

A Journal of the Gesellschaft Deutscher Chemiker A Deutscher Chemiker GDCh International Edition www.angewandte.org

Accepted Article

- Title: Ammonia Synthesis Under Ambient Conditions: Selective Electroreduction of Dinitrogen to Ammonia on Black Phosphorus Nanosheets
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This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Angew. Chem. Int. Ed. 10.1002/anie.201813174 Angew. Chem. 10.1002/ange.201813174

Link to VoR: http://dx.doi.org/10.1002/anie.201813174 http://dx.doi.org/10.1002/ange.201813174

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Ammonia Synthesis Under Ambient Conditions: Selective Electroreduction of Dinitrogen to Ammonia on Black Phosphorus Nanosheets

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Abstract: Constructing efficient catalysts for the N₂ reduction reaction (NRR) is a major challenge for artificial nitrogen fixation under ambient conditions. Herein, inspired by the principle of "like dissolves like", we demonstrate that, a member of the nitrogen family, well-exfoliated few-layer black phosphorus nanosheets (FL-BP NSs) can be used as an efficient nonmetallic catalyst for electrochemical nitrogen reduction. The catalyst can achieve a high ammonia yield of 31.37 µg h⁻¹ mg⁻¹_{cat.} under ambient conditions. Density functional theory calculations reveal that the active orbital and electrons of zigzag and diff-zigzag type edges of FL-BP NSs enable selective electrocatalysis of N₂ to NH₃ via an alternating hydrogenation pathway. This work proves the feasibility of using a nonmetallic simple substance as a nitrogen-fixing catalyst and thus opening a new avenue towards the development of more efficient metal-free catalysts.

Ammonia (NH₃) is a basic raw chemical material used in modern industry and agriculture.^[1] At present, the energy-intensive Haber-Bosch process is the main artificial synthesis route for ammonia, and this process uses more than 1 % of global annual energy consumption and produces carbon dioxide emissions.^[2,3] In contrast, electrochemical reduction of nitrogen into ammonia under ambient conditions is a potential strategy for sustainable ammonia production.^[4-6] However, due to the strong dipole moment of the N=N triple bond and the vigorous hydrogen evolution reaction (HER) competing,^[7-11] the development of highly effective catalysts with sufficient activity and selectivity is essential.

According to available experimental and theoretical NRR data, an active center that can easily adsorb nitrogen molecules and sufficiently activate the N=N triple bond is very desirable.^[12-15] To this end, the search for an electrocatalytic NRR center in recent years has mainly focused on transition-metal-based materials.^[8,14-23] Specifically, benefiting from the unoccupied and occupied *d* orbitals of transition metals, the electron density from N₂ is synergically accepted with appropriate energy and symmetry, and then, the transition metal donates electrons to

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the π^* orbital of N=N, strengthening N₂ adsorption and weakening the N=N bond.^[7] It is worthwhile to note that although an unoccupied nonbonding orbital and electron donor site with abundant electron cloud density are prerequisites for a NRR catalyst, the *d* orbital electrons in transition metals also benefit the formation of metal-H bonds, which will exacerbate the competitive hydrogen evolution reaction and limit the nitrogen reduction selectivity and catalytic efficiency.^[24]

Compared to transition metals, the weak hydrogen adsorption of nonmetallic elements and their abundant valence electrons should provide a more ideal nitrogen activation center.^[25,26] Some recent studies have shown that the use of nonmetallic components as active centers may be an effective way to obtain high selectivity.^[27-31] For example, Yu et al. reported a high NH₃ production rate and faradaic efficiency by using boron-doped graphene as a metal-free NRR catalyst under ambient conditions.^[29] Similar nitrogen reduction activity was also observed on metal-free boron carbide nanosheets.^[30] Nevertheless, restricted by the number of effective active sites or doping concentration or poor conductivity, many reported nonmetallic electrocatalysts have not shown their deserved activity for nitrogen activation. In addition, all of the recent studies on metal-free catalysts for the NRR have mainly focused on nonmetallic compounds or complexes, which create complex catalyst active centers and are difficult to purposefully optimize. Therefore, the development of nonmetallic electrocatalysts with high-concentration active centers and more efficient strategies to utilize their intrinsic catalytic activity are highly desired.

Here, for the first time, we focus our attention on a nonmetallic simple substance and demonstrate that orthorhombic black phosphorus in the form of few-layer nanosheets is a superior metal-free single element electrocatalyst for nitrogen reduction under ambient conditions. More specifically, in addition to the characteristics of single elements, black phosphorus is attractive as a catalyst for nitrogen reduction because its valence electron structure is similar to that of nitrogen $(3s^2 3p^3 and 2s^2 2p^3)$, respectively) and it has an anisotropic lattice structure.^[32] In particular, black phosphorus is a type of layered crystal (Figure 1a,b, Figure S1) with monolayers stacked together via weak, interlayer van der Waals interactions;^[33,34] these interactions allow black phosphorus to be exfoliated into monolayer phosphorene or few-layer black phosphorus, releasing the maximum number of intrinsic active sites.^[35-40] Notably, such inherent features should facilitate chemisorption of N2 molecules and provide sufficient electrons for activation of the inert N≡N triple bond. As a proof of concept, few-layer black phosphorus nanosheets have a faradaic efficiency and NH₃ production rate for the NRR in an acidic aqueous solution (0.01 M HCl) as high as 5.07 % and 31.37 μ g h⁻¹ mg⁻¹_{cat.}, respectively.

10.1002/anie.201813174

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Figure 1. (a) Schematic of black phosphorus (BP). (b) SEM image of bulk BP. (c) TEM images, (d) HR-TEM image and SAED pattern, (e) Raman spectra, (f) Height-mode AFM image and (g) XPS spectra of FL-BP NSs.

Few-layer black phosphorus nanosheets (FL-BP NSs) were obtained from bulk black phosphorus (BP) by a facile liquid exfoliation method (experiment details are given in the section of supplementary methods in Supporting Information). The colossal difference between the photographs of BP slurry and FL-BP NSs suspension (Figure S2) foreshadows a successful exfoliation of BP. The scanning electron microscopy (SEM) images in Figure S3 confirm the sheet structure of the exfoliated FL-BP NSs. A representative transmission electron microscopy (TEM) image of a FL-BP NS (Figure 1c) and the higher magnification image in the inset of Figure 1c further reveal the few-layer property of the exfoliated BP. Additionally, clear lattice fringes in the highresolution TEM (HR-TEM) image along with the corresponding selective area electron diffraction (SAED) patterns (Figure 1d) indicate that the FL-BP NSs inherit the intact layer structure and crystal merits of BP. The X-ray diffraction (XRD) pattern of FL-BP NSs in Figure S4 shows two typical diffraction peaks at 16.9° and 34.2°, which are consistent with diffraction of the (002) and (004) crystal planes, respectively, confirming that the FL-BP NSs produced by liquid exfoliation retain the initial crystalline state.^[41] The comparative Raman spectra of FL-BP NSs and BP precipitants (without successful exfoliation) are also provided and shown in Figure 1e. Based on previous reports, the three Raman peaks at 361 cm⁻¹, 441 cm⁻¹ and 468 cm⁻¹ from the BP precipitants correspond to A_g^1 , B_{2g} and A_g^2 modes, respectively. And, a blueshift in the A_{g}^{1} , B_{2g} and A_{g}^{2} Raman peaks of the FL-BP NSs is clear compared to those of the BP precipitants, suggesting a reduction in the number of layers.^[34] Moreover, according to the atomic force microscopy (AFM) analysis in Figure 1f, the exfoliated BP NSs have a thickness of ~4.1 nm (5-7 layers), which is consistent with that of the FL-BP NSs (Figure S5). The further chemical composition analysis of the FL-BP NSs was performed using X-ray photoelectron spectroscopy (XPS). As shown in Figure 1g, the FL-BP NSs exhibit a P 2p^{3/2}

(130.5 eV) and P $2p^{1/2}$ (131.3 eV) doublet, which represents the characteristic binding energies of crystalline BP. The weak oxidized phosphorus (PO_x) peak at 134.5 eV is in agreement with previous reports on electronic-grade BP.^[35] The above characterization fully confirmed the successful preparation of FL-BP NSs.

The NRR electrocatalytic activity of FL-BP NSs (supported on carbon fiber, and denoted as FL-BP NSs/CF) was performed in a high purity N₂-saturated 0.01 M HCl solution using a gas-tight two-compartment cell (Figure S6). And the potential ammonia product was detected and quantified by using indophenol blue method and 1H nuclear magnetic resonance (1H NMR). Figure S7 shows the chronoamperometry curves of electrolysis for 2 h at different applied potentials (from -0.4 to -0.8 V) under ambient conditions. The corresponding UV-vis absorption spectra of the product solutions stained with indophenol indicator are shown in Figure 2a. According to the standard curve at λ =660 nm (Figure S8), the maximum faradaic efficiency of 5.07 % for ammonia synthesis on the FL-BP NSs/CF catalyst electrode was achieved at -0.6 V (Figure 2b) and the highest NH₃ yield rate was 31.37 μ g h⁻¹ mg⁻¹_{cat.} at -0.7 V (Figure 2c), which is significantly higher than that on bulk BP and powdery BP (grated bulk BP) catalyst electrodes (Figure S9,10), as well as most nonmetallic and metal-based catalysts reported at present (Table S1). Furthermore, no apparent byproduct (N₂H₄) was detected in the product solutions (Figure S11,12), which indicates that the FL-BP NSs/CF has a good selectivity for N₂ electroreduction into NH₃. Based on the nitrogen adsorption-desorption isotherms (Figure S13a) and TPD spectra (Figure S13b) of bulk BP and exfoliated sample, we speculate that the superior nitrogen reduction properties of the FL-BP NSs are mainly due to the rich nitrogen-adsorption active sites brought about by the lamellar structure formed by the full exfoliation of the bulk BP.

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Figure 2. NRR behavior of FL-BP NSs/CF. (a) Corresponding UV-vis absorption spectra of the electrolyte (electrolysis at different potentials) stained with indophenol indicator. (b) Faradaic efficiency and (c) NH_3 yield rate at various potentials. (d) 1H NMR spectra (600 MHz) of both ${}^{14}NH_4^+$ and ${}^{15}NH_4^+$ produced from the NRR reaction (at -0.6 V vs. RHE) using ${}^{14}N_2$ or ${}^{15}N_2$ as the N₂ source. (e) Corresponding UV-vis absorption spectra of the electrolyte (electrolysis on recycled catalyst) stained with indophenol indicator. (f) Cycling stability results at -0.6 V (vs. RHE).

To verify the source of ammonia, some necessary comparative experiments were carried out at the optimal potential of -0.6 V, including using Ar instead of nitrogen as the feed gas, CF without FL-BP NSs as the working electrode, and $^{15}\text{N}_2$ as the feed gas. Specifically, no apparent NH_4^+ was detected in the electrolyte after two hours of electrolysis when N₂ was replaced by Ar, and when a carbon fiber without the FL-BP NSs was used as a catalyst electrode, respectively (Figure S14). By contrast, typical ¹⁵NH₄⁺ signal was detected in the presence of continuous ¹⁵N₂ bubbling (based on the 1H NMR spectra, Figure 2d). Moreover, the corresponding 1H NMR spectra had only a double peak of ¹⁵NH₄⁺, which confirms that the formation of NH₃ was completely derived from the electrochemical reduction of N₂ in the presence of FL-BP NSs catalyst (Figure S15-17). Considering that the peak area of nuclear magnetic resonance is directly related to the content of ammonia, the concentration of ¹⁵NH₄⁺ was further quantitatively determined by 1H NMR with external standards (Figure S18,19). As expected, the calculated peak area and corresponding ammonia yield were very close to the quantitative results from the indophenol blue method (Table S2) and 1H NMR spectra of ¹⁴NH₄⁺ when the electrolysis was performed using $^{14}\mathrm{N}_2$ as the feed gas (Figure S20). This result further confirmed the high efficiency catalytic activity of FL-BP NSs for NRR.

The durability of the FL-BP NSs catalyst for NRR was first assessed by 5 consecutive electrolysis cycles. As shown in Figure 2e,f and Figure S21, the faradaic efficiency and yield rate for NH₃ production only decrease slightly after five cycles of chronoamperometric runs (about 90% performance retention at -0.6 V), which is indicative of a good stability of the FL-BP NSs in NRR electrocatalysis during the continuous electrolytic reaction. Time-dependent electrolytic test further confirmed the good stability of the FL-BP NSs for NRR. From Figure S22, it can be clearly seen that the time-dependent yield of NH₃ during nitrogen reduction increases linearly with increased electrolysis time. To

verify this result, the linear dependence between NH₃ production and reaction time was also quantitatively determined by 1H NMR spectra of ¹⁵NH₄⁺ when the electrolysis was performed for 6 h using ¹⁵N₂ as feed gas (Figure S22d, Table S3). Here the good linearity also means that NH₃ can be produced sustainably by consuming the dissolved nitrogen. Moreover, considered about the inherent property of this catalyst, that is, the FL-BP NSs may be not stable in the presence of water and oxygen molecules (although the above experiments were performed under oxygen-free condition), we also characterize the spent catalyst to determine whether the structure and composition have changed during NRR. The typical sheet structure characteristic in AFM image shows that the FL-BP NSs have good structural stability (Figure S23). However, the slightly blurred lattice fringe in the TEM image of the spent catalyst (Figure S24), and the blueshift of the A_g^1 , B_{2g} and A_g^2 Raman peaks (Figure S25a), as well as the enhanced oxidation peak (PO_x) intensity located at the binding energy of 134.5 eV (Figure S25b), indicating that the surface of the FL-BP NSs does suffer partial oxidation decay during the electrolysis process. Accordingly, to explore the effect of the PO_x on electrochemical ammonia synthesis, control experiment using Oxidized-FL-BP NSs/CF as the working electrode in N2-saturated solution was conducted. As shown in Figure S26, the electrochemical performance of ammonia synthesis on the Oxidized-FL-BP NSs/CF is significantly lower than that on the FL-BP NSs/CF, indicating that the increased POx in the FL-BP NSs catalyst does not benefit for ammonia synthesis from electrochemical nitrogen reduction (Table S4). The conclusion was also confirmed by theoretical calculation (Figure S27). Thus, further improvements in preventing BP degradation in the electrolyte will be beneficial for the long-term durability of the electrocatalyst for NRR.



Figure 3. (a) Structure of ideal FL-BP NSs (top view). The green balls represent five active sites (surface, zigzag, armchair-1, diff-zigzag and armchair-2 edge). (b) LUMO (yellow) and HOMO (blue) of FL-BP NSs. (c) Schematic diagram of the possible reaction mechanisms (solid line: low-energy route, dotted line: unfavorable route) for electrochemical reduction of N₂ to NH₃ at the zigzag edge (zz, top view) of FL-BP NSs under N₂ atmosphere.

In addition, to identify the intrinsic nitrogen adsorption active sites and understand the possibility mechanism of nitrogen reduction, we performed density functional theory (DFT) calculations for the molecular orbitals of FL-BP NSs (Figure 3a,b), which due to the electron distribution in the molecular orbital of the catalyst is the key factor to determine the active sites for nitrogen fixation.^[7,13] As shown in Figure 3b, the lowest unoccupied molecular orbital (LUMO, vellow) and the highest occupied molecular orbital (HOMO, blue) present a nonlocalized, asymmetric electron distribution. The electron densities of the HOMO and LUMO are obviously concentrated on the zigzag and diff-zigzag edges (Figure S28), and at the edges, the active orbitals are beneficial for adsorbing N2 and boosting the NRR performance. For the zigzag and diff-zigzag edges (denoted as zz and diff-zz, respectively), an alternating hydrogenation pathway in an association mechanism is the plausible lowenergy NRR pathway (Figure 3c, Figure S29), which can be

described as follows (using zigzag active sites as an example): $zz+N_2 \rightarrow zz^*N_2 \xrightarrow{H^+} zz^*NNH \xrightarrow{H^+} zz^*HNNH \xrightarrow{H^+} zz^*HNNH_2 \xrightarrow{H^+} zz^*H_2NNH_2$ $\xrightarrow{H^+} zz^*H_2N+NH_3(I) \xrightarrow{H^+} zz+NH_3(I)$

In contrast with the feasible hydrogenation reduction of $*H_2NNH_2$ to $*NH_2$ and NH_3 at zigzag (-0.14 eV) and diff-zigzag edges (0.1 eV) (Figure 4), the desorption of $*H_2NNH_2$ is predicted to be energetically unfavorable (0.56 eV and 1.61 eV, respectively). Such a difference indicates that the hydrogenation route to NH_3 is the dominant pathway for FL-BP NSs, as observed experimentally.

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Figure 4. DFT-calculated reaction pathways and the corresponding energy changes for the NRR on zigzag-edge (A) and diff-zigzag-edge (B) active sites of FL-BP NSs/CF.

In summary, we have demonstrated that BP with a few-layer nanosheet structure is a superior nonmetallic electrocatalyst for nitrogen reduction under ambient conditions. Isotopic tracer experiments confirmed that the synthetic ammonia was completely derived from the supplied nitrogen. DFT calculations support that the zigzag and diff-zigzag edges of the FL-BP NSs are active centers for nitrogen adsorption and N=N triple bond activation, which enable electroreduction of N₂ to NH₃ via an alternating hydrogenation pathway. This work not only proves the feasibility of using a nonmetallic simple substance as a nitrogen-fixing catalyst, but also provides a model for more accurate studies on the reaction mechanism of nitrogen reduction on nonmetallic materials. Overall, we expect this work to play a role in the development of more efficient metal-free nitrogen-fixing catalysts.

Acknowledgements

We gratefully acknowledge financial support from the National Natural Science Foundation of China (21776099), the Pearl River and S&T Nova Program of Guangzhou (201610010076), National Key R&D Program (2016YFA0202601) and Fundamental Research Funds for the Central Universities.

Keywords: ammonia synthesis • nitrogen reduction reaction • electrocatalysis • metal-free • black phosphorus

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