Altering the rate-determining step over cobalt single clusters leading to highly efficient ammonia synthesis

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ABSTRACT

Activation of high-energy triple-bonds of N₂ is the most significant bottleneck of ammonia synthesis under ambient conditions. Here, by importing cobalt single clusters as strong electron-donating promoter into the catalyst, the rate-determining step of ammonia synthesis is altered to the subsequent proton addition so that the barrier of N₂ dissociation can be successfully overcome. As revealed by density functional theory calculations, the N₂ dissociation becomes exothermic over the cobalt single cluster upon the strong electron backdonation from metal to the N₂ antibonding orbitals. The energy barrier of the positively shifted rate-determining step is also greatly reduced. At the same time, advanced sampling molecular dynamics simulations indicate a barrier-less process of the N₂ approaching the active sites that greatly facilitates the mass transfer. With suitable thermodynamic and dynamic property, a high ammonia yield rate of 76.2 μg h⁻¹ mg⁻¹ cat and superior Faradaic efficiency of 52.9% were simultaneously achieved.

Keywords: nitrogen reduction reaction, rate-determining step, cobalt single cluster, mass transfer, molecular dynamics simulations

INTRODUCTION

Ammonia (NH₃) is widely considered as a critical chemical whether in agriculture or transportation [1,2], since it is the main ingredient for fertilizer production and a carbon-free energy storage intermediate with high-energy density [3]. Although an infinite nitrogen (N₂) source from the atmosphere can be easily obtained, large scale ammonia production is hindered by the chemical stability of the N≡N bond (bond energy: 940.95 kJ mol⁻¹) [4,5]. To date, the traditional Haber-Bosch process using transition metal as catalyst under drastic reaction conditions still dominates the industrial market of NH₃ synthesis [6–8]. However, this typical strategy can only reach a relatively low conversion ratio (~15%) and consumes nearly 5% of the world’s natural gas [9,10]. The use of fossil fuels, at the same time, accounts for large quantities of CO₂ generation into the atmosphere [11]. Therefore, a clean and sustainable strategy for NH₃ production is urgently demanded for both the global population and energy.

The electrocatalytic N₂ reduction reaction (NRR), using protons from water as the hydrogen source and powered by renewable electricity sources, is an alternative method to achieving N₂ fixation under ambient conditions [12–16]. Theoretically, common mechanisms of the NRR start with N₂ chemisorption on the catalyst’s surface, followed by the cleavage of N≡N bond and consecutive proton addition to form NH₃ [17]. Yet, strong bonding energy, high ionization potential, broad HOMO-LUMO gap as well as poor electron affinity of N₂ do not favor any electron transfer process, and the N₂ activation process is thus commonly considered as the rate-determining step [18,19]. A catalyst which features active sites with suitable energy and symmetry of orbitals is able to bind with N₂ molecules through accepting electron density from, and backdonating to, N₂ [20]. The backdonation, known as the π backbonding, strengthens the catalyst–nitrogen bond, weakens the N≡N bond, and thus contributes to lowering the energy barrier of N₂ activation and positively shifting the rate-determining step [19]. This process could be enhanced by strong electron-donating ability, which enables the smooth electron transfer from the active site to the N₂ antibonding π-orbitals,
termed the electronic promoting effect [21–23], and further benefits the eventual N₂ dissociation. Unfortunately, only very few catalysts reported to date can efficiently reduce the nitrogen activation barrier, leaving the ammonia production rate and Faradaic efficiency in low level [23–25]. Hence, searching for highly active catalysts that could alter the rate-determining step of electrochemical ammonia synthesis is still a challenging goal.

Herein, we successfully demonstrate that deliberately introducing cobalt single clusters as electron-donating promoter in nitrogen-doped carbon alters the rate-determining step of ammonia synthesis from N₂ cleavage to proton addition (Fig. 1a). An excellent ammonia yield rate (76.2 μg h⁻¹ mg⁻¹ cat.) and a superior Faradaic efficiency (52.9%) were simultaneously obtained under ambient conditions. Isotopic labeling experiments and control experiments are combined to confirm that all the NH₃ produced is from the N₂ electrochemical reduction. Also, the catalyst is steady enough to suffer consecutive electrolysis recycle with negligible attenuation in the NRR activity and selectivity. Density functional theory (DFT) calculations reveal that N₂ activation is transferred into a strong thermodynamically exothermic process on cobalt single clusters, so that it is no longer the rate-determining step of ammonia synthesis. Instead, only small energy barriers exist upon NHₓ formation in the whole nitrogen fixation process. Also, the approaching process of N₂ molecules towards the single cluster sites is confirmed to be barrier-less by molecular dynamics (MD) simulations, which greatly favor the whole nitrogen reduction process. Altering the rate-determining step of nitrogen reduction effectively leads to a desirable NRR performance, and thus provides a powerful guidance for future design of catalysts.

RESULTS AND DISCUSSION

Characterization of the CoSC-N-C catalyst

The cobalt single clusters dispersed in nitrogen-doped carbon (CoSC-N-C) were fabricated and carefully characterized. The transmission electron microscopy (TEM) image (Supplementary Fig. 1) and dark-field TEM image (Fig. 1b) of CoSC-N-C clearly show highly dispersed cobalt single clusters in the catalyst, with corresponding element

Figure 1. (a) Schematic illustration for the mechanism of enhanced NRR activity by introducing Co single cluster in nitrogen-doped carbon. The cyan, red, purple and gray spheres represent C, N, Co and H atoms, respectively. (b) Dark-field TEM image of CoSC-N-C showing highly dispersed Co single clusters in the material and (c) corresponding element maps showing the distribution of Co (blue), N (orange) and C (red). (d) Co K-edge X-ray absorption near-edge structure (XANES) and (e) Fourier-transformed (FT) k³-weighted extended X-ray absorption fine structure (EXAFS) spectra of CoSC-N-C, CoNP-N-C and Co foil.
Co-Co coordination is detected in CoNP-N-C, so Co-Co, respectively. In great contrast, only a strong interaction with cobalt nanoparticles (CoNP-N-C) and without metal (N-C) were also synthesized by replacing the Co2+/Zn2+ mixture with single Co2+ and Zn2+, respectively, under otherwise identical conditions (Supplementary Figs 3 and 4). As shown in the X-ray powder diffraction (XRD) patterns (Supplementary Fig. 5), CoNP-N-C exhibits distinct metallic cobalt diffraction, whereas the cobalt single clusters in CoSC-N-C exist as amorphous phase. The increased content of Co accounts for the improved graphitization degree, as evaluated by the Raman spectra (Supplementary Fig. 6).

To confirm the chemical state of Co species in different samples, X-ray absorption fine structure (XAFS) measurements were conducted with Co foil as reference. The Co K-edge X-ray absorption near-edge structure (XANES) shows that the absorption edge of CoSC-N-C exhibits a positive shift compared with that of Co foil, reflecting that the average valence state of Co atoms is at positive level and is higher than that in CoNP-N-C (Fig. 1d). The Fourier-transformed (FT) k3-weighted extended X-ray absorption fine structure (EXAFS) spectrum of the CoSC-N-C (Fig. 1e) shows two main peaks at about 1.5 Å and 2.2 Å, attributing to Co-N and Co-Co, respectively. In great contrast, only a strong Co-Co coordination is detected in CoNP-N-C, so that the C atoms are present as nanoparticles in the carbon framework. The surface chemistry of different samples was further investigated by X-ray photoelectron spectroscopy (XPS, Supplementary Fig. 7). The coexistence of four different N species in different samples, namely pyridinic-N, pyrrolic-N, graphitic-N and N-oxides, was confirmed by the high-resolution N 1s spectra (Supplementary Fig. 8) [26,27]. The high-resolution Co 2p spectra (Supplementary Fig. 9) show higher valence states of Co in CoSC-N-C compared with CoNP-N-C [28,29], indicating the coordination of cobalt and nitrogen, which is in accordance with the XAFS responses. The XPS results and the XAFS responses are combined to confirm the existence of nitrogen-stabilized cobalt single clusters in CoSC-N-C. In addition, CoSC-N-C possesses a large surface area of 287.1 m² g⁻¹, as determined by the Brunauer-Emmett-Teller (BET) method (Supplementary Fig. 10).

**Electroreduction of N₂ to NH₃ on the CoSC-N-C catalyst**

To evaluate the NRR activity of different samples, linear sweep voltammetry (LSV) curves were first measured (Supplementary Fig. 11). The current density difference between Ar and N2 clearly affirms the contribution from the nitrogen reduction. Without cobalt sites, N-C exhibits the weakest NRR and hydrogen evolution reaction (HER) activity. While, compared with CoNP-N-C, the bigger current density gap between Ar and N2 and lower HER current density of CoSC-N-C indicate that the introduction of cobalt single clusters leads to much more improved NRR activity and selectivity than those of the cobalt nanoparticles. Then, a quantified study of the NRR ability for different samples was carried out via chronoamperometry measurement using an H-shape electrochemical cell [30]. Here, the most rigorous experimental protocol was followed for reliable proof of the NRR performance [31]. The nitrogen gas was sufficiently purified before use to avoid the possible existence of NH3 and NOx. Possible reduction products including NH3 and N2H4 were both tested (Supplementary Figs 12–15), whereas only NH3 was detected in this work (Supplementary Fig. 16). Before the NRR test, several control experiments were first carried out to ensure that no contamination was present in the feeding gas or the equipment, and the carbon paper (CP) as current collector of the cathode did not have NRR activity, so that NH3 could only be produced by N2 reduction in the presence of cobalt sites. Detailed comparison of the NH3 yield rates and corresponding Faradaic efficiencies of CoSC-N-C, CoNP-N-C and N-C under various applied potentials is displayed in Fig. 2b and c. Clearly, pristine N-C exhibits only negligible NRR performance. After incorporating cobalt single clusters, the CoSC-N-C, with an optimized loading of 0.5 mg cm⁻² (Supplementary Fig. 17), exhibits the highest NH3 yield rate of 76.2 μg h⁻¹ mg⁻¹ at −0.2 V versus reversible hydrogen electrode (vs. RHE), far exceeding the peak value of CoNP-N-C (22.5 μg h⁻¹ mg⁻¹) realized at an even more negative potential (−0.3 V vs. RHE). Notably, the maximal NRR Faradaic efficiency of CoSC-N-C is also obtained at −0.2 V vs. RHE (52.9%), which is more than one order of magnitude higher than the counterparts. Detailed chronoamperometry responses are shown in Supplementary Fig. 18. Also, the electrochemical active surface area (EASA) of each sample was determined by double-layer...
capacitance ($C_{dl}$, Supplementary Fig. 19). Expectedly, the surface-area-normalized ammonia production rate of CoSC-N-C shows an obvious advantage over other samples (Supplementary Fig. 20). The NRR activity and selectivity of CoSC-N-C remarkably stands at the top level of reported catalysts under mild conditions (Supplementary Table 1), and is thus of great significance in energy utilization. Based on the nitrogen temperature-programmed desorption ($N_2$-TPD) spectra (Supplementary Fig. 21), CoSC-N-C exhibits the strongest $N_2$ adsorption ability, confirming that cobalt single clusters are superior nitrogen-adsorption active sites compared with cobalt nanoparticles or nitrogen-doped carbon [32]. The gradual decrease of the NRR Faradaic efficiency of CoSC-N-C as the applied potential becomes more negative than $-0.2$ V vs. RHE is mainly due to the increased HER [33], as evaluated by the gas chromatography (GC) responses (Fig. 2d and Supplementary Fig. 22). In terms of selectivity, CoSC-N-C shows a much smaller proportion of the competing HER compared with CoNP-N-C and N-C, and is more inclined to proceed NRR (Supplementary Fig. 23). Based on the above results, CoSC-N-C has a prominent advantage in nitrogen reduction, especially at $-0.2$ V vs. RHE (Fig. 2e and Supplementary Table 2).

Careful examination of the N source for produced NH$_3$ is helpful in getting an in-depth understanding of the catalyzing mechanism. Thus, isotope-labeling experiments were systematically conducted [34–37]. The $^{15}N_2$ gas was also sufficiently purified before use. As shown in the ultraviolet-visible (UV–vis) absorption spectra (Fig. 3a), no NH$_3$ can be detected when $^{15}N_2$ is fed unless an electrocatalytic potential was applied to the CoSC-N-C working electrode. Then, the produced NH$_3$ was distinguished using $^1$H nuclear magnetic resonance ($^1$H NMR) spectra (Fig. 3b). After a continuous electrolysis under $-0.2$ V vs. RHE using $^{15}N_2$ as feeding gas, only a doublet signal ($\sim73$ Hz) representing $^{15}NH_4^+$ is detected in the spectrum instead of the triplet signal ($\sim52$ Hz) of $^{14}NH_4^+$. When Ar was used for electrolysis, no NH$_3$ signal was detected in the NMR spectrum, indicating the obtained ammonia is totally from the $N_2$ electroreduction process. For accuracy of the performance data, NMR method was also employed for ammonia quantification (Fig. 3c and Supplementary Fig. 24). The NH$_3$ yield rate and Faradaic efficiency obtained by quantitative $^1$H NMR and colorimetric method using both $^{14}N_2$ and $^{15}N_2$ exhibit good consistency (Fig. 3d), thus demonstrating the reliability of the experimental results.
Figure 3. (a) The UV-vis absorption spectra of the electrolytes after electrolysis using $^{15}$N$_2$ as feeding gas under different conditions. (b) $^1$H nuclear magnetic resonance (NMR) spectra of both $^{14}$NH$_4^+$ and $^{15}$NH$_4^+$ produced from the NRR using $^{14}$N$_2$ and $^{15}$N$_2$ as feeding gas, respectively. (c) $^1$H NMR spectra of the NRR product at $0.2$ V vs. RHE using NMR quantification method. (d) Comparison of NH$_3$ yield rate and Faradaic efficiency for NRR at $0.2$ V vs. RHE using different quantification methods. The error bars correspond to the standard deviations of the obtained data over three separately conducted electrochemical measurements under the same conditions.

Stability is another vital parameter for an electrocatalyst. Thus, the durability of Co$_{SC}$-N-C was consecutively tested by electrolyzing at a constant potential of $0.2$ V vs. RHE for 10 cycles. The Co$_{SC}$-N-C catalyst can keep the superior Faradaic efficiency of NH$_3$ production unchanged even after 10 cycles of continuous electrolysis (Supplementary Fig. 25), manifesting its broad prospect for practical applications. Simultaneously, TEM image, corresponding element maps and Raman spectra (Supplementary Figs 26 and 27) exhibit no variation in the morphology and structural properties of Co$_{SC}$-N-C after the NRR process. Its chemical state is also well maintained as confirmed by the high-resolution XPS spectra analyses (Supplementary Fig. 28), demonstrating that the Co$_{SC}$-N-C is robust enough for long-term NRR electrocatalysis.

Computational studies

Computational studies on both thermodynamics and dynamics were carried out to investigate the mechanism of ammonia synthesis over the Co$_{SC}$-N-C catalyst. The thermodynamic process of different models was first studied by DFT calculations. As confirmed by catalyst characterizations, the cobalt in Co$_{SC}$-N-C mainly exists as single clusters. Accordingly, several possible models of cobalt single cluster with different numbers of cobalt atoms on nitrogen-doped carbon (Co$_x$N$_4$-C, $x = 2$ to 6) were systematically proposed, and pure nitrogen-doped carbon (N$_4$-C) was also calculated for comparison (Supplementary Fig. 29). For N$_4$-C, the nitrogen adsorption is a strong endothermic process with a step-by-step uphill trend of Gibbs free energy (Supplementary Fig. 30). The introduction of cobalt single clusters is able to turn the nitrogen adsorption into exothermic process without energy barriers, suggesting that the cobalt single clusters are superior nitrogen-adsorption active sites. Notably, all of the structures with cobalt single clusters are able to alter the rate-determining step to the subsequent nitrogen hydrogenation with relatively small energy barriers (Supplementary Figs 31 and 32). Taking Co$_4$-N$_4$-C for example, as clearly shown in Fig. 4a, starting from a favored side-on mode N$_2$ adsorption, the preferred NRR approach of Co$_4$-N$_4$-C is verified to be the associative alternating pathway instead of the associative distal pathway (Supplementary Fig. 33a). When chemically adsorbed on Co cluster, N$_2$ is spontaneously activated and experiences a significant weakening of the N≡N bond due to the strong electron backdonation from the metal to the N$_2$ antibonding orbitals, and the N$_2$ dissociation becomes an exothermic process over the cobalt single cluster. In addition, the energy released from the N$_2$ adsorption step greatly benefits the following N$_2$ cleavage, according to the ‘hot atom’ mechanism [19,38]. Thus, the rate-determining step has been successfully shifted from the usual N$_2$ activation to the subsequent hydrogenation with only a small energy barrier of 0.85 eV. In great contrast, without the Co single cluster, the N$_4$-C model not only suffers a severely endothermic N$_2$ adsorption process, but also possesses high NRR rate-limiting barriers of 2.04 eV and 1.84 eV for the alternating and distal pathways, respectively, indicating a weak activity towards NRR (Fig. 4b and Supplementary Fig. 33b). On the other hand, N$_2$ has priority in the adsorption competition with $^1$H on Co$_4$-N$_4$-C. As shown in Fig. 5a and b, the N$_2$ chemisorption on Co$_4$-N$_4$-C is strongly exothermic ($-0.82$ eV) with a step-by-step downhill trend of the Gibbs free energy, whereas the H chemisorption suffers an extremely high energy barrier of 2.53 eV due to the water dissociation process. Even if $^1$H is adsorbed, its desorption to form H$_2$ is still an endothermic reaction (Supplementary Fig. 34), which is also beneficial to promoting the NRR Faradaic efficiency.

From a dynamic point of view, the N$_2$ approaching process towards Co$_4$-N$_4$-C was then explored.
Figure 4. Free energy diagram and models represent the corresponding adsorbates on (a) Co₄-N₄/C and (b) N₄/C through the associative alternating pathway. The cyan, red, purple and gray spheres represent C, N, Co and H atoms, respectively.

The system was set up by randomly placing 6 K⁺, 6 OH⁻ and 3000 water molecules in the simulation box, with a Co₄-N₄/C model fixed perpendicular to the z-axis at the center of the simulation system. The N₂ molecule initially located at 1.5 nm above the geometric center of the upper three Co atoms. Then, the N₂ molecule was pulled towards the Co₄-N₄/C along the z-axis at a rate of 0.01 nm ps⁻¹ under a harmonic force constant to generate configurations for umbrella-sampling (Fig. 5c). The potential of the mean force (PMF) as a function of distance and the corresponding snapshots (Fig. 5d and Supplementary Fig. 35) illustrate that the approaching process of N₂ molecule is nearly barrierless with only a small energy hill at approximately 0.52 nm. This clearly indicates that the cobalt single cluster as active site is accessible to the N₂ molecule, which can greatly promote the following N₂ chemisorption, and is thus contributory to the entire NRR process. The above computational conclusions well explain the experimental results, and further highlight the contribution of the cobalt single cluster as an important promoter for ambient N₂ fixation.

CONCLUSION

In summary, we have successfully altered the rate-determining step of ambient NH₃ synthesis by deliberate introduction of cobalt single clusters as electron-donating promoter in nitrogen-doped carbon, and achieved outstanding ammonia yield rate of 76.2 μg h⁻¹ mg⁻¹ and superior Faradaic efficiency of 52.9%. The Co₄C-N-C is steady enough for long-term NRR electrocatalysis with negligible decay of the amazingly high Faradaic efficiency through consecutive electrolysis recycle. The ¹⁵N isotopic labeling experiments and control experiments are combined to confirm that the N source of N₂-to-NH₃ conversion is completely from the feeding gas instead of any activated N species in the catalyst. First-principles simulations demonstrate a strong exothermic process of N₂ chemisorption on the cobalt...
single cluster site, which greatly promotes the following $\text{N}_2$ dissociation. The $\text{N}_2$ activation, therefore, becomes exothermic, and the rate-determining step has been successfully altered to the subsequent nitrogen hydrogenation. A smooth $\text{N}_2$ approaching process with almost no energy hill towards the catalyst paves the way for the $\text{N}_2$ mass transfer, as confirmed by the MD simulations. Our work overcomes the obstacle of ambient ammonia synthesis, and contributes to the guiding of future catalyst design for sustainable NRR systems.

**SUPPLEMENTARY DATA**

Supplementary data are available at NSR online.

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**AUTHOR CONTRIBUTIONS**

T.Q. conceived and designed this work. C.Y. supervised the project. S.L. prepared materials and performed the material characterizations and electrochemical measurements. S.L. and M.W. participated in analyzing the experimental results. H.J. conducted the theoretical calculations. X.S. offered help in the material characterizations. S.L. wrote this paper with feedback from the other...
authors. All authors discussed the results and commented on the manuscript.

Conflict of interest statement. None declared.

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