Atomically ordered PdCu electrocatalysts for selective and stable electrochemical nitrate reduction

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Abstract

Electrochemical nitrate reduction (NO₃ RR) has attracted attention as an emerging approach to mitigate nitrate pollution in groundwater. Here, we report that a highly ordered PdCu alloy-based electrocatalyst exhibits selective (91% N₂), stable (480 hours), and near complete (94%) removal of nitrate without loss of catalyst. In situ and ex situ XAS provide evidence that structural ordering between Pd and Cu improves long-term catalyst stability during NO₃RR. In contrast, we also report that
a disordered PdCu alloy-based electrocatalyst exhibits non-selective (49% N\textsubscript{2} and 49% NH\textsubscript{4}\textsuperscript{+}), unstable, and incomplete removal of nitrate. The copper within disordered PdCu alloys is vulnerable to accepting electrons from hydrogenated neighboring Pd atoms. This resulted in copper catalyst losses which were 10x greater than that of the ordered catalyst. The design of stable catalysts is imperative for water treatment because loss of the catalyst adds to the system cost and environmental impacts.

**Keywords**

Electrochemical nitrate reduction, nitrogen, ammonia, intermetallic PdCu, in-situ XAS, long-term stability
The introduction of anthropogenic nitrogen fertilizers has increased nitrate accumulation in groundwater, negatively affecting human health.\textsuperscript{1,2} The World Health Organization has regulated a maximum contaminant level of 10 mg L\textsuperscript{-1} for NO\textsubscript{3}\textsuperscript{-} and 0.3 mg L\textsuperscript{-1} for NO\textsubscript{2}\textsuperscript{-} in drinking water. Although biological treatment at centralized wastewater treatment facilities is the dominant nitrate treatment approach, there is growing interest in designing technologies to treat nitrate contamination near the source of the pollution. Electrochemical conversion of nitrate pollution is an emerging approach that is designed to meet this need.\textsuperscript{3,4} However, most catalyst examinations related to the electrocatalytic conversion of nitrate focus solely on designing a highly selective catalyst.\textsuperscript{1} While selectivity is important, the use of downstream separations can aid in the tuning of product purity. Therefore, from a catalysis perspective, material stability may be most important to reduce the cost of the system and prevent additional contamination.\textsuperscript{5}

Copper is the state-of-art high activity catalyst for NO\textsubscript{3}\textsuperscript{-} RR in neutral and alkaline media.\textsuperscript{6} Whether copper is incorporated in a solid molecular hybrid catalyst or appears as an oxide, the element achieves effective nitrate conversion with good selectivity toward ammonia.\textsuperscript{7,8} However, copper passivation is common in the presence of chloride and copper oxide is desabilized in the presence of ammonium through the formation of a soluble [Cu(NH\textsubscript{3})\textsubscript{6}]\textsuperscript{2+} complex.\textsuperscript{9} This results in rapid deactivation and loss of Cu, which could inhibit the practical long-term use of Cu for the reduction of nitrate.\textsuperscript{6,10} The most common approach to stabilizing copper is to incorporate copper into an alloy.

Pd-Cu-based alloys have been found to be potentially ideal for NO\textsubscript{3}\textsuperscript{-} conversion to nitrogen gas.\textsuperscript{11–15} The primary advantage of binary PdCu alloys is that Cu strongly adsorbs nitrate, reducing NO\textsubscript{3}\textsuperscript{-} to NO\textsubscript{2}\textsuperscript{-} and NO. Then, NO spills from the Cu site to the Pd sites, where NO couples to form N\textsubscript{2}.\textsuperscript{16,17} Here, hydrogenated Pd sites are essential to directly convert NO\textsubscript{2}\textsuperscript{-} to N\textsubscript{2} and recover metallic Cu from CuO. Cu sites have a tendency to act as an electron donor to reduce NO\textsubscript{3}\textsuperscript{-}.\textsuperscript{14,18–20} Despite the clear promise of intermetallic electrocatalyst\textsuperscript{21–25} few mechanistic studies and long-term stability investigations have been carried out to assess
catalyst stability during reduction of nitrate and nitrite.

Here, we examine the electrochemical and catalytic mechanisms that promote instability of PdCu alloys. We specifically examine how the ordered atomic level can allow for high degrees of selectivity and stability during NO$_3^-$ conversion. The use of ex situ and in situ XAS provides insight into the mechanism responsible for catalyst loss in disordered PdCu alloys.

To obtain the atomic-level PdCu alloy structure, we first prepared randomly disordered PdCu NPs on a carbon support (denoted D-PdCu / C) and then annealed the catalysts at temperatures ranging from 200 to 600 °C. We characterized the crystal phase by XRD (Supplementary Figure S1). The face-centered cubic (FCC) phase peaks at 41.4°, 48.2°, 70.5°, and 85.3° correspond to (111), (200), (220), and (311) facets. The body-centered cubic (BCC) phase peaks at 29.8°, 42.7°, 52.8°, 62.0° and 78.0° correspond to (100), (110), (111), (200), and (211) facets. The D-PdCu / C catalyst showed a BCC structure, with the main peak at 42.7° represented for the (110) facet. With increasing annealing temperature, the phase of the FCC(111) and the CsCl structure typed BCC(110) of PdCu emerge. The peaks at higher temperatures were very sharp, mainly because of the larger nanoparticle (NP) size formed by agglomeration. The degree of ordering and crystallinity depend on the annealing temperature, and this was used to control the ratio of FCC and BCC phase structure (F/B). Here, we will focus on examining two highly ordered structures of PdCu obtained by annealing the prepared D-PdCu/C catalyst at 500 °C (denoted O1-PdCu / C) and 600 °C (denoted O2-PdCu / C). O2-PdCu/C showed a higher F / B ratio (0.96) compared to O1-PdCu / C (0.76) and D-PdCu / C (0), as estimated by the two main exposed peaks at 41.5° and 42.8°.

The uniformly distributed D-PdCu NPs on the carbon support showed an average NP size (4.3 nm), as measured by TEM images (Supplementary Fig. 2). After annealing at 500 °C, the O1-PdCu / C catalysts showed an average NP size of 5.3 nm. O2-PdCu / C (annealed at 600 °C) exhibited a large average NP size (9.5 nm) and included the largest
Fig. 1. Morphology of O1-PdCu/C (annealed at 500 °C). HRTEM, STEM, fast Fourier transform (FFT) images of O1-PdCu NPs (a-i). Atomically well-ordered structure of Pd and Cu atoms in HRTEM, STEM and EDS mapping results (j-l). NPs over 20 nm. As the annealing temperature increased above 500 °C, the catalyst showed severe NP agglomeration within the heating range between 500 and 600 °C, resulting in the transformation of the more FCC structure from the original BCC structure.
Aberration-corrected bright-field (BF) and high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) images and energy-dispersive X-ray spectroscopy (EDS) maps in Fig. 1 clearly demonstrate the ordered phase at the atomic level of O1-PdCu NPs. Representative small NPs and large NP showed both ordered cubic CsCl structure typed BCC(110) phases. The alternating contrast between atomic columns in the HAADF-STEM image is consistent with Pd and Cu ordering atoms (Fig. 1j, k), as confirmed by the EDS mapping results in Fig. 1l that display the alternating atomic columns of Pd (green) and Cu (red). The chemical composition of the pristine O2-PdCu / C, O1-PdCu / C and D-PdCu / C powder catalysts showed a ratio close to 1: 1 for Pd and Cu, measured by ICP-MS (Supplementary Table 1).

Next, we will evaluate the electrocatalytic performance of nitrate (NO$_3$RR) and nitrite reduction (NO$_2$RR) (Fig. 2a, b), with the activity reported in terms of a partial current density collected at -0.5 $V_{RHE}$ (Supplementary Fig. 4). Commercial Pd / C showed the highest hydrogen evolution reaction (HER) activity (5.53 mA cm$^{-2}$) as well as NO$_3$RR activity (9.03 mA cm$^{-2}$). D-PdCu / C exhibited lower HER activity (3.90 mA cm$^{-2}$) than commercial Pd / C because Cu prohibits the proton adsorption necessary for HER. The D-PdCu/C catalyst showed higher NO$_3$RR activity (15.5 mA cm$^{-2}$) than commercial Pd / C. O1-PdCu / C exhibited the highest NO$_3$RR activity (20.2 mA cm$^{-2}$) and an obvious reduction peak of NO$_2^−$ around -0.5 $V_{RHE}$, while HER activity (4.13 mA cm$^{-2}$) was slightly higher than that of D-PdCu/C (3.90 mA cm$^{-2}$). This indicates that the atomically ordered structure of Pd and Cu showed a higher NO$_3$RR performance due to the creation of multiple active sites on the exposed Pd and Cu atoms, as well as due to electronic modifications. The O2-PdCu/C catalyst showed the lowest current density toward both HER (0.86 mA cm$^{-2}$) and NO$_3$RR (1.06 mA cm$^{-2}$); however, this was largely attributed to the size of NP that significantly reduced the ECSA.

Regarding nitrite reduction, commercial Pd / C unsurprisingly showed the best NO$_2$RR performance (8.84 mA cm$^{-2}$) because the Pd catalyst is favorable for NO$_2$RR. The D-
Fig. 2. Electrocatalytic performance of (a) NO$_3$RR and (b) NO$_2$RR. Blank LSV curves (dashed line) for HER were collected in Ar-purged 0.05 M Na$_2$SO$_4$ electrolyte in absence of nitrate and nitrite ions. NO$_3$RR and NO$_2$RR activity (solid line) were measured in Ar-purged 0.05 M Na$_2$SO$_4$ + 20 mM NO$_3^-$ and 0.05 M Na$_2$SO$_4$ + 2 mM NO$_2^-$. (c) PdO reduction method to estimate ECSAs of O2-PdCu/C, O1-PdCu/C, D-PdCu/C, and commercial Pd/C catalysts. O1-PdCu/C: (d) NO$_3^-$ conversion yield and N$_2$/NH$_4^+$ selectivity, and (e) stability. D-PdCu/C: (f) NO$_3^-$ conversion yield and N$_2$/NH$_4^+$ selectivity, and (g) stability. Each measurement was 24 h of electrolysis in an Ar purged 0.05 M Na$_2$SO$_4$ + 100 ppm NO$_3^-$-N electrolyte.

PdCu/C demonstrated indistinguishable NO$_2$RR activity (4.44 mA cm$^{-2}$) and HER activity (3.90 mA cm$^{-2}$). The larger O2-PdCu/C catalyst showed the lowest current density for NO$_2$RR (1.12 mA cm$^{-2}$). Overall the O2-PdCu/C catalyst had nearly identical performance for nitrate and nitrite reduction (Fig. 2a,b). We should note that we estimated the ECSAs for all catalysts using PdO reduction area measurement and TEM analysis, and summarize the values in Supplementary Table 2.

The O1-PdCu/C catalyst showed the highest NO$_3^-$ conversion (98%) at -0.5 V$_{RHE}$ (Fig. 2c).
2d), which is in agreement with the LSV curves for NO$_3$RR (Fig. 2a). O1-PdCu/C produced the highest N$_2$ selectivity (92%) at 0.5 V$_{RHE}$ (Fig. 2d). Thus, the atomically ordered structure of Pd and Cu is favorable for electrochemical denitrification, not for NH$_4^+$ synthesis. The D-PdCu/C catalyst exhibited 59.4% of NO$_3^-$ conversion with 55% of the formed products being N$_2$ and 34% of of the formed products being NH$_4^+$ (Fig. 2f). Disordered PdCu NPs have more Cu clusters on the surface than well-ordered PdCu NPs. Cu clusters are known to catalyze and guide a pathway from NO$_3^-$ to NH$_4^+$ rather than N$_2$.

During electrolysis, we connected in situ mass spectrometry with the sealed chamber to verify gaseous products (Supplementary Fig. 5-7). The O1-PdCu / C and commercial Pd / C electrodes both released H$_2$ and N$_2$ as the main gaseous products, but no N$_2$O gas is detected. It should be noted that the D-PdCu / C electrode exhibited not only H$_2$ and N$_2$ as the main gaseous products, but also generated N$_2$O gas. This indicated that Cu clusters placed far from Pd sites on the surface may be responsible for the production of N$_2$O gas. The Cu sites in the highly ordered structure (O1-PdCu/C) have a close connection with their neighboring Pd atoms, which allows for the reduction of adsorbed N$_2$O to N$_2$, resulting in high N$_2$ selectivity.

Long-term electrolysis is necessary to achieve a practical application. O1-PdCu/C electrode showed outstanding stability with a uniform NO$_3^-$ conversion (93-98%) and N$_2$ selectivity (85-92%) over 20 cycles of repeated electrolysis tests for 480 h electrolysis. The final cycle electrolysis of O1-PdCu/C showed excellent NO$_3^-$ conversion (94%) and N$_2$ selectivity (91%). On the other hand, the D-PdCu / C electrode exhibited a dynamic change in terms of the NO$_3^-$ conversion and N$_2$/NH$_4^+$ selectivity. The initial 8 cycles showed a slight enhancement in the conversion of NO$_3^-$ (59%→65%) and NH$_4^+$ selectivity (34%→49%). There is also a slight decrease in selectivity for N$_2$ (55%→44%). This finding implies that surface Cu atoms could undergo an oxidation process more easily with the disordered catalyst during the NO$_3$RR electrolysis. Prior reports have shown that oxidized copper has excellent NH$_4^+$ selectivity and NO$_3^-$ conversion. From 8 to 20 cycles, we found a continuous decay of NO$_3^-$
conversion (65% → 44%) and NH$_4^+$ selectivity (49% → 18%) while there is an enhancement of N$_2$ selectivity (44% → 79%). For the D-PdCu/C catalyst, a dissolution of the oxidized Cu occurred, which leached into the electrolyte. Thus, eventually more Pd surfaces are evolving during the long-term NO$_3$RR electrolysis, contributing to the transition in selectivity from NH$_4^+$ to N$_2$. We proposed a mechanism for O1-PdCu / C and D-PdCu / C during long-term electrochemical NO$_3$ RR in Supplementary Figure 8.

We examine the excellent structure stability of O1-PdCu/C through ICP-MS (Supplementary Table 3) and STEM results (Supplementary Fig. S9). After continuous electrolysis for up to 20 cycles, we measured the concentration of Cu and Pd in the electrolytes. D-PdCu/C represented not only a higher Cu leaching concentration (547 ppb), but also a higher Pd leaching concentration (18.2 ppb) compared to O1-PdCu/C (Cu: 42.3 ppb, Pd: 4.64 ppb). The representative of O1-PdCu NP maintained the ordered structure well after 20 repeated cycles (Supplementary Fig. S9). These findings demonstrated that O1-PdCu/C showed highly efficient NO$_3^-$ conversion and excellent N$_2$ selectivity with outstanding lifetimes in electrochemical NO$_3$RR operations.

We performed X-ray absorption spectroscopy (XAS) to examine changes in the oxidation states and coordination environment near the Pd and Cu atoms. We first demonstrated the role of PdCu ordered structure during NO$_3$RR through ex-situ and in-situ XAS measurements by using our customized cell. In situ measurements show the oxidation of Cu clusters in D-PdCu / C compared to Cu sites in O1-PdCu / C. This is ascribed to poor coordination with hydrogenated Pd sites. This is because Cu sites which provide electrons to reduce NO$_3^-$ to NO$_2^-$ become more oxidized, but neighboring hydrogenated Pd atoms are easily accessible and reduced to lower Cu oxidation states.$^{14,30,31}$ The pristine powder samples (Fig. 3 e, f) and open circuit potential (OCP) spectra (Fig. initially for both D-PdCu/C and O1-PdCu/C catalysts have slightly oxidized surfaces for Cu sites (CuOx). Using negative potentials from 0.1 to -0.7 V$_{RHE}$, the XANES spectra showed a trend for CuOx reduction to metallic Cu regardless of catalysts or the existence of NO$_3^-$ (Fig. 3a, d). This finding concluded that
Fig. 3. XAS analysis of D-PdCu/C and O1-PdCu/C catalysts. The in-situ XAS measurement of Cu K-edge for (a) D-PdCu/C and (d) O1-PdCu/C during NO₃RR in absence and presence of NO₃⁻ ions in 0.05 M Na₂SO₄ electrolyte. Normalized XANES at the (b) Pd K-edge and (e) Cu K-edge for D-PdCu/C and O1-PdCu/C catalysts before and after long-term electrolysis tests. The corresponding FT-EXAFS spectra of the (c) Pd K-edge and (f) Cu K-edge derived from (b) and (e).

1. The applied negative reduction potentials are more dominant than the oxidation of the Cu sites, as they provide electrons to reduce NO₃⁻. For ex situ measurement, Pd K-edge spectra indicated that there were no changes for both D-PdCu/C and O1-PdCu/C catalysts before and after the long-term NO₃RR operations (Fig. 3b, c). However, the ex situ characteristics of the Cu K edge after long-term electrolysis (Fig. 3e, f), D-PdCu/C showed a significant change due to the higher Cu oxidation states than that of pristine catalyst. However, the O1-PdCu/C spectra did not alter, which implies constant oxidation states before and after long-term electrolysis. These stable states of O1-PdCu/C demonstrated that intermetallic Pd and Cu nanoparticles have robust stability for long-term NO₃RR operations.

2. The structurally ordered O1-PdCu/C catalyst which featured both BCC(110) and FCC(111)
phase structures exhibited high NO$_3^-$ conversion (98%), high N$_2$ selectivity (92%), and was stable throughout the entire test period. After long-term electrolysis, ex situ XAS analysis proved that the ordered structure of PdCu remained the same and the oxidation state of copper was (Cu$_2$O). The disordered structure exhibited a higher oxidation state of Cu (CuO), resulting in severe dissolution of the copper and loss of catalyst. The intermetallic structure of PdCu provides superior interactions between the Cu and Pd sites, which contributes to excellent stability during the electrochemical conversion of nitrate.
Methods

Materials.

Palladium(II) acetylacetonate (Pd(acac)$_2$, 99%), copper(II) acetylacetonate (Cu(acac)$_2$, ≥99%), L-Ascorbic acid (C$_6$H$_8$O$_6$, 99%), and oleylamine (OA, C$_{18}$H$_{37}$N, 70%) were used for synthesizing PdCu bimetallic nanoparticles. Sodium sulfate (Na$_2$SO$_4$, ≥99%), sodium nitrate (NaNO$_3$, ≥99%), and sodium nitrite (NaNO$_2$, ≥99%) were utilized as neutral pH electrolytes, nitrate, and nitrite sources. Phosphoric acid (H$_3$PO$_4$, ≥85%), sulfanilamide (C$_6$H$_8$N$_2$O$_2$S, ≥98%), and N-(1-Naphthyl) ethylenediamine dihydrochloride (C$_{12}$H$_{14}$N$_2$, ≥98%) were used for a color agent for nitrite measurement. Sodium hydroxide (NaOH, ≥97%), salicylic acid (C$_7$H$_6$O$_3$, ≥99%), sodium citrate dihydrate (C$_6$H$_5$Na$_3$O$_7$.2H$_2$O, ≥99%), sodium nitroferricyanide(III) dihydrate (C$_5$FeN$_6$Na$_2$O.2H$_2$O, ≥99%), and sodium hypochlorite solution (NaClO, ≥98%) were considered as the indophenol blue method for ammonium measurement. Above all materials were purchased from Sigma-Aldrich. Nitarte TNTplus test kit was obtained from HACH and Vulcan XC-72R carbon support was purchased from Cabot Corporation. Nafion membrane was obtained from Fuel Cell Store Company. Ultrapure water (18.2 MΩ) was purified from Millipore Milli-Q.

Synthesis of ordered PdCu bimetals.

The procedure to synthesize the ordered structure of PdCu comprises two steps. First, we prepared randomly disordered PdCu bimetallic nanoparticles supported by Vulcan XC-72R carbon (D-PdCu/C) by means of simple one-pot method. The D-PdCu/C catalyst was synthesized without using any capping agents and surfactants. In detail, 15.2 mg of Pd (acac)$_2$, 26.6 mg of Cu (acac)$_2$, 71.2 mg of L-ascorbic acid (AA), 13 mL of oleylamine (OA), and 40 mg of Vulcan XC-72R were used as Pd and Cu precursors, reducing agent, solvent, and carbon support. After a solvothermal reduction process at 200 °C for 12 h, the disordered PdCu alloy catalyst was obtained and the bimetal NPs were uniformly dispersed.
on the carbon support. We conducted various heat treatments from 200 to 500 °C for 1 h under the reductive atmosphere (4 % H₂, and 96 % Ar flow) to search the atomically ordered nanoparticles of Pd and Cu.

**Characterization of ordered PdCu catalysts.**

X-ray powder diffraction (XRD) patterns were collected using PANalytical Empyrean XRD system for crystalline identification with Cu Kα radiation (λ = 1.54051 Å). TEM images were obtained by FEI Tecnai F20 at 200 kV operation. The aberration corrected high-angle annular dark-field scanning TEM (HAADF-STEM) combined with complementary energy dispersive X-ray spectroscopy (EDS) was performed on a JEOL NEOARM operated at 200 kV. All TEM grid samples were prepared by drop casting on a gold grid (Electron Microscopy Science Co.), and then dried under ambient conditions. Inductively coupled plasma mass spectrometer (ICP-MS, PerkinElmer Elan DRC) was used to determine the ratio of Pd and Cu atoms, and measure the leaching concentrations of Pd and Cu after long-term electrolysis. The X-ray absorption spectroscopy (XAS) spectra at Pd k-edge and Cu k-edge were measured from 8-ID (ISS) Beamline National Synchrotron Light Source II at Brookhaven National Laboratory, using a Si (111) double crystal monochromator and a passivated implanted planar silicon fluorescence detector at room temperature, with energy calibrated using Pd foil and Cu foil. The catalyst samples were sealed in Kapton films for ex-situ XAS measurements and our customizing designed cell was used for in-situ XAS measurements. All X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) data were analyzed using the Athena and Artemis software for conversion of raw data to μ(E) spectra, background subtraction and normalization, Fourier transformation and plotting, and fitting in k-space and R-space.
Electrochemical performance test on ordered PdCu catalysts.

Electrochemical NO$_3$RR and NO$_2$RR were measured using the three-electrode electrochemical cell (Pine Research Instrumentation) connected with a potentiostat. We prepared catalyst inks to deposit on a glassy carbon electrode as a working electrode for measurement by ring disk electrode (RDE). Each catalyst was dissolved into each solvent, which is an addition of Nafion ionomer solution (5 wt%, 20 $\mu$L mL$^{-1}$) in a mixture of ultrapurewater and isopropanol alcohol (1.5 mg mL$^{-1}$). The Pd metal loading on the GCE was set to 15 $\mu$g$_{Pd}$ cm$^{-2}$ confirmed by ICP-MS and the deposited ink was dried under ambient conditions. Ag/AgCl (saturated potassium chloride) and Pt wire were selected as a reference electrode and counter electrode, respectively. All reported potentials were reversible hydrogen electrode (RHE) calibrated by using hydrogen gas purging into the electrolyte and Pt electrode. We collected all LSV curves after electrochemical surface cleaning by sweeping potentials from -0.4 to 0.8 V$_{RHE}$ for 200 cycles in 0.05 M Na$_2$SO$_4$ solution. To avoid the possible attached hydrogen bubble produced by HER during the NO$_3$RR and NO$_2$RR measurement, we rotated the RDE at 1000 rpm and operated the LSV experiments at a scan rate of 50 mV s$^{-1}$. The LSV experiment was initiated at 0.2 V$_{RHE}$ and repeated in a potential range of -0.2 to 0.8 V$_{RHE}$. Ar gas was continuously purged in the electrolyte to establish inert conditions by eliminating any oxygen that might remain in the electrolyte. For screening of NO$_3$RR and NO$_2$RR activity for all catalysts, we added 20 mM NO$_3$ or 2 mM NO$_2$ into 0.05 M Na$_2$SO$_4$ electrolyte and collected the LSV data from the first LSV curve. During the 50 cycles operation, no significant changes of LSV curves were detected. We examined the possible ion and gaseous products for selectivity of all catalysts by using electrolysis tests in a two-chamber electrolytic cell that connected with the potentiostat and in-situ mass spectrometry. The working electrode (0.25 cm$^2$) and Ag/AgCl reference electrode were placed in the cathode chamber under Ar condition. The Pt wire counter electrode was placed in the anode chamber. The electrolytes in the cathode were 0.05 M Na$_2$SO$_4$ + 100 ppm of NO$_3^-$-N electrolyte, and the anode chamber was 0.05 M Na$_2$SO$_4$ electrolyte. We measured
NO$_3^-$ conversion yield, and selectivity of N$_2$, NO$_2^-$, and NH$_4^+$ for D-PdCu/C and O1-PdCu/C catalysts in different applied potentials through Chronoamperometry (CA) at -0.1, -0.3, -0.5, and -0.7 VRHE. After the electrolysis for 24 h at each applied potential, we measured remained NO$_3^-$ from the initial 100 ppm of NO$_3^-$ in the electrolyte to calculate the NO$_3^-$ conversion yield. Long-term electrolysis for stability testing was conducted at -0.5 VRHE electrolysis for 24 h and repeated for 20 cycles (total 480 h electrolysis).

**ECSA calculation.**

The ECSA$_{PdO}$ values were calculated from the integration of the Pd oxide reduction region around 0.6 VRHE in Fig. 2c. This is the most extended approach to determine ECSA of Pd-based catalysts.$^{32,33}$ We also estimated the ECSAs for all catalysts measured by TEM measurement. We counted the diameter of nanoparticles ($d_i$) over 200 individual nanoparticles and measured the number($l_i$)-averaged particle sizes, $d_N$.

$$d_N = \frac{\sum_i^n l_i \cdot d_i}{\sum_i^n l_i}$$  \hspace{1cm} (1)

We used $d_S$ for the surface averaged diameter and metal density ($\rho_{metal}$) of Pd (12.02 g cm$^{-3}$) and Cu (8.96 g cm$^{-3}$) to calculate ECSA$_{TEM}$, assuming all nanoparticles have a spherical shape.

$$\text{ECSA}_{TEM} = \frac{6}{\rho_{metal} \cdot d_S}$$  \hspace{1cm} (2)

$$d_S = \frac{\sum_i^n l_i \cdot d_i^3}{\sum_i^n l_i \cdot d_i^2}$$  \hspace{1cm} (3)
Product analysis.

Titration technique was used to quantify the ion concentrations of \( \text{NO}_3^- \), \( \text{NO}_2^- \) and \( \text{NH}_4^+ \). The extracted small amount of solutions from the electrolysis were properly diluted and placed into the thin-layer quartz cuvettes to measure the adsorption intensity detected by the ultraviolet-visible (UV-Vis) spectrophotometer. Each calibration curve was collected from each adsorption intensity and wavelength (345 nm for \( \text{NO}_3^- \), 540 nm for \( \text{NO}_2^- \), and 655 nm for \( \text{NH}_4^+ \)). The details for preparing color agents and each ion product measurements were described in our previously reported paper.\textsuperscript{34,35} We attached an in-situ mass spectrometer (Cirrus 2, MKS Instruments) to the sealed chamber cell for investigating the gaseous products. After stabilizing the gas analyzer signal, we operated the gas analyzer during the electrolysis purged by ultrahigh purity Ar carrier gas at a 20 mL min\(^{-1}\).

Calculation of \( \text{NO}_3^- \) conversion rate and \( \text{N}_2 \) selectivity.

\[
\text{NO}_3^- \text{ Conversion rate} = \frac{\Delta C(\text{NO}_3^-)}{C_0(\text{NO}_3^- - N)} \times 100\% \quad (4)
\]

\[
S(\text{NO}_2^-)\% = \frac{C_t(\text{NO}_2^- - N)}{\Delta C(\text{NO}_3^- - N)} \times 100\% \quad (5)
\]

\[
S(\text{NH}_4^+)\% = \frac{C_t(\text{NH}_4^+ - N)}{\Delta C(\text{NO}_3^- - N)} \times 100\% \quad (6)
\]

\[
S(\text{N}_2)\% = \frac{\Delta C(\text{NO}_3^- - N) - C_t(\text{NO}_2^- - N) - C_t(\text{NH}_4^+ - N)}{\Delta C(\text{NO}_3^- - N)} \times 100\% \quad (7)
\]
\( \Delta C_0(\text{NO}_3^-) \) is the difference of \( \text{NO}_3^- \) concentrations between before and after the electrolysis tests, \( C_0 \) is the initial \( \text{NO}_3^- \) concentration. The \( C_t \) is a change of concentration after the electrochemical reduction time, and \( \text{N}_2 \) selectivity is estimated from the total nitrogen mass balance, considering \( \text{NO}_3^- \)-N, \( \text{NO}_2^- \)-N and \( \text{NH}_4^+ \)-N as main products. The electrolyte volume in the cathode compartment is 20 mL of 0.05 M \( \text{Na}_2\text{SO}_4 \) including 100 ppm of \( \text{NO}_3^- \)-N.

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**Supporting Information Available**

Methods of are presented in the supporting information.

The material is available and free of charge via the Internet at https://pubs.acs.org/

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