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- Authors: Xien Liu, Haeseong Jang, Ping Li, Jia Wang, Qing Qin, Min Gyu Kim, Guangkai Li, and Jaephil Cho

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Antimony-Based Composites Loading on Phosphorus-Doped Carbon for Boosting Faradaic Efficiency of the Electrochemical Nitrogen Reduction Reaction

Xien Liu,*^[a] Haeseong Jang,^[b] Ping Li,^[a] Jia Wang,^[a] Qing Qin,*^[a] Min Gyu Kim,^[c] Guangkai Li,^[a] and Jaephil Cho*^[b]

Abstract: The ammonia synthesis from nitrogen by electrochemical route with high selectivity on a large scale at room temperature and atmospheric pressure is highly desirable but challenging. Herein, a new nanocomposite of PC/Sb/SbPO4 (PC, phosphorus-doped carbon) exhibits a high activity and an excellent selectivity for efficient electrocatalytic conversion of N2 to NH3 in both acidic and neutral electrolytes under ambient conditions. At a low reductive potential of - 0.15 V versus the reversible hydrogen electrode (RHE), the PC/Sb/SbPO₄ catalyst achieves a high Faradaic efficiency (FE) of 31 % for ammonia production in 0.1 M HCl under mild conditions. In particular, a remarkably high FE value of 34 % is achieved at a lower reductive potential of - 0.1 V (vs. RHE) in a 0.1 M Na₂SO₄ solution, which is better than most reported electrocatalysts towards nitrogen reduction reaction (NRR) in neutral electrolyte under mild conditions. The change in surface species and electrocatalytic performance before and after N2 reduction is explored by ex-situ method. PC and SbPO₄ are both considered as the active species that enhanced the performance of NRR.

Scientists have been developing novel ammonia synthetic routes under mild conditions to replace the energy-intensive, harmful and unsustainable Haber-Bosch process. Ammonia synthesis by electrocatalytic NRR at room temperature and atmospheric pressure is considered a promising route and has become a very hot research topic.^[1] Noble metal-based materials are commonly used to catalyze the NRR. In this context, Zeng et al. reported that the Ru single-atom catalyst, Ru SAs/N-C, exhibited a FE of 29.6 % for ammonia synthesis at - 0.20 V (*vs.* RHE) under ambient conditions,^[2] and the Ru single atoms were considered to be the key active sites. Very recently, Sun's group also reported a Ru single-atom catalyst, Ru@ZrO₂/NC, that enhanced the yield rate of ammonia up to 3.66 mg_{NH3}h⁻¹mg_{Ru}⁻¹ at a potential of - 0.21 V. However, the use of noble metal-based catalysts in large-scale

[a]	Prof. X. Liu, P. Li, J. Wang, Dr. Q. Qin, G. Li,
	State Key Laboratory Base of Eco-Chemical Engineering, College of
	Chemical Engineering, College of Chemistry and Molecular
	Engineering, Qingdao University of Science and Technology
	Qingdao 266042, China
	E-mail: liuxien@qust.edu.cn; qinqing@qust.edu.cn
[b]	H. Jang, Prof. J. Cho
	Department of Energy Engineering and School of Energy and
	Chemical Engineering, Ulsan National Institute of Science and
	Technology (UNIST)
	Ulsan 689-798, South Korea
	E-mail: jpcho@unist.ac.kr
[c]	Prof. M. Kim
	Beamline Research Division, Pohang Accelerator Laboratory (PAL)
	Pohang 790-784, Korea
	Supporting information for this article is given via a link at the end of the document.((Please delete this text if not appropriate))

is limited by their expensive and rare attributes. Compared to noble metal-based catalysts, non-noble metal-based and metal-free catalysts, such as MoO₃/GCE,^[3] Fe₂O₃-CNT,^[4] polymeric carbon nitride (PCN)^[5] and nitrogen-doped carbon nanospikes,^[6] are earth abundant and more favorable due to their low cost and high FE. To suppress the competitive hydrogen evolution reaction (HER), the use of an organic electrolyte, particularly an ionic liquid, was demonstrated to be highly effective. Using 1-butyl-1-methylpyrrolidinium tris (pentafluoroethyl) trifluorophosphate ([C₄mpyr] [eFAP]) as the electrolyte, MacFarlane et al. reported that an α -Fe@Fe₃O₄ NRR catalyst exhibited an excellent FE of 32 %, which was further enhanced up to 60 % by using an ionic liquid as the electrolyte.^[7] Obviously, however, the use of an ionic liquid is not economic and sustainable.

Very recently, Hao et.al. reported a strategy for promoting NRR selectivity and activity by using bismuth nanocrystals and potassium cations, leading to a record high FE of 66 % in acid electrolyte.^[8] Thus, one of the attractive options is to develop composite catalysts of a high FE and selectivity for NRR. For this purpose, antimony-based and carbon-based materials are attractive components of choice as they are not highly active for the HER, and hence good for NRR. Besides, carbon-based nanomaterials, such as PCN and nitrogen-doped carbon nanospikes, have demonstrated FEs beyond 10 %. However, PCN itself contains C-N bonds, which are more easily broken than the triple bond of N₂ to affect the yield rate of ammonia and FE. Although isotopic labeling measurements using ¹⁵N₂-enriched gas have been used to examine the actual N source of NH₃, this technique is expensive and not available at all laboratories. Therefore, it highly desirable to develop antimony- and carbonbased N-free composite materials that can achieve a high FE and selectivity for ammonia synthesis, though antimony- and carbonbased composite containing with or without N has yet to be reported in the literature.

In this study, we synthesized the first NRR electrocatalyst composed of PC/Sb/SbPO₄ that achieved a high FE of 31 % at a low reductive potential of - 0.15 V (*vs.* RHE) and a high ammonia yield rate of 25 μ g h⁻¹ mg_{cat}.⁻¹ at - 0.25 V in 0.1 M HCl under ambient conditions. In neutral electrolytes, the catalyst outperformed all reported non-noble metal-based catalysts for the conversion of N₂ to NH₃ with a remarkably high FE of 34 % at a low reductive potential of - 0.1 V. Our *ex*-situ electrochemical study indicated that PC and SbPO₄ were both served as the active sites for enhancing the NRR performance of PC/Sb/SbPO₄.

 $PC/Sb/SbPO_4$ was prepared by annealing $C/Sb/Sb_2O_3$ and sodium hypophosphite monohydrate under an argon atmosphere (see Supporting Information for details). Figure S1 shows the Xray diffraction (XRD) pattern for the $C/Sb/Sb_2O_3$. A typical scanning electron microscopy (SEM) image in Figure 1a shows the three-dimensional honeycomb structure of the as-synthesized

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PC/Sb/SbPO₄ catalyst. As shown in Figure 1b, all the XRD peaks (black plot) of the as-prepared catalyst can be well indexed to rhombohedral Sb (green plot at the bottom of Figure 1b, JCPDS No. 05-0562) and monoclinic SbPO₄ (red plot at the bottom of Figure 1b, JCPDS No.35-0829). The characteristic peaks of PC are not present, which may be caused by the poor crystallinity of the carbon substrate relative to that of Sb and SbPO₄. After N₂ reduction at - 0.15 V (vs. RHE) in 0.1 M HCl for 1 h, the diffraction peaks corresponding to SbPO4 disappeared, and the peaks in Figure 1b highlighted by the green lines can be attributed to metallic Sb, which may be caused by partial dissolution of SbPO₄ into the electrolyte and amorphization upon NRR. As shown in Figure S2, the HRTEM image of PC/Sb/SbPO₄ after the NRR testing shows blurred lattice fringes, and the contents of elemental Sb, P and O decreased obviously after the NRR measurement (Figure S3). The high-resolution transmission electron microscopy (HRTEM) image of the catalyst is shown in Figure 1c, which corresponds to the region marked with a white circle in Figure S4. The clear fringe with a lattice spacing of 0.33 nm can be indexed to the (101) plane of SbPO₄. The energy-dispersive X-ray spectroscopy (EDS) analysis in Figure 1d-h further confirms the component of the prepared catalyst and the uniform distribution of C, Sb, P and O in the structure.



Figure 1. a) SEM image of PC/Sb/SbPO4. b) XRD patterns of PC/Sb/SbPO4 before and after NRR testing. The vertical bars in the bottom corresponded to the XRD standard cards (red plot: SbPO4, green plot: Sb), c) HRTEM image of PC/Sb/SbPO4. d-h) STEM-EDS elemental mapping of PC/Sb/SbPO4.

X-ray photoelectron spectroscopy (XPS), X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure spectroscopy (EXAFS) measurements were conducted to further verify the composition and electronic states of PC/Sb/SbPO₄. As demonstrated by Figure S5a, C, O, P and Sb are observed in the XPS survey spectrum of PC/Sb/SbPO₄. Before N₂ reduction, no N signal is observed both in the XPS survey spectrum and the high-resolution XPS spectrum of N 1s (Figure S5b). The Sb 3d core level XPS spectrum of the asprepared PC/Sb/SbPO₄ in Figure 2a (plots at the bottom) was deconvoluted into two peaks located at 530.3 eV and 539.7 eV, which can be assigned to Sb 3d_{5/2} and Sb 3d_{3/2} of SbPO₄, respectively, corresponding to the Sb(III) state.^[9] However, no Sb⁰ peaks, which should be located at approximately 537.5 and 528.2 eV for Sb $3d_{3/2}$ and Sb $3d_{5/2}$,^[10] are observed, indicating that the metallic Sb is covered by SbPO4 and is consistent with the HRTEM result. The small peak at a binding energy (BE) of 531.8 eV can be ascribed to O 1s.^[9] After the NRR testing, as shown in Figure 2a (plots at the top), the peaks of Sb 3d_{5/2} and Sb 3d_{3/2} are slightly shifted to higher binding energies, indicating the formation of Sb species with a higher valence state on the surface of the catalyst.^[11] After the NRR testing, two peaks appeared at BEs of 402.5 eV and 400.3 eV in N 1s spectrum (Figure S5c) can be assigned to NH₂ and NH₄^{+,[12]} respectively, indicating the production of NH₃ is from N₂, instead of other NH₃ source in reaction vessel. The P 2p spectrum in Figure 2b can be deconvoluted into two components at BEs of 133.0 and 134.0 eV, corresponding to P 2p_{3/2} and P 2p_{1/2} for the P-C and P-O bonds in P-doped carbon and SbPO₄,^[13] respectively. After N₂ reduction, the relative contents of P-O and P-C were obviously changed, further confirming the content decrease of SbPO₄ in the hybrids. By contrast, the BEs of C=O/P=O and C-O-P in O 1s spectra display almost no shift after the NRR testing (Figure S5d). The peaks centered at 284.4 eV and 286.2 eV in C 1s spectrum (Figure S5e) can be assigned to C=C and C-P interactions, respectively.^[14] After the NRR testing, three new peaks were observed at approximately 290-293 eV, belonging to the C species in the Nafion binder introduced for the electrochemical measurements. Otherwise, the BEs of C=C and C-P have no obvious change before and after the NRR testing.



Figure 2. a) High-resolution XPS spectra of Sb 3d for PC/Sb/SbPO₄. The spectrum shown at the bottom refers to the as-prepared samples, while the one shown at top corresponds to the samples after N₂ reduction at -0.15 V (vs. RHE) in 0.1 M HCl for 1 h. b) High-resolution XPS spectra of P 2p before and after N₂ reduction. c) The XANES spectra of PC/Sb/SbPO₄ before and after N₂ reduction. d) The *k*²-weighted Fourier transform of EXAFS spectra of PC/Sb/SbPO₄ before and after N₂ reduction.

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The XANES spectrum of Sb K-edge for PC/Sb/SbPO₄ (red plot in Figure 2c) shows a main peak at 30502 eV, which is similar to that of reported Sb³⁺ species.^[15] After the NRR testing, the main peak slightly shifted to a higher photon energy (blue plot in Figure 2c), indicating the appearance of Sb species with a higher valence state on the surface of the catalyst,^[16] which is consistent with the XPS analysis result. The radial distribution function of PC/Sb/SbPO₄ in Figure 2d shows the peaks centered at 0.98 and 1.48 Å belonging to Sb-O bonds, while the adjacent peak featured at 2.73 Å resulted from the Sb-Sb interaction. After the NRR, the two peaks of the Sb-O bonds shifted to smaller interatomic distances of 0.91 and 1.42 Å due to the formation of Sb species with a higher valence state, while the interatomic distance of the Sb-Sb bond increased and right-shifted to 2.76 Å. By combining these advanced characteristic techniques, the prepared catalyst was unequivocally determined to be the PC/Sb/SbPO₄ nanocomposite, in which SbPO₄ species covered the surface of metallic Sb to form Sb/SbPO4 nanoparticles supported on Pdoped carbon.



Figure 3. a) Time-current density curves for PC/Sb/SbPO₄ at different potentials for 3600 s in 0.1 M HCl. b) NH₃ yields and Faradaic efficiencies for PC/Sb/SbPO₄ at corresponding potentials. c) NH₃ yields of PC/Sb/SbPO₄, C/Sb/Sb₂O₃ and PC electrodes at potential of - 0.15 V (vs. RHE) after 1 h electrolysis under ambient conditions. d) Recycling test of NH₃ yields and Faradaic efficiencies over PC/Sb/SbPO₄ electrodes for five times at potential of - 0.15 V (vs. RHE).

The NRR testing were first performed in a 0.1 M HCI solution under ambient conditions using a gas-tight H-type cell, which was separated from the counter electrode by a Nafion 117 membrane. Carbon paper coated with the catalyst was used as the cathode. For comparison, the NRR activities of PC and PC/Sb/Sb₂O₃ were also tested under the same conditions. Figure S6a shows the linear sweep voltammetry (LSV) curves of PC/Sb/SbPO₄ in both N₂- and Ar-saturated 0.1 M HCl media. The larger current density at a lower potential under a N2 atmosphere demonstrated a higher NRR activity. After a continuous potentiostatic electrolysis at the constant potentials (Figure 3a), NH₄⁺-contained products were carefully detected by indophenol blue method, as shown in Figure S6b, and the corresponding calibration curves are shown in Figure S7. No by-product N₂H₄ was detectable by the Watt and Chrisp method (Figure S8), suggesting the good selectivity of PC/Sb/SbPO₄ for the NRR. As illustrated in Figure 3b, the highest yield rate of 25 µg h⁻¹ mg_{cat}⁻¹ for ammonia was obtained at a potential of - 0.25 V (vs. RHE). The FE of the PC/Sb/SbPO₄ catalyst for ammonia production reached 31 % at a low applied potential of - 0.15 V, which even exceeded those of some noble metal-based catalysts, including Au/CeOx-RGO (10.1 % at - 0.2 V vs. RHE),^[17] Au/TiO₂ (8.11 % at - 0.2 V vs. RHE),^[18] Ru@ZrO₂/NC (21 % at - 0.11 V vs. RHE), [19] Ru SAs/N-C (29.6% at - 0.2 V vs. RHE)^[20] and Au SAs-NDPCs (12.3 % at - 0.2 V vs. RHE).^[21] Notably, the PC/Sb/SbPO₄ catalyst delivered an ammonia yield rate of 16.7 µg h⁻¹ mg_{cat.}⁻¹ at - 0.15 V, which is over four times higher than that of C/Sb/Sb₂O₃ (4.1 µg h⁻¹ mg_{cat.}⁻¹) (Figure 3c). In contrast, without the Sb/SbPO₄ nanoparticles, PC delivers poorer NRR activity, characterized by an smaller NH₃ formation rate of 7.4 µg h⁻¹ mg_{cat}⁻¹. Because of the coverage of Sb⁰ by SbPO₄ layer, the Sb⁰ species are not directly taking part in the catalytic process. Hence, the PC and SbPO₄ are both the active sites for NRR, synergistically enhance the NRR activity of the PC/Sb/SbPO₄. As reported by previous studies, heteroatom P doping into carbon can effectively tailor the electron structure of carbon,[14a, 22] significantly improving the conductivity of the catalyst. Moreover, the SbPO₄ nanoparticles anchored on the PC substrate can effectively prevent them from aggregation, favoring high stability for long-term NRR process. The recycling tests were performed at - 0.15 V (vs. RHE) for 1 h. The chronoamperometry results were shown in Figure S9. Evidently, both the NH₃ yield rate and FE have no obvious degradation experiencing five cycling tests (Figure 3d). As shown in Figure S10, the current density of PC/Sb/SbPO₄ remained stable during the continuous NRR at -0.15 V in acid media for 24 h because the current density of HER was majority. However, the concentration of NH₃ in the electrolyte presented a nonlinear increase from the initial concentration of 0.215 μg mL $^{-1}$ at 6 th h to 0.395 μg mL $^{-1},$ 0.547 μg mL $^{-1},$ and 0.658 µg mL⁻¹ at 12th h, 18th h, and 24th h, respectively (Figure S11a), and the corresponding yield rate of NH3 exhibited a gradual decrease from 12.55 μ g h⁻¹ mg_{cat.}⁻¹ to 7.10 μ g h⁻¹ mg_{cat.}⁻¹ after consecutive electrolysis (Figure S11b), indicating a loss of the NRR activity of 43 % after electrolysis for 24 h. The loss of the NRR activity of PC/Sb/SbPO4 is attributed to three possible reasons: First, the loss of the active sites caused by the partial dissolution of SbPO₄ into electrolyte and amorphization; Second, the N-contained species, NH_x bind to the catalyst (Figure S5c) during the NRR process, making the catalyst deactivation; Third, the NH_3 formation reaction is a reversible reaction. When the ammonia concentration reaches a certain value, the reaction is in equilibrium, which also leads to the decrease of the NH₃ yield rate. We also quantified the hydrogen by gas chromatography (GC) after NRR testing at - 0.15 V for 6 h and the FE of H_2 was calculated to be 68.7 % (Figure S12), while the FE of NH_3 was determined to be 14.6 %. The possible reasons for that the sum of H₂ and NH₃ FEs is less than 100 % are the reduction of catalyst itself (from Sb³⁺ to Sb⁰ evidenced by comparing XRD before and after NRR), as well as the capacitance of the carbon support.^[23]

Time-depended ICP-AES analysis results (Table S1) revealed that the concentration of antimony in electrolyte was 0.021 ppm after electrolysis for 6 h and then increased very slowly over long period, demonstrating the residual amorphous layer was relatively stable that wrapped the inner Sb⁰ moiety, which effectively prevented the Sb⁰ from the cathodic corrosion. Even so, as more catalyst combined with the NH_x, as well as the

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negative effect of the higher ammonia concentration on chemical reaction direction, the activity of the catalyst still gradually declined. We also compared NRR performance of PC/Sb/SbPO₄ with those of reported catalysts in an acidic electrolyte, as listed in Table S2. The activity of PC/Sb/SbPO₄ is one of the highest among the listed catalysts for the NRR.

To verify that the detected NH₃ was solely generated via the NRR on PC/Sb/SbPO₄, three control experiments were performed: i) using carbon paper without catalyst loading as the working electrode; ii) continuously feeding N₂ to the testing apparatus at the open-circuit potential; and iii) testing the PC/Sb/SbPO₄ electrode under an Ar gas atmosphere. As evidenced by the corresponding UV-vis absorption spectra shown in Figure S13-S17, no NH₃ product was detected under these conditions, indicating that the NH₃ product is indeed produced by the NRR on PC/Sb/SbPO₄.



Figure 4. a) LSV curves of PC/Sb/SbPO₄ in Ar- and N₂-saturated 0.1 M Na₂SO₄ with a scan rate of 10 mV s⁻¹. b) Time-dependent current density curves for PC/Sb/SbPO₄ at different potentials for 1 h in 0.1 M Na₂SO₄. c) UV-Vis absorption spectra of the electrolytes stained with indophenol indicator after electrolysis at a series of potentials for 1 h. d) NH₃ yields and FEs for PC/Sb/SbPO₄ at corresponding potentials.

The electrocatalytic performance of the PC/Sb/SbPO₄ toward the NRR in 0.1 M Na₂SO₄ solution was also measured.^[24] The NH₃ was determined by spectrophotometry method using salicylic acid as a color agent.^[25] The corresponding calibration curves for the NH₃ concentration-dependent absorbance are shown in Figure S18. LSV curves in Figure 4a showed the increased current density in the N₂ atmosphere compared to that in the Arsaturated electrolyte indicated that PC/Sb/SbPO₄ is active for the NRR. The i-t curves in Figure 4b were recorded at five given potentials. The corresponding UV-vis absorption spectra of the electrolytes colored with indophenol indicator after the NRR testing are shown in Figure 4c. Surprisingly, as shown in Figure 4d, the highest FE is up to 34 % at a lower potential of - 0.1 V (vs. RHE), to the best of our knowledge, which is the highest value of FEs among those of all the reported non-noble metal-based catalysts for the N2 NRR in neutral electrolyte under mild conditions. We compared the NRR performance of our catalyst with the reported catalysts in neutral conditions in Table S3. The

maximum NH₃ yield rate reach to 23 μ g h⁻¹ mg_{cat.}⁻¹ at - 0.3 V. As evidenced by Figure S19a, the NH₃ yield rate of PC/Sb/SbPO₄ was 13.5 μ g h⁻¹ mg_{cat.}⁻¹ at - 0.1 V, which is much higher than those of the C/Sb/Sb₂O₃ (2.2 µg h⁻¹ mg_{cat.}⁻¹) and PC (8.6 µg h⁻¹ mg_{cat.}⁻¹), and suggests a synergistic effect of PC and SbPO₄ resulting in the high electrocatalytic activity. The durability and stability of PC/Sb/SbPO₄ toward the NRR were also evaluated by cycling tests and long-term continuous potentiostatic electrolysis. The recycling tests were performed at - 0.10 V (vs. RHE) for 1 h. The chronoamperometry results were shown in Figure S19b. After five parallel tests, the NH₃ formation rate and the corresponding FEs presented only a slight decrease relative to their initial values (Figure S19c). Continuous potentiostatic electrolysis at - 0.1 V for 24 h did not result in any apparent change in the current density of PC/Sb/SbPO₄ (Figure S20). The controlled experiments were carried out to test that the detected NH₃ was only from the NRR. The testing results under different conditions are collected in Figure S21-25, all these results confirmed that NH₃ is from the NRR.

The XRD, HRTEM, XPS and XANES measurements were adopted to monitor the changes of structure and composition of PC/Sb/SbPO₄ catalyst before and after the NRR testing. Evidently. the components of SbPO₄ and PC in the hybrids were active for the NRR, ensuring sufficient active sites for the adsorption and activation of N₂ molecules,^[26] in which the N₂ reduction occurred at the active sites of Sb in SbPO₄ and positively charged P in carbon substrate.^[27] The doping of P into carbon effectively tuned the electronic structure of the hybrid catalyst, resulted in enhanced conductivity.^[28] Meanwhile, the Sb/SbPO₄ particles were anchored on the P-doped carbon substrate, preventing aggregation of the Sb/SbPO4 particles and benefiting high exposure of active sites during the NRR process, [29] which led to excellent electrochemical durability and structural stability. The Sb⁰ species were not served as active sites for directly participating in the NRR due to the surface coverage by SbPO₄. However, as an effective support, the existence of Sb⁰ species significantly increased the exposure of the external SbPO4, thereby producing positive effect on the NRR performance. Although the SbPO₄ moiety went through a partial dissolution into electrolyte during the NRR process, which was not bringing significant impact on the electrocatalytic activity and stability of PC/Sb/SbPO₄ toward NH₃ electrosynthesis.

In summary, the PC/Sb/SbPO₄ catalyst was successfully synthesized *via* a facile solid-state phosphorization reaction with C/Sb/Sb₂O₃ as precursor under an Ar flow. Benefiting from the integrated advantages of the active sites of PC and SbPO₄, as well as the conductivity enhanced by PC, the resultant PC/Sb/SbPO₄ exhibited high activities, excellent FEs and nice stability for the electrocatalytic N₂ to NH₃ conversion in both acidic and neutral electrolytes under ambient conditions. A peak FE of 31 % was achieved with PC/Sb/SbPO₄ at a lower potential of - 0.15 V (vs. RHE) in 0.1 M HCl electrolyte, as well as 34 % at a lower potential of - 0.1 V in 0.1 M Na₂SO₄ solution, both significantly exceeding most of the reported NRR electrocatalysts. This study provides a new design strategy of coupling different active species to one advanced structure to enhance the performance of a catalyst for artificial N₂ transformation to NH₃.

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- a) G.-F. Chen, S. Ren, L. Zhang, H. Cheng, Y. Luo, K. Zhu, L.-X. Ding, H. Wang, *Small Methods* 2018, 1800337; b) D. Yan, H. Li, C. Chen, Y. Zou, S. Wang, *Small Methods* 2018, 1800331.
- [2] Z. G. Geng, Y. Liu, X. D. Kong, P. Li, K. Li, Z. Y. Liu, J. J. Du, M. Shu, R. Si, J. Zeng, *Adv. Mater.* **2018**, *30*, 1803498.
- [3] J. Han, X. Ji, X. Ren, G. Cui, L. Li, F. Xie, H. Wang, B. Li, X. Sun, J. Mater. Chem. A 2018, 6, 12974-12977.
- [4] S. M. Chen, S. Perathoner, C. Ampelli, C. Mebrahtu, D. S. Su, G. Centi, Acs Sustain. Chem. Eng. 2017, 5, 7393-7400.
- [5] C. Lv, Y. Qian, C. Yan, Y. Ding, Y. Liu, G. Chen, G. Yu, Angew. Chem. Int. Ed. 2018, 57, 10246-10250.
- [6] Y. Song, D. Johnson, R. Peng, D. K. Hensley, P. V. Bonnesen, L. B. Liang, J. S. Huang, F. C. Yang, F. Zhang, R. Qiao, A. P. Baddorf, T. J. Tschaplinski, N. L. Engle, M. C. Hatzell, Z. L. Wu, D. A. Cullen, H. M. Meyer, B. G. Sumpter, A. J. Rondinone, *Sci. Adv.* **2018**, *4*, 1700336.
- [7] F. L. Zhou, L. M. Azofra, M. Ali, M. Kar, A. N. Simonov, C. McDonnell-Worth, C. H. Sun, X. Y. Zhang, D. R. MacFarlane, *Energ. Environ. Sci.* 2017, *10*, 2516-2520.
- [8] Y.-C. Hao, Y. Guo, L.-W. Chen, M. Shu, X.-Y. Wang, T.-A. Bu, W.-Y. Gao, N. Zhang, X. Su, X. Feng, J.-W. Zhou, B. Wang, C.-W. Hu, A.-X. Yin, R. Si, Y.-W. Zhang, C.-H. Yan, *Nat. Catal.* **2019**, doi.org/10.1038/s41929-019-0241-7.
- [9] J. Pan, S. Chen, Q. Fu, Y. Sun, Y. Zhang, N. Lin, P. Gao, J. Yang, Y. Qian, ACS Nano 2018, 12, 12869-12878.
- [10] H. Bryngelsson, J. Eskhult, L. Nyholm, M. Herranen, K. Edström, Chem. Mater. 2017, 19, 1170-1180.
- [11] F. Garbassi, Surf. Interface Anal. 2010, 2, 165-169.
- a) D. B. Cairns, S. P. Armes, *Resp. Res.* **1999**, *15*, 1-13; b) J. J. Benítez,
 M. A. San-Miguel, S. Domínguez-Meister, J. A. Heredia-Guerrero, M.

Salmeron, J. Phys. Chem. C 2011, 115, 19716-19723; c) Y. Zheng, Y. Jiao, L. H. Li, T. Xing, Y. Chen, M. Jaroniec, S. Z. Qiao, ACS Nano 2014, 8, 5290-5296.

- [13] a) S. Chen, Y. Di, T. Li, L. Feng, C. Wei, *CrystEngComm* 2018, *20*, 4305-4312; b) R. Gao, P. Lun, H. W. Wang, X. W. Zhang, L. Wang, J. J. Zou, *Acs Catal.* 2018, *8*, 8420-8429; c) Q. Qin, H. Jang, L. Chen, G. Nam, X. Liu, J. Cho, *Adv. Energy Mater.* 2018, *8*, 1801478.
- [14] a) Q. Qin, H. Jang, P. Li, B. Yuan, X. Liu, J. Cho, *Adv. Energy Mater.* **2018**, 1803312; b) J. Zhang, L. Qu, G. Shi, J. Liu, J. Chen, L. Dai, *Angew. Chem. Int. Ed.* **2016**, 55, 2230-2234.
- [15] D. S. Bhachu, R. G. Egdell, G. Sankar, C. J. Carmalt, I. P. Parkin, J. Mater. Chem. C 2017, 5, 9694-9701.
- [16] a) B. Ma, A. Fernandez-Martinez, B. Madé, N. Findling, E. Markelova, E. Salas-Colera, T. G. G. Maffeis, A. R. Lewis, D. Tisserand, S. Bureau, L. Charlet, *Environ. Sci. Technol.* **2018**, *52*, 11931-11940; b) W. Ni, A. Krammer, C. S. Hsu, H. M. Chen, A. Schueler, X. Hu, *Angew. Chem. Int. Ed.* **2019**, *58*, 7445-7449.
- [17] S. J. Li, D. Bao, M. M. Shi, B. R. Wulan, J. M. Yan, Q. Jiang, *Adv. Mater.* 2017, 29, 1700001.
- [18] M. M. Shi, D. Bao, B. R. Wulan, Y. H. Li, Y. F. Zhang, J. M. Yan, Q. Jiang, *Adv. Mater.* 2017, 29, 1606550.
- [19] H. Tao, C. Choi, L.-X. Ding, Z. Jiang, Z. Han, M. Jia, Q. Fan, Y. Gao, H. Wang, A. W. Robertson, S. Hong, Y. Jung, S. Liu, Z. Sun, *Chem* 2019, 5, 204-214.
- [20] Z. Geng, Y. Liu, X. Kong, P. Li, K. Li, Z. Liu, J. Du, M. Shu, R. Si, J. Zeng, Adv. Mater. 2018, 1803498.
- [21] Q. Qin, T. Heil, M. Antonietti, M. Oschatz, *Small Methods* 2018, 1800202.
 [22] L. Xia, X. Wu, Y. Wang, Z. Niu, Q. Liu, T. Li, X. Shi, A. M. Asiri, X. Sun, *Small Methods* 2018, 1800251.
- [23] J. Wang, L. Yu, L. Hu, G. Chen, H. Xin, X. Feng, Nat. Commun. 2018, 9, 1795.
- [24] J.-X. Yao, D. Bao, Q. Zhang, M.-M. Shi, Y. Wang, R. Gao, J.-M. Yan, Q. Jiang, *Small Methods* **2018**, 1800333.
- [25] G. W. Watt, J. D. Chrisp, Anal. Chem. **1952**, 24, 2006-2008.
- [26] D. Yan, H. Li, C. Chen, Y. Zou, S. Wang, Small Methods 2018, 1800331.
- [27] R. Paul, F. Du, L. Dai, Y. Ding, Z. L. Wang, F. Wei, A. Roy, Adv. Mater. 2019, 31, 1805598.
- [28] a) B. Yuan, G. Nam, P. Li, S. Wang, H. Jang, T. Wei, Q. Qin, X. Liu, J.
 Cho, J. Power Sources 2019, 421, 109-115; b) Q. Qin, J. Hao, W. Zheng,
 ACS Appl. Mater. Interfaces 2018, 10, 17827-17834.
- [29] Z. Pu, I. S. Amiinu, Z. Kou, W. Li, S. Mu, Angew. Chem. Int. Ed. 2017, 56, 11559-11564.

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Antimony-based composites loading on phosphorus-doped carbon exhibits excellent faradaic efficiency for the conversion of nitrogen to ammonia under ambient condition in both acidic and neutral electrolyte. Two active species including P-doped carbon and antimony phosphate synergistically improve nitrogen reduction reaction performance



Xien Liu,* Haeseong Jang, Ping Li, Jia Wang, Qing Qin,* Min Gyu Kim, Guangkai Li, and Jaephil Cho*

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Antimony-Based Composites Loading on Phosphorus-Doped Carbon for Boosting Faradaic Efficiency of the Electrochemical Nitrogen Reduction Reaction