Article type: RESEARCH ARTICLE

Graphdiyne based metal atomic catalysts for synthesizing ammonia

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ABSTRACT

Exploring new catalysts for nitrogen reduction at ambient pressures and temperatures with ultrahigh ammonia (NH₃) yield and selectivity is still a giant challenge. In this work, atomic catalysts with separated Pd atoms on graphdiyne (Pd-GDY) have been synthesized and show fascinating electrocatalytic properties for nitrogen reduction. Outstandingly, the catalyst shows the highest average NH₃ yield of 4.45 ± 0.30 mg NH₃ mg⁻¹ Pd⁻¹ h⁻¹, almost tens of orders larger than previously reported ones, and 100% reaction selectivity in neutral media. And Pd-GDY exhibits almost no decreases in the NH₃ yield and Faradaic efficiency. Density functional theory calculations show that the reaction pathway prefers to perform at the (Pd, C1, C2) active area due to the strongly coupled (Pd, C1, C2) which elevates the selectivity via enhanced electron-transfer. By adjusting the p-d coupling accurately, the reduction of self-activated nitrogen is promoted by anchoring atom selection, and the side effects are minimized.

Keywords: graphdiyne, atomic catalyst, two dimensional carbon material, ammonia, nitrogen reduction reaction
INTRODUCTION

Ammonia (NH$_3$), an indispensable raw material in industrial production, has always occupied an important position in basic chemical industry, and is also an important source of chemical fertilizer in agricultural production [1–3]. Unfortunately, traditional production of NH$_3$ must operate at high pressures and temperatures, which is very energy consuming. Electrochemical catalytic nitrogen reduction reaction (ECNRR) in aqueous electrolytes at ambient conditions provides an idea method for clean and efficient conversion of N$_2$ to energy-rich NH$_3$ [4–7]. However, up to now, there are still some key scientific and technical issues to be solved, and the NH$_3$ yield (Y$_{NH3}$) and Faradic Efficiency (FE) are still very low. In order to solve these major issues perfectly and promoting the efficient conversion of N$_2$ to NH$_3$, efficient catalysts that can drive ECNRR at low overpotential with high selectivity, Y$_{NH3}$, FE, and stability are in great demand.

Electrocatalysts comprising of singly-dispersed metal atoms and supporting materials have shown high catalytic activity and selectivity in various reactions, because of the atomically distributed active sites [8–21]. Although the rapid development of single-atom catalysts brings many new science, new knowledge and new concepts to the development of catalytic science, there are still some important scientific issues to be solved in this field, such as the precise structure of the support materials, the valence of the supported metal atoms and the structure, the high dispersion distribution of the metal single atoms and so on, are key issues and challenges to be addressed in this field. For a better understanding of the issues, very recently, Li and coworkers reported the first zero-valent atomic catalysts (AC) [20,21], an important finding is that zero-valent metal atoms can be anchored on graphdiyne surfaces and have drawn great attention [22–31]. The AC exhibits high stability and catalytic activity and represents the emergence of a new generation of catalysts. The emergence of the new concept catalysts provides new inspiration for
understanding the mechanism, reaction process and properties of atomic catalysis. In this study, we demonstrate that highly selective and active NH$_3$ production can be achieved by using a zero-valence atom catalyst based on graphdiyne, Pd-GDY, to activate the N$_2$ and react with water at room temperatures and pressures. Experimental and theoretical results solidly confirm the unique chemical structure and electronic structure and zero-valence state of this electrocatalysts. The strong orbital interactions between Pd atoms and neighboring C sites leads to a strong electronegative reduction character for ECNRR. The downshifted s-band from the electronic structure arises from the elimination non-bonding lone-pair N2-2s orbitals through N-hydrogenation to suppress HER electronically. The designed Pd-GDY AC presents significantly improved ECNRR performances compared with reported ones. This study might provide a promising strategy for designing and synthesizing highly efficient electrocatalysts for producing NH$_3$ at room temperature and ambient pressures.

RESULTS AND DISCUSSION

Pd-GDY was synthesized through a self-reduction strategy. Fig. 1 shows the synthesis and reusability schematic of Pd-GDY for the electrochemical nitrogen reduction reaction. As can be seen from the scanning electron microscopy (SEM) images (Supplementary Fig. S1, available as Supplementary Data at NSR online), graphdiyne fibers with porous surface interweave in a three-dimensional manner forming three-dimensional flexible electrodes.
**Figure 1.** Schematic of the synthesis (central green circle) and resuability of the Pd-GDY electrocatalyst for the ammonia production.

SEM (Fig. 2a and Supplementary Fig. S2, available as Supplementary Data at NSR online), high-resolution transmission electron microscopy (HRTEM) (Fig. 2b and Supplementary Fig. S3, available as Supplementary Data at NSR online), scanning transmission electron microscopy (STEM, Fig. 2c) and high-angle annular dark-field (HAADF) STEM (Figs. 2d-g and Supplementary Fig. S4, available as Supplementary Data at NSR online) images show that no Pd particles or clusters can be observed. Energy-dispersive X-ray spectroscopy mapping results (Fig. 2c) reveal the uniform distribution of Pd and C atoms in the sample. In HAADF images, the bright dots gave an average size of 0.36 ± 0.01 nm (Supplementary Fig. S5, available as Supplementary Data at NSR online), confirming that each dot is an individual Pd atom. The possible anchoring sites of Pd atoms
on GDY (Supplementary Fig. S6, available as Supplementary Data at NSR online), as revealed by our detailed computational calculations, in which the all the possible placements of the Pd on GDY have been fully examined. The anchoring site is determined based on the formation energies comparison between different anchoring sites. Notably, the lowest formation energy of the anchoring site of -0.99 eV as the presented position will be the undoubtfully optimal placement for Pd on GDY. Inductively coupled plasma optical emission spectroscopy (ICP-OES) measurements showed an average mass loading of 1.02 ± 0.04 wt.%.

**Figs. 2h and 2i** show the X-ray absorption near-edge structure (XANES) profiles for Pd-GDY along with corresponding reference samples (Pd foil and PdO). For the Pd K-edge spectrum, the absorption threshold position of Pd-GDY located at the same position to Pd metal and more negative position than the PdO (Fig. 2h). In addition, the first derivative XANES for Pd-GDY is similar to that of metallic Pd (Fig. 2i). These results strongly indicate that the valence states for the Pd atoms in Pd-GDY metals are zero. The extended x-ray absorption fine structure (EXAFS) spectrometry results (Supplementary Fig. S7, available as Supplementary Data at NSR online) showed that there was only one peak appeared around 1.5 to 2 Å arising from the Pd-C contribution, and no peak contributed to the Pd-Pd (around 2~3 Å) could be observed. These demonstrate that the Pd atoms individually anchored on GDY and exhibited zero-valence state (Supplementary Fig. S8, available as Supplementary Data at NSR online).

We used X-ray photoelectron spectroscopy (XPS) and Raman spectrum to characterize the chemical composition and quality of as-synthesized samples. The XPS survey spectra shows the only existence of carbon (Supplementary Fig. S9, available as Supplementary Data at NSR online), except for oxygen signal from the adsorption of air. The C 1s XPS spectrum of Pd-GDY can be divided into sp²-C (284.5 eV), sp-C (285.1 eV), C=O (288.3 eV), COO (286.7 eV), and π-π transition (291.2 eV) peaks (Supplementary Fig. S10a, available as Supplementary Data at NSR online). Compared with pure GDY
(Supplementary Fig. S10b, available as Supplementary Data at NSR online), a newly-formed peak at 291.2 eV was observed, which can be attributed to the electronic transitions induced by the anchoring of Pd atoms. The ratio of intensity of sp\(^2\)/sp-carbon is 0.5, revealing the integrity of GDY structure in Pd-GDY. As shown in Supplementary Fig. S11 (available as Supplementary Data at NSR online), the Pd-GDY shows the lower valence band (VB) with a smaller energy at 1.73 eV than that of pure GDY (2.26 eV), indicating the enhanced conductivity of Pd-GDY. Raman spectra provide information on the structural changes of carbon materials. The intensity of the D and G bands of GDY and Pd-GDY changed (Supplementary Fig. S12, available as Supplementary Data at NSR online). The D band to G band intensity ratio increased from 0.73 (GDY) to 0.82 (Pd-GDY), which suggests the presence of more defective sites in Pd-GDY, indicating the formation of more active sites, which have been demonstrated to be helpful for improving catalytic activity [32,33].
Figure 2. (a) SEM, (b) HRTEM, (c) elemental mapping, and (d,f) HADDF-STEM images of Pd-GDY. (e,g) Enlarged images of the red square areas in image (d) and (f), respectively. (h) The experimental K-edge XANES spectra (inset: magnified image) and (i) the first derivative curves of Pd-GDY, Pd foil and PdO.

Based on the above inspiring findings, the ECNRR experiments were carried out in 0.1 M Na$_2$SO$_4$ (pH 7) aqueous solution at room temperature and atmospheric pressure by using a H-type electrolytic cell separated by the Nafion 117 membrane (Supplementary Fig. S13, available as Supplementary Data at NSR online). The catalyst loading of Pd-GDY is 2.7 μg$_{\text{metal}}$ cm$^{-2}$, and the geometric area is 2.0 cm$^2$, respectively. The NH$_3$ was determined using
an indophenol blue method [34] and the calibration curves with reliable sensitivity and good linear relationship were obtained (Supplementary Fig. S14, available as Supplementary Data at NSR online). The ECNRR of Pd-GDY starts at around 0.2 V versus RHE in N₂-saturated 0.1 M Na₂SO₄ solution (Supplementary Fig. S15, available as Supplementary Data at NSR online). Only NH₃ (no by-product of N₂H₄) can be detected in this work (Supplementary Figs. S16 and S17, available as Supplementary Data at NSR online), revealing the ultra-high selectivity of Pd-GDY in the ECNRR process. The NH₃ yielding rate (Y_{NH₃}) and the Faradic efficiency (FE) raise with the increasing of cathodic potential until -0.16 V versus RHE (Figs. 3a and 3b), at which the highest Y_{NH₃} of 4.45 ± 0.30 mg_{NH₃} mg_{Pd}^{-1} h^{-1} (1.97 ± 0.13×10^{-10} mol cm⁻² s⁻¹, normalized by geometric surface area) and FE up to 31.62 ± 1.06% were achieved (Supplementary Table S1, available as Supplementary Data at NSR online). These values are larger than all reported ECNRR catalysts worked under ambient conditions including Au/TiO₂ (Y_{NH₃} = 21.4 μg_{NH₃} mg_{cat.}⁻¹ h⁻¹, FE = 8.11%) [6], THH Au NRs (Y_{NH₃} = 2.69×10⁻¹¹ mol cm⁻² s⁻¹, FE = 4.02%) [35], Bi₄V₂O₁₁/CeO₂ (Y_{NH₃} = 23.21 μg_{NH₃} mg_{cat.}⁻¹ h⁻¹, FE = 10.16%) [36], Ru SAs/N-C (Y_{NH₃} = 120 μg_{NH₃} mg_{cat.}⁻¹ h⁻¹, FE = 29.6%) [37], and Ru NC (Y_{NH₃} = 3.6 mg_{NH₃} mg_{cat.}⁻¹ h⁻¹, FE = 21%) [38], and Pd-based ECNRR catalysts such as Pd/C (Y_{NH₃} = 4.9 μg_{NH₃} mg_{cat.}⁻¹ h⁻¹, FE = 8.2%) [39], Pd₀.₂Cu₀.₈/rGO (Y_{NH₃}=2.8 μg_{NH₃} mg_{cat.}⁻¹ h⁻¹, FE = 4.5%) [40], Pd₃Cu₁ alloy (Y_{NH₃}=39.9 μg_{NH₃} mg_{cat.}⁻¹ h⁻¹, FE = 1.22%) [41], and even compared favourable to those worked at higher temperatures/pressures (Fig. 3c; Supplementary Tables S2 and S3, available as Supplementary Data at NSR online) [42]. With the further increasing of the negative potentials, the Y_{NH₃} and FE decreased sharply, which can be attributed to the competition between ECNRR and HER [21,43]. Control experiments were performed to determine the origin of the detected NH₃. The pristine GDY yielded limited NH₃ (Y_{NH₃}: 5.44×10⁻¹² mol cm⁻² s⁻¹; FE: 1.65%; Supplementary Figs. S17a and 7b, available as Supplementary Data at NSR online) and CC substrate yielded almost no NH₃ (Supplementary Fig. S17a, available as Supplementary Data at NSR online). No NH₃
can be detected in Ar-saturated electrolyte (Supplementary Fig. S17c, available as Supplementary Data at NSR online) and at the open-circuit potential (Supplementary Fig. S17d, available as Supplementary Data at NSR online). $^{15}$N-labeling experiments were performed using $^{15}$N$_2$ as the feeding gas to confirm the ammonium formed from the reduction of N$_2$. Only $^{15}$NH$_4^+$ (doublet peak) was observed from the $^1$H nuclear magnetic resonance ($^1$H-NMR) results (Fig. 3d). These revealed that all detected NH$_3$ comes from the reduction of N$_2$ molecular by Pd-GDY catalyst. The fact that the Y$_{NH3}$ and FE of Pd-GDY are almost 10 and 3 times larger than that of palladium nanoparticles modified GDY (Pd NP/GDY, Supplementary Fig. S18, available as Supplementary Data at NSR online) demonstrates the superiority of isolated zero-valence Pd atoms than bulk Pd nanoparticles toward efficiently catalysing ECNRR (Fig. 3e). In addition to the excellent catalytic activity and selectivity, long-term stability is another essential criterion for an electrocatalyst in practical application. It was observed that the NH$_3$ yield rate and FE of Pd-GDY exhibited no obvious change after successive six catalytic cycles (Fig. 3f, Supplementary Fig. S19, available as Supplementary Data at NSR online), and the total NH$_3$ yield increased linearly with reaction time (Supplementary Fig. S20, available as Supplementary Data at NSR online). Comprehensive characterizations (Supplementary Fig. S21, available as Supplementary Data at NSR online) on the sample obtained after stability test showed the well preservation of the morphology and structure, revealing its robust nature.
Figure 3. (a) UV-Vis absorption spectra of the 0.1 M Na$_2$SO$_4$ electrolytes after ECNRR at different potentials for 2 h. (b) $Y_{\text{NH}_3}$ and FEs at applied potentials in 0.1 M Na$_2$SO$_4$. Error bars represent calculated standard deviation from independent experiments (at least three times). (c) Comparison of the ECNRR performance of Pd-GDY with others. Error bars represent calculated standard deviation from independent experiments (at least three times). (d) $^1$H-$^{15}$N NMR spectra of 0.1 M Na$_2$SO$_4$ after ECNRR under $^{15}$N$_2$ with Pd-GDY as catalyst. (e) $Y_{\text{NH}_3}$, FEs and corresponding UV-Vis absorption spectra (inset) of Pd-GDY and Pd NP/GDY catalysts after 2 h electrolysis at −0.40 V. (f) Stability test of Pd-GDY at −0.4 V in 0.1 M Na$_2$SO$_4$ under ambient conditions.
Figure 4. (a) UV-Vis absorption spectra of the 0.1 M HCl electrolytes after ECNRR at different potentials for 2 h. (b) $Y_{\text{NH}_3}$ and FE at applied potentials in 0.1 M HCl. (c) $^1\text{H}$-$^{15}\text{N}$ NMR spectra of 0.1 M HCl after ECNRR under $^{15}\text{N}_2$ with Pd-GDY as catalyst. (d) Stability test of Pd-GDY at $-0.26$ V versus RHE under ambient conditions. (e) Measured and fitted impedance data of the samples. (f) Plot of current density versus scan rates of 20, 40, 60, 80, 100 and 120 mV s$^{-1}$, respectively.

Electrolytes are considered to have significant effects on the ECNRR selectivity and activity [39,43–45]. The electrolytes, such as neutral and basic electrolytes, with limited proton transfer rate can effectively improve the ECNRR selectivity. While in the acidic electrolytes, the ECNRR
selectivity would be kinetically limited due to the high proton availability; the rate of the HER increases significantly with the increasing of applied potentials, in which most protons or H$_2$O are converted to H$_2$ rather than NH$_3$, resulting in great decreases in reaction selectivity. Many efforts have recently been devoted to improve the ECNRR performances in acidic electrolytes [37,44,46–48]. However, the Y$_{\text{NH}_3}$ and Faradaic efficiencies of these reported ECNRR electrocatalysts are still very low (Supplementary Tables S2 and S3, available as Supplementary Data at NSR online). Owing to these limitations, it is of significant importance to develop an electrocatalyst with high selectivity and activity in acidic electrolytes for efficient ECNRR.

We then study the ECNRR activity of Pd-GDY in 0.1 M HCl solution (Fig. 4a, Supplementary Fig. S22, available as Supplementary Data at NSR online). The NH$_3$ and N$_2$H$_4$ were determined using spectrophotometry method, and the calibration curves were shown in Supplementary Fig. S23 (available as Supplementary Data at NSR online). Pd-GDY also shows high selectivity toward the formation of NH$_3$ (without N$_2$H$_4$ formation) in acidic media (Supplementary Figs. S22b and S24, available as Supplementary Data at NSR online). As shown in Fig. 4b, the average NH$_3$ yield rate reaches the maximum value of 1.58 ± 0.05 mg$_{\text{NH}_3}$ mg$_{\text{Pd}}$ h$^{-1}$ [(6.99 ± 0.22) × 10$^{-11}$ mol cm$^{-2}$ s$^{-1}$ at −0.26 V versus RHE]. While it achieves the highest FE of 4.32 ± 0.49% at a cathodic potential of −0.06 V versus RHE (Supplementary Tables S1, available as Supplementary Data at NSR online). The $^{15}$N isotope labelling experiments confirmed that the NH$_3$ was formed from the reduction of N$_2$ (Fig. 4c), which indicates that the Pd-GDY is highly selective and active toward ECNRR in acidic media. The FE value keeps decreasing with the applied potentials becomes more negative, which can be attributed to the competition of the HER in acidic media. The rapid increasing of current densities in polarization curves recorded in both N$_2$- and Ar-saturated 0.1 M HCl (Supplementary Fig. S25, available as Supplementary Data at NSR online) also give a supportive evidence for this major interference. Despite all this, the ECNRR activity of
Pd-GDY in acidic conditions still compared favourably to most of reported catalysts (Supplementary Tables S2 and S3, available as Supplementary Data at NSR online) such as MoS$_2$ ($\gamma_{\text{NH}_3}=8.48^{\pm}11$ mol cm$^{-2}$ s$^{-1}$, FE=0.096%). In addition, both $\gamma_{\text{NH}_3}$ and FE of Pd-GDY shows negligible degradation after six consecutive tests, confirming a reliable stability of Pd-GDY in acidic media (Fig. 4d). Electrochemical impedance spectroscopy (EIS) was conducted to offer more insight into the catalytic behaviours. The impedance data was recorded and analysed using R(QR)(QR) equivalent circuit model (Supplementary Table S4, available as Supplementary Data at NSR online). As shown in Fig. 4e, Pd-GDY shows the lowest solution resistance ($R_s$, 10.41 $\Omega$) and charge transfer resistance ($R_{ct}$, 3501 $\Omega$) than GDY ($R_s$, 15.70 $\Omega$; $R_{ct}$, 4658 $\Omega$), CC ($R_s$, 26.5 $\Omega$; $R_{ct}$, 8933 $\Omega$), indicating the more kinetically favourable ECNRR for Pd-GDY than others. Electrochemically active surface area (ECSA) was further estimated by determining the electrochemical double-layer capacitance ($C_{dl}$) through cyclic voltammetry method (Supplementary Fig. S26, available as Supplementary Data at NSR online). The $C_{dl}$ value of Pd-GDY is 2.1 mF cm$^{-2}$ (Fig. 4f), which is larger than that of pure GDY (1.7 mF cm$^{-2}$) and CC (1.3 mF cm$^{-2}$), respectively, implying the increase of the active site number in Pd-GDY catalyst.

**Figure 5.** (a) PDOSs evolutions of site-dependent energetic preference N-fixation on the GDY-Pd system. The energetic preference sequence follows the sequence of blue (strongly
favourable) green, pink and red (unfavourable) shaded area. (b) The variation behaviour of the Pd-4d band centre, Pd-4d band peak position, and N\textsubscript{2}-2p BA splitting with related to the N\textsubscript{2}-adsorption energy. (c) PDOSs of s- and p- bands of all related N-species and adsorbing H among the ECNRR steps. (d) PDOSs of p-orbitals of C0, and C1-C4. The C0 is the C-site of benzene ring and C1-C4 are labelled sequentially following the C0 along the C-chain bonding with Pd. (e) PDOSs of s, p, and d orbitals from Pd-(C1, C2) bonding motifs from GDY-Pd with consideration of different charge populations. (f) The orbital potential energy projections ($U_{\text{out}1}$ and $U_{\text{out}2}$) for Pd-4d within singly anchoring site under the planar and round constant electrode potential distribution.

The origin of the outstanding catalytic activities of the samples were further studied by using the computational calculations (see Methods for details). The bonding and anti-bonding orbitals near the Fermi level ($E_F$) are demonstrated for the case of Pd-GDY, HER, and ECNRR respectively. We find the (Pd, C1, C2) sites are the electron-rich region exhibiting the localized $p$-$d$ coupled electronic orbital. The variation of the real-spatial distribution of charge density distribution indicates the site-to-site charge migration and redistribution between the Pd-GDY and N/H-species (Fig. 5a). The interplay of Pd-4d and N\textsubscript{2}-2p orbitals has been illustrated with the projected partial density of states (PDOSs). We find that the preference of N\textsubscript{2}-adsorption on the Pd-GDY interacting with Pd-4d orbitals indeed follows the farthest $p$-$d$ separation instead of the $p$-$d$ orbital overlapping. This is evidently different from the adsorption preference of O-species. Such anomalous trend implies the on-site effective screening Coulomb repulsion potential is a determining factor existing between Pd-4d\textsuperscript{10} and N\textsubscript{2}-(2s\textsuperscript{2}, 2p\textsuperscript{3}). This arises because the non-bonding lone-pair N\textsubscript{2}-2s-orbitals are highly active participating within ECNRR process for hydrogenation-bonding. The fulfilled Pd-4d\textsuperscript{10} is an electron-rich center for evident site-to-site charge migrations exhibiting substantially strong electronegative activity (ENA). Such strong ENA induces high chemical potential contrast for
favorite directional electron-transfer, which favors electron-transfer from Pd onto N-species for N-hydrogenation rather than HER. We further interpret the underlying electronic mechanism for redirect HER-suppression trend. The $p$-$d$ coupled effective negative correlation energy matters the subtle interplay between on-site Coulomb repulsion and ENA, which overcomes on-site Coulomb repulsion and being energetically favorable to accumulate ENA (Fig. 5a). The Pd-4d band center, Pd-4d band dominant peak, and splitting gap between bonding and anti-bonding (BA) of $N_2$-$2p$-band all exhibit the same trend to monotonically decrease with $N_2$-adsorption energy increased. The deep localized Pd-4d$^{10-1t_{2g}}$ component strongly couples with $N_2$-$2p$ band, resulting in a narrowing of the $N_2$-$2p$ band BA splitting gap (Fig. 5b). We further demonstrate the s- and p- band variations among the N-hydrogenation process. The downshifted s-band arises from the elimination non-bonding lone-pair $N_2$-$2s$ orbitals through N-hydrogenation. The N-hydrogenation performs 0.8 eV more than the H-adsorption on the C-site. Therefore, the original HER performance has been electronically suppressed (Fig. 5c). Considering the contribution of individual C-site within Pd-GDY, both C1 and C2 sites clearly show a strong 2p electronic state at $E_v$-$5.0$ eV as rely-center-like level promoting the electron-transfer between Pd and (C1, C2). The evident bonding and anti-bonding splitting feature at C1-site confirms the strong Pd-C1 interaction is indeed enhanced and further stabilized via charge-transfer (Fig. 5d). The PDOSs of Pd-4d and (C1, C2)-2p orbitals presents a large overlapping extent near the $E_F$ and the two dominant BA orbitals of (C1, C2) coupled the Pd-4d bands. The metallic fcc-Pd$^0$, Pd$^{0-\delta}$, and Pd$^{0+\delta}$ states ($0<\delta<1$) have been compared within the PDOSs. The Pd$^{0-\delta}$ shows 1 eV lower than the fcc-Pd$^0$ while Pd$^{0+\delta}$ stays 1.5 eV higher. This reveals the Pd-GDY preserves Pd$^0$ state and possesses an even higher ENA than the fcc-Pd$^0$, which dominates the strong electronegative reduction character for ECNRR (Fig. 5e). We further reasoned the Pd-4d orbital information under the electrode potential of the planar and round constant potential distributions. Strong orbital interaction between Pd and neighboring C sites induces a close shell effect in way of crossover. The
crossover orbital energy turns to be equivalent point for repulsion and ENA energetic competition, which is staying at 6.55 eV beyond the original energy found from fcc-Pd (2.51 eV). This implies the ENA has been more promoted by the negative correlation to overcome the orbital repulsion (Fig. 5f).

Figure 6. (a) ECNRR energetic pathway on the GDY-Pd. (b) Formation energies of H-adsorption on C-sites of GDY-Pd. (c) H-chemisorption energies on C-sites of GDY-Pd. (d) Structural configuration evolution of ECNRR catalysis process.

We further move onto the energetic preference of ECNRR. Benchmark from different adsorption configuration, the pathway prefers to perform at the (Pd, C1, C2) active area. This is due to the strongly coupled (Pd, C1, C2) elevates the selectivity via enhanced electron-transfer as discussed above. The Pd-site dominated preferable pathway has been considered. The Pd-GDY possesses the potential of $U=-0.37$ V for ECNRR and shows mainly downhill energetic trend. Between these two parts, the Pd-site dominates the optimal N-fixation and the C-sites along the C-chain distribute the H-adsorption. For the $U=-0.37$ V, the overall energy gain is $-3.01$ eV where the NH$_3$-desorption nearly barrier-free of merely 0.03 eV for each NH$_3$. For the $U=0$ V, the path confronts barrier at the asymmetrical N-hydrogenation step until the formation of $*$NH-NH$_2$+3(H$^+$+e$^-$), which starts downhill trend. This hydrogenation
step determines the overall reaction barrier of 0.66 eV. The formation of \( ^*\text{N} = \text{NH} + 5(\text{H}^+ + \text{e}^-) \) also shows an uphill step while a lower barrier of 0.45 eV. Therefore, the asymmetric H-desorption from the (C1, C2) sites controls the barrier acting as potential determining step (PDS) for the ECNRR (Fig. 6a). We compared site-dependent H-adsorption energies. The C1 and C2 sites are confirmed as energetic favorable sites for H-adsorption. Further H-chemisorption energies summarize that both C1 and C2 contribute two optimal active sites for H-adsorption for efficient proton-electron charge exchange (Fig. 6b,c). From pathway analysis, we found the ECNRR prefers parallel hydrogenation (late N-N cleavage) instead of serial hydrogenation (early N-N cleavage). Further local structural configurations of ECNRR process demonstrate the late N-N bond dissociation starts at the step of \( \text{NH}_2 \rightarrow \text{NH}^+ (\text{H}^+ + \text{e}^-) \), which is advantageous for better HER suppression. This shows consistent trend that the intermediate nitrogen-nitrogen bonding (i.e. N=N and N-N) variation ensures the energetic compensation for H-desorption from the local active adsorption sites (Fig. 6d).

CONCLUSIONS

In summary, our experimental and theoretical results strongly support such a zero-valence state of the palladium atom that can be anchored on graphdiyne surfaces. The anchoring site of a zero-valence metal atom was observed directly by XANES, and the position of atomic site in sight is in agreement with the theoretical calculation. The derivative X-ray absorption near-edge structure (XANES) of Pd-GDY is similar to that of metallic Pd which confirms the stable valence state of Pd atoms in sample is zero. The zero-valence Pd atoms separated from graphdiyne show high ECNRR activity and selectivity with highest \( \text{N}_2 \) reduction activity and the average yield of \( \text{NH}_3 \) is \( 4.45 \pm 0.30 \text{ mg}_{\text{NH}_3} \text{ mg}_{\text{Pd}}^{-1} \text{ h}^{-1} \) under environmental conditions. Our work represents a new concept of catalysis, which is of great significance for a deeper understanding of the catalytic process and mechanism of zero-valence atomic catalysts, especially the discovery of highly selective atomic catalysts for the conversion of nitrogen to ammonia at high efficiency.
We note the rapid development of single-atom catalysts in recent years, which has led to the rapid development of catalytic science. Prof. Tao Zhang [8, 9, 11], Prof. Jun Li [11, 49, 50] and Prof. Yadong Li [16, 17, 19] et al. have made many contributions in the basic and applied research of single atom catalysts leading the progress in this field. Our study cleverly utilizes the advantages of the electronic and chemical structures of graphdiyne to successfully anchor transition metal and noble metal zero-valent atoms on graphdiyne, so we call it atomic catalyst. Loading zero-valent metal atoms has been an important challenge in the field of catalysts, especially for anchoring transition metals atoms. The success of loading zero-valent metal atoms on graphdiyne expands the synthesis methodology of single-atom catalysts and enriches the types of functional catalysts. The birth of zero-valent atomic catalysts is of great academic significance for us to clearly understand the anchoring process of single atoms on the support, the new catalytic process and mechanism, the interaction of metal atoms with the support, the energy, electron transfer and conversion in the system, and the relationship between the catalytic performance and the above scientific content. The emergence of zero-valent catalysts is a real insight into the strategies involved in the development of new single-atom catalysts: the following important strategies are the principles of our later design and synthesis of highly efficient catalysts: (i) the design of support is an important basic strategy related to catalyst stability, selectivity and efficiency. (ii) Consider the energy transfer and electron transport between the support and different metal atoms. (iii) Development of systems theory for single-atom and atomic catalysts, and how to use machine learning to screen and functionalized catalysts. (iv) In particular, it is necessary to develop highly conjugated supports to form donor-acceptor (D-A) systems with metal atoms, understand the mode of interaction of metal atoms and supports, and better understand the regular of structure and performance of the system. (v) Consider how to control the amount of charge transfer in a single-atom system to realize the regulation of catalyst activity.
METHODS

Preparation of GDY electrode

GDY electrodes were prepared according to previous studies [20,21,23]. Typically, 50 mL pyridinic solution of hexaethynylbenzene (HEB, 0.4 mg mL⁻¹) was added very slowly into a three-necked flask containing several pieces of copper foil and carbon cloth (CC) at 110 °C. After a 3-day reaction (110 °C, protected from air and light), the CC was washed with hot acetone, DMF, KOH (4 M), HCl (6 M), KOH (4 M) and water, sequentially, followed by drying in 40 °C vacuum oven for 12 hours. The GDY electrodes were obtained.

Preparation of Pd-GDY

A piece of the freshly-prepared GDY electrode was immersed into 35 mL H₂SO₄ aqueous solution containing 12 mg PdCl₂. During this process, the Pd atoms could be spontaneously anchored on GDY surface. After a 4-hour reaction, the samples were washed with 0.5 M H₂SO₄ and water in sequence, and then immediately used for ECNRR.

Characterizations

SEM images were obtained from an S-4800 field emission scanning electron microscope. TEM, HRTEM and EDX mapping data were collected using a JEM-2100F electron microscope operating at 200 kV. (HAADF) STEM measurements were conducted on aberration-corrected cubed FET Titan Cubed Themis G2 300 or JEM-ARM200F (JEOL, Tokyo, Japan) XRD patterns were recorded using a D/max-2500 rotation anode X-ray diffractometer (Rigaku, Japan) with Cu Kα radiation (λ = 1.54178 Å). Raman measurements were performed on a Renishaw-2000 Raman spectrometer (473 nm excitation laser source). And a Thermo Scientific ESCALab 250Xi instrument with monochromatic Al Kα X-ray radiation was used to perform the XPS measurement.

ECNRR measurements
ECNRR measurements were carried out on an electrochemical workstation (CHI 660E) with H-type electrolytic cell, which was separated by the Nafion 117 membrane into two chambers. The freshly-prepared Pd-GDY (or other reference sample) was used as working electrode. The catalyst loading of Pd-GDY catalyst is 2.7 μg\textsubscript{metal} cm\textsuperscript{-2}, and the geometric area is 2 cm\textsuperscript{2}, respectively. The graphite rod and saturated calomel electrode were used as the counter and reference electrodes, respectively. 30 mL N\textsubscript{2}–saturated electrolyte (0.1 M Na\textsubscript{2}SO\textsubscript{4} or 0.1 M HCl) was added into the chambers. N\textsubscript{2} flow was continuously fed into cathodic side with proper position. The comparison of the catalytic activities of Pd-GDY normalized by geometric area and catalyst loading with other recently reported catalysts, respectively. The chronoamperometry tests were performed in ambient condition at different potentials.

SUPPLEMENTARY DATA

Supplementary data are available at NSR online.

ACKNOWLEDGEMENTS

We would like to thank Professor Jun Luo at Tianjin University of Technology for his assistance in the HAADF imaging measurements. We also thank the BL14W1 XAFS beamline at the Shanghai Synchrotron Radiation Facility.

FUNDING

This work was supported by the National Nature Science Foundation of China (21790050, 21790051 and 21771156), the National Key Research and Development Project of China (2016YFA0200104 and 2018YFA0703501), and the Key Program of the Chinese Academy of Sciences (QYZDY-SSW-SLH015) and the Early Career Scheme (ECS) fund (Grant No.: PolyU 253026/16P) from the Research Grant Council (RGC) in Hong Kong.

Conflict of interest statement. The authors declare no conflict of interest
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A novel 3D flexible atomic catalyst with high-density palladium atoms anchored on graphdiyne for highly selective and active conversion of nitrogen to ammonia at ambient conditions is synthesized. The catalyst shows a determined chemical structure, valence state, and a strong electronegative activity, resulting in an outstanding NH$_3$ yield of $4.45 \pm 0.30$ mg$_{\text{NH}_3}$ mg$_{\text{Pd}}^{-1}$ h$^{-1}$ in neutral media.

**Keyword**

graphdiyne, atomic catalyst, two dimensional carbon material, ammonia production

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**Highly Efficient Ammonia Production on Graphdiyne Atomic Catalysts**

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