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Improving the electrocatalytic N₂ reduction activity of Pd nanoparticles through surface modification⁺

Guorong Deng,^{ab} Ting Wang,^b ^c Abdulmohsen Ali Alshehri,^d Khalid Ahmad Alzahrani,^d Yan Wang,^{*b} Hejiang Ye,^e Yonglan Luo^b*^c and Xuping Sun^{*}

Industrially, NH₃ production mainly relies on the energy-intensive Haber–Bosch process with the release of a large amount of CO₂. Electrochemical fixation of N₂ to NH₃ under ambient conditions is an environmentally friendly and sustainable alternative, but the N₂ reduction reaction (NRR) requires stable and efficient electrocatalysts. In this work, we report that the electrocatalytic NRR activity of Pd nanoparticles can be improved by surface modification with oxygenrich tannic acid. The electrochemical test results in 0.1 M Na₂SO₄ suggest that such a catalyst achieves a large NH₃ yield of 24.12 µg h⁻¹ mg_{cat.}⁻¹ and a high faradaic efficiency of 9.49% at -0.45 V vs. the reversible hydrogen electrode (RHE), rivaling the performances of most of the reported aqueous-based NRR electrocatalysts. In addition, it also shows strong long-term electrochemical stability.

As one of the most important inorganic chemicals, NH₃ plays a key role in the Earth's ecosystem and it is widely used in the manufacture of fertilizers, medicaments, dyes, explosives, and resin.¹ NH₃ is also a carbon-free energy carrier with a low liquefying pressure and high H₂ density.² Due to the strong N \equiv N bond with a bond energy of 941 kJ mol⁻¹, low polarizability, and lack of a dipole moment, N₂ is rather inert and its conversion to NH₃ faces difficulty.³ N₂ fixation occurs under ambient conditions over natural Mo-dependent nitrogenases *via* multiple proton and electron transfer steps and is enabled by energy input from ATP hydrolysis.⁴ However, the Haber–Bosch process for industrial-scale NH_3 production must operate at high temperatures and high pressure using N_2 and H_2 as the feed gases and consumes a large amount of energy with heavy CO_2 emission.⁵ In this regard, energy-saving and environmentally benign NH_3 synthesis is in great demand.

Electrochemical N2 reduction using water as a proton source has emerged as a promising alternative to the Haber-Bosch process for ambient artificial N2-to-NH3 fixation, but its efficiency requires the identification of efficient and stable electrocatalysts for the N₂ reduction reaction.⁶⁻⁹ Au, Ru and Rh catalysts perform efficiently for the NRR, but their scarcity and high cost hinder their wide use.¹⁰⁻¹⁴ Pd has a higher abundance than Ru and Rh, and its price is lower than that of Au. Recently, Pd has also emerged as an interesting element with the ability to catalyze electrochemical N2 fixation. Wang et al. reported ambient electrochemical reduction of N2 to NH3 on carbon black-supported Pd nanoparticles (Pd/C) with an NH₃ yield of 4.5 μ g h⁻¹ mg_{cat.}⁻¹ and a faradaic efficiency (FE) of 8.2%.¹⁵ Yan and co-workers demonstrated that amorphous PdCu nanoclusters on reduced graphene oxide (Pd_{0.2}Cu_{0.8}/rGO) electrocatalyzes the NRR with an NH₃ yield of 2.80 μ g h⁻¹ mg_{cat.}⁻¹, superior to that of its Pd/rGO counterpart.16 Pd-based NRR catalysts simultaneously achieving large NH3 yields and high FE are still urgently needed.

As a plant derived polyphenolic compound, tannic acid (TA) is inexpensive and has been widely utilized as a stabilizer for noble metal nanoparticles.¹⁷ In this communication, we report on our recent effort in this direction in developing oxygen-rich TAmodified Pd nanoparticles (Pd-TA) toward enhanced electrochemical N₂ reduction for ambient NH₃ synthesis. When tested in 0.1 M Na₂SO₄, the resulting Pd-TA catalyst achieves a large NH₃ yield of 24.12 μ g h⁻¹ mg_{cat.}⁻¹ and a high FE of 9.49% at -0.45 V ν s. the reversible hydrogen electrode (RHE), outperforming pure Pd nanoparticles and reported Pd-based catalysts as well as other aqueous NRR electrocatalysts. Notably, it also shows high electrochemical and structural stability.

The X-ray diffraction (XRD) pattern of Pd-TA (Fig. 1a) presents diffraction peaks at $2\theta = 40.118^{\circ}$, 46.658° , 68.119° , and

^aInstitute of Fundamental and Frontier Sciences, University of Electronic Science and Technology of China, Chengdu 610054, Sichuan, China. E-mail: xpsun@uestc.edu.cn ^bSchool of Materials and Energy, University of Electronic Science and Technology of China, Chengdu 611731, Sichuan, China. E-mail: wy@uestc.edu.cn

^cChemical Synthesis and Pollution Control Key Laboratory of Sichuan Province, College of Chemistry and Chemical Engineering, China West Normal University, Nanchong 637002, Sichuan, China. E-mail: luoylcwnu@hotmail.com

^dChemistry Department, Faculty of Science, King Abdulaziz University, P.O. Box 80203, Jeddah 21589, Saudi Arabia

^eHospital of Chengdu University of Traditional Chinese Medicine, Chengdu 610072, Sichuan, China

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Fig. 1 (a) XRD pattern of Pd-TA nanoparticles. (b) TEM image for Pd-TA nanoparticles. (c) Size distribution of Pd-TA nanoparticles. (d) HRTEM image taken from one single Pd-TA nanoparticle.

82.098° indexed to the (111), (200), (220) and (311) planes of Pd (JCPDS no. 46-1043), respectively. Pure Pd nanoparticles were prepared by the same method without addition of TA and their XRD pattern shows basically the same diffraction peaks as that of Pd-TA nanoparticles (Fig. S1†). Fig. 1b displays the transmission electron microscopy (TEM) image of Pd-TA, which confirms the formation of nanoscale particles. However, obvious agglomeration occurs for Pd nanoparticles without TA modification (Fig. S2†). Fig. 1c shows that Pd-TA nanoparticle sizes have a distribution between 7 and 16 nm, with an average size of around 11 nm. The high-resolution TEM (HRTEM) image taken from a single Pd-TA nanoparticle (Fig. 1d) reveals a well-resolved lattice fringe with an interplanar distance of 0.223 nm corresponding to the (111) plane of Pd, which is consistent with that of pure Pd nanoparticles (Fig. S2b†).

Fig. 2a shows the X-ray photoelectron spectroscopy (XPS) survey spectrum of Pd-TA nanoparticles, evidencing the presence of Pd, C, and O elements. In the Pd 3d region (Fig. 2b), as observed, there are two pairs of spin-orbit doublets, indicating the existence of Pd⁰ (Pd-Pd bonding energy peaks at 341 and 335.6 eV) and Pd^{δ^+} (Pd–O bonding energy peaks at 343.1 and 338.9 eV).18,19 Compared with pure Pd, which shows sharp peaks at BEs of 341 eV and 335.4 eV corresponding to Pd 3d_{3/2} and 3d_{5/2} from Pd⁰ respectively (Fig. S3[†]), the electron density of Pd-TA nanoparticles is redistributed, leading to electron deficiency. As for the XPS spectrum of C1s (Fig. 2c), three typical peaks at BEs of 284.5, 285.8 and 288.5 eV are separately assigned to C-H, C-O and O=C-O.20 The O 1s spectrum (Fig. 2d) can be resolved into three peaks at BEs of 531.4, 532.3 and 533.1 eV, which are assigned to the C=O, O-H and C-O species, respectively.21 These results provide a piece of clear evidence to support the formation of TA-modified Pd nanoparticles. In the Fourier transform infrared (FT-IR) spectra (Fig. S4[†]), the broad peak in the region of 3100–3600 cm⁻¹ for Pd-TA can be attributed to the stretching vibration of the abundant aromatic hydroxyls in TA. Other



Fig. 2 (a) XPS survey spectrum of Pd-TA nanoparticles. XPS spectra of Pd-TA nanoparticles in the (b) Pd 3d, (c) C 1s, and (d) O 1s regions of Pd-TA.

characteristic peaks, such as 1714 cm⁻¹ (conjugated C=O stretching vibration), 1447 cm⁻¹ (aromatic C=C stretching vibration), 1317 cm⁻¹, 1196 cm⁻¹ (C–O stretching), and 756 cm⁻¹ (C–H out-plane bending) appeared in the spectrum of Pd-TA, also confirming the successful modification of Pd by TA.²²

To evaluate the NRR performance of Pd-TA nanoparticles, electrochemical measurements were carried out in N2-saturated 0.1 M Na₂SO₄ solution using a two-compartment electrochemical cell separated by a Nafion 117 membrane. Pd-TA nanoparticles deposited on carbon paper (Pd-TA/CP; Pd-TA loading: 0.2 mg cm^{-2}) was used as the working electrode and Ag/AgCl and a graphite rod were used as the reference electrode and counter electrode, respectively. All NRR tests were carried out under ambient conditions and the potentials were all reported on a RHE scale. The desired product NH₃ and possible byproduct N₂H₄ were determined according to previous reports.23,24 Their detecting calibration curves are shown in Fig. S5 and S6.[†] Fig. S7[†] shows the linear sweep voltammetry (LSV) curves for Pd-TA/CP in Ar- and N2-saturated 0.1 M Na2SO4 solution. It is clearly seen that Pd-TA/CP attains a higher current density in N2-saturated solution, indicating that it is active to catalyze N2 electroreduction. As shown in Fig. 3a, timedependent current density curves for Pd-TA/CP in N2-saturated 0.1 M Na₂SO₄ indicate that the current densities remain almost unchanged for 2 h. Fig. 3b shows the UV-vis absorption spectra at different potentials after 2 h electrolysis. Clearly, the electrocatalytic NRR process occurs in a potential range from -0.30 V to -0.55 V. When electrolyzed at -0.45 V, the electrolyte shows the highest absorbance intensity. Corresponding NH₃ yields and FEs at various potentials are plotted in Fig. 3c. With the potential decreasing to -0.45 V, the maximum NH₃ yield and the highest FE reach 24.12 $\mu g \ h^{-1} \ m g_{cat.}^{~-1}$ and 9.49%, respectively. When the potential is more negative, both the NH₃ yield and FE decrease considerably, which is due to the competitive reaction of N2 and H2 on the working electrode



Fig. 3 (a) Time-dependent current density curves of Pd-TA nanoparticles at a series of potentials for 2 h in N₂-saturated 0.1 M Na₂SO₄. (b) UV-vis absorption spectra of the electrolytes stained with indophenol indicator after NRR electrolysis at different potentials for 2 h. (c) FEs and NH₃ yields of Pd-TA/CP for the NRR at different potentials. (d) Amounts of NH₃ generated with different electrodes after 2 h electrolysis at a potential of -0.45 V.

surface.^{25,26} Therefore, the potential at -0.45 V is selected as the optimum potential of the reaction for further studies. Of note, the performance of this catalyst rivals the performances of reported noble-metal Au nanorods (6.04 μ g h⁻¹ mg_{cat.}⁻¹; 4.0%),¹² Au sub-nanoclusters on TiO₂ (21.4 μ g h⁻¹ mg_{cat.}⁻¹; 8.11%),¹³ Pd/ C (4.5 μ g h⁻¹ mg_{cat.}⁻¹; 8.2%),¹⁶ Pd_{0.2}Cu_{0.8}/rGO (2.80 μ g h⁻¹ $mg_{cat.}^{-1}$; N/A),¹⁷ and Ag nanosheets (2.83 µg h⁻¹ mg_{cat.}⁻¹; 4.8%),²⁷ as well as many other reported earth-abundant NRR electrocatalysts, including hexagonal BN nanosheets (22.4 µg h^{-1} mg_{cat.}⁻¹; 4.7%),²⁴ γ -Fe₂O₃ (0.21 µg h^{-1} mg_{cat.}⁻¹; 1.9%),²⁸ MnO (7.92 µg h⁻¹ mg_{cat.}⁻¹; 8.02%),²⁹ Ti₃C₂T_x (T = F, OH) MXene nanosheets (20.4 μ g h⁻¹ mg_{cat.}⁻¹; 9.3%),³⁰ CoP hollow nanocages (10.78 $\mu g~h^{-1}~mg_{cat.}^{-1};$ 7.36%), 31 cubic sub-micron SnO_2 $(4.03 \ \mu g \ h^{-1} \ m g_{cat.}^{-1}; 2.17\%)$,³² boron nanosheets (13.22 $\mu g \ h^{-1}$ $mg_{cat.}{}^{-1}\!;$ 4.04%), 33 Mn_3O_4 nanoparticles@reduced graphene oxide (17.4 μ g h⁻¹ mg_{cat.}⁻¹; 3.52%),³⁴ oxygen-doped carbon nanosheets (20.15 μ g h⁻¹ mg_{cat.}⁻¹; 4.97%),³⁵ etc. Table S1† gives a detailed comparison of NRR performances with some reported aqueous-based NRR catalysts under ambient conditions. Fig. 3d compares the amount of NH₃ generated $(m_{\rm NH_2})$ over bare CP, Pd nanoparticles deposited on CP (Pd/CP) and Pd-TA/CP. Obviously, bare CP shows poor activity and Pd-TA/CP is much superior in NRR activity compared to Pd/PC. Of note, N2H4 was not detected in the electrolytes after 2 h electrolysis at all potentials and after 24 h electrolysis at -0.45 V (Fig. S8[†]), indicating that Pd-TA/CP is highly selective for NH₃ formation.

Considering the possible presence of NH_3 in the supplying gas and atmosphere, we tested Pd-TA/CP in N₂-saturated solution at an open circuit potential and Ar-saturated solution at -0.45 V. No apparent NH_3 was detected for both cases (Fig. S9 and S10†), confirming that the detected NH_3 was indeed generated from the NRR process over Pd-TA/CP. To further verify that there are no impurities that were stained with indophenol indicator and had an effect on the measurement results, we further performed NRR electrolysis at -0.45 V with alternating 2 h cycles between N₂-saturated and Ar-saturated electrolytes for a total of 12 h. As observed in Fig. 4a, NH₃ was only obtained in N₂-saturated electrolyte. Fig. 4b shows the relationship between NH₃ yield and reaction time at -0.45 V over Pd-TA/CP, revealing that NH₃ yield increases almost linearly with the reaction time. All these results indicate that the NH₃ generated is indeed derived from the NRR process of Pd-TA nanoparticles rather than other impurities.

Durability and stability are also important factors in evaluating the catalytic performance of an electrocatalyst. As shown in Fig. 4c, both NH₃ yields and FEs of Pd-TA/CP have a small variation during consecutive recycling tests performed 7 times at -0.45 V, proving the high stability of Pd-TA/CP for the electrochemical NRR. Under sustained N2, 24 h electrolysis of Pd-TA/CP at a potential of -0.45 V only leads to a slight decrease in current density (Fig. 4d), further indicating the excellent stability of Pd-TA/CP with current densities maintained for 24 h during the electrochemical NRR process. We further determined the NRR performance after the 2 h NRR test at -0.45 V in a fresh N2-saturated electrolyte using Pd-TA/CP that has already been used in 24 h NRR electrolysis. As shown in Fig. S11,† the UV-vis absorption spectrum for the electrolyte has approximately the same intensity as that shown in Fig. 3b, suggesting that Pd-TA/CP is still highly active for the NRR. Furthermore, we provided the photographs of pH test papers of the Na₂SO₄ aqueous solution before and after 2 h electrolysis (Fig. S12[†]). Results indicate that there is almost no change of pH in our experiment. Meanwhile, the TEM image of Pd-TA nanoparticles after the stability test (Fig. S13[†]) shows almost no obvious change in morphology. The XRD pattern (Fig. S14†) also remains unchanged after NRR electrolysis. Moreover, XPS analyses (Fig. S15[†]) reveal that the valence states remain



Fig. 4 (a) NH₃ yields and FEs of Pd-TA nanoparticles at a potential of -0.45 V with alternating 2 h cycles between N₂-saturated and Arsaturated electrolytes with a total of 12 h. (b) Curve of NH₃ production vs. reaction time at -0.45 V over Pd-TA/CP. (c) NH₃ yields and FEs at -0.45 V during the recycling test performed 7 times. (d) Time-dependent current density curve for Pd-TA/CP at -0.45 V.

unchanged after the long-term stability test. The results indicate that there is almost no change of pH in our experiment. All these results confirm that Pd-TA nanoparticles are an extraordinarily stable NRR electrocatalyst under ambient conditions.

In summary, the Pd-TA nanoparticles have been proven experimentally to be an efficient electrocatalyst for ambient N₂ fixation to NH₃ with excellent selectivity. In 0.1 M Na₂SO₄, they achieve a large NH₃ yield of 24.12 μ g h⁻¹ mg_{cat.}⁻¹ with a high FE of 9.49% at a potential of -0.45 V vs. RHE. Notably, they also exhibit strong electrochemical and structural stability. This work not only provides us an attractive catalyst material for efficient NH₃ electrosynthesis, but would open up an exciting new avenue to explore small molecules for surface modification of metal catalysts toward enhanced N₂ fixation.

Conflicts of interest

There are no conflicts to declare.

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