathway, which is thermodynamically more favorable than that through the distal pathway (Fig. 5f and Supplementary Fig. S47). Moreover, the hydrogenation of *NNH to *NHNH is the potential-determining step (PDS) of 0.05 eV, which determines the onset potential of

NRR[42]. Thus, it can be seen that the corresponding calculated onset potential is -0.05 V, further confirming the superior catalytic activity of NRR towards Ru SAs/GDY/G at -0.1 V. Consequently, the dual-active sites and hydrogen radicals-transferring mechanism result in the improved FE and NH_3 yield rate on Ru SAs/GDY/G.

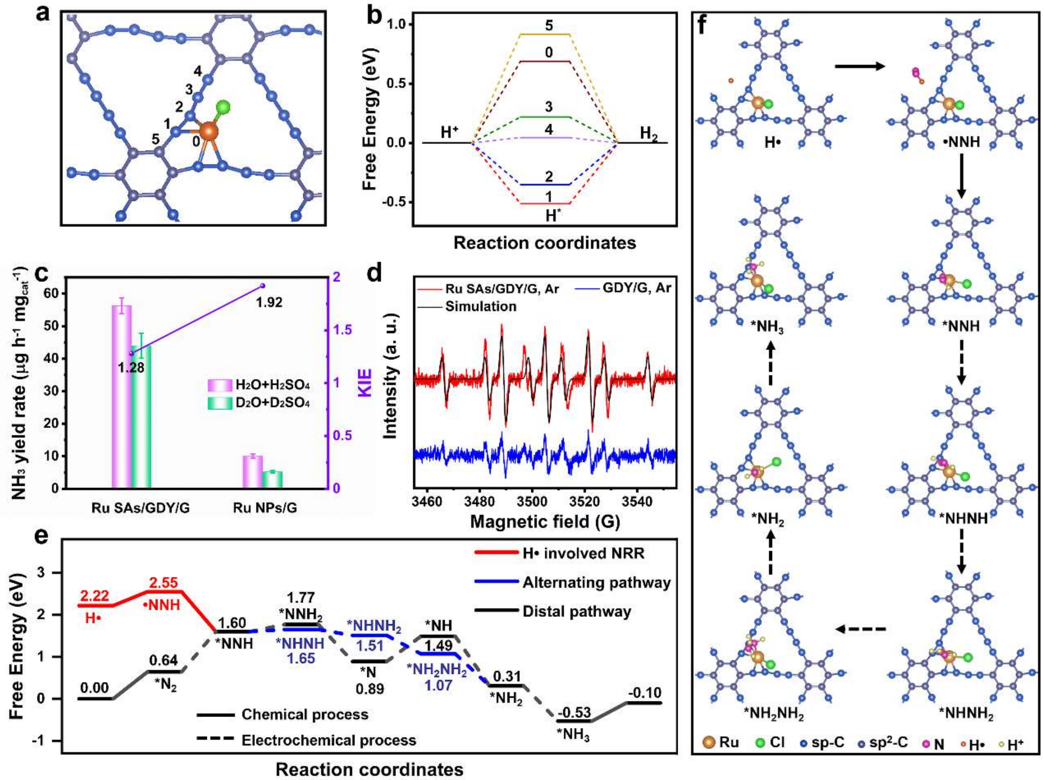


Fig. 5. Insights into the mechanism of NRR on Ru SAs/GDY/G. a The structure of Ru SAs/GDY/G. **b** Free energy diagram of the intermediates generated during HER over the Ru SAs/GDY/G at different active sites annotated in Fig. 5a. **c** KIE of H/D and NH_3 yield rate over Ru SAs/GDY/G and Ru NPs/G at -0.1 V**. d** EPR spectra of the solutions obtained after 10 min NRR tests by Ru SAs/GDY/G and GDY/G under Ar. **e** Free energy diagrams of NRR on Ru SAs/GDY/G. **f** The structure of the intermediates for the H• involved NRR process.

Conclusions

Our finding demonstrates that Ru SAs/GDY/G is an efficient electrocatalyst for NRR, showing an exceptionally high NH_3 yield rate of 56.8 μg h^{-1} $mg_{cat.}^{-1}$ (4.7 mg h^{-1} mg_{Ru}^{-1}) and FE of 37.6% at -0.1 V. The experiments and DFT calculations suggest that the Ru single atoms function as active sites for hydrogenation process of NRR. The GDY not only inhibits H covering on Ru single atoms, but also produces H• to accelerate the kinetics of hydrogenation process. To our knowledge, the H•-transferring mechanism is a wholly new observation in NRR. Our designed catalysts are conceptually similar, opening new possibilities for the design of highly selective and active electrocatalysts for electrocatalytic hydrogenation reactions.

ASSOCIATED CONTENT

Supporting Information

Experimental section, construction of models and computation details, structural characterization, photograph of setup for NRR measurement, additional electrochemical results and performance comparison.

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Notes

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