BNL-229312-2026-JAAM

Decoupling size and surface effects of intermetallic CuPd nanocrystals for electrocatalytic nitrate reduction to ammonia

L. Zhang, L. Ma

To be published in "Chem Catalysis"

December 2025

Photon Sciences

Brookhaven National Laboratory

U.S. Department of Energy

USDOE Office of Science (SC), Basic Energy Sciences (BES). Scientific User Facilities (SUF)

DISCLAIMER

Decoupling Size and Surface Effects of Intermetallic CuPd Nanocrystals for Electrocatalytic Nitrate Reduction to Ammonia

Liyue Zhang[1,6], Zaheer Masood[2,6], Qiang Gao[1], Min-chul Kang[3], Xiangru Wei[1], Yulu Zhang[1], Zhanrong Guo[1], Yizhen Chen[1], Lu Ma[4], Huiyuan Zhu[1], Lin Zhou[3,5], Bin Wang[2]*, Sen Zhang[1,7]*

[1] Department of Chemistry, University of Virginia, Charlottesville, VA 22904, USA
[2] School of Sustainable Chemical, Biological and Materials Engineering, University of Oklahoma, Norman, OK 73019, USA
[3] Ames National Laboratory, Ames, IA 50011, USA
[4] National Synchrotron Light Source II, Brookhaven National Laboratory, Upton, NY 11973, USA
[5] Department of Materials Science and Engineering, Iowa State University, IA 50011, USA
[6] These authors contributed equally
[7] Lead contact
* Correspondence: B.W: wang_cbme@ou.edu; S.Z: sz3t@virginia.edu

The lead contact of this work is Prof. Sen Zhang (sz3t@virginia.edu).

Summary

Nitrate pollution poses a major environmental challenge, but its electrochemical conversion to ammonia offers a sustainable waste-to-value solution. Here, we synthesized monodisperse, size-tunable B2-phase CuPd intermetallic nanocrystals (6–46 nm) and studied their performance in the electrochemical nitrate reduction reaction (eNO_3RR). By using bromide ions to modulate Pd reduction and applying mild annealing, we achieved phase-pure B2 structures across all sizes. Catalytic testing revealed a volcano-like trend in ammonia yield, peaking at 33 nm nanocubes with a rate of 6.97 mol h^{-1} g^{-1} at −0.6 V vs. RHE. This optimum reflects a balance between the increased surface area of smaller particles and the enhanced exposure of active (100) facets in larger ones. Theoretical calculations indicated that the B2-CuPd (100) facet is favorable for nitrate adsorption, thereby supporting the high activity of nanocubes. Our results highlight the critical role of tuning both nanoparticle size and surface structure to maximize eNO_3RR efficiency.

Introduction

Nitrate from agricultural runoff and industrial discharge is a major contributor to eutrophication in aquatic systems, leading to severe environmental and ecological consequences[1, 2]. To help mitigate

nitrate pollution and restore the human-disrupted nitrogen cycle, the electrochemical nitrate reduction reaction (eNO_3RR) has emerged as a promising waste-to-value strategy that converts nitrate into valuable products, particularly ammonia[3-6]. Ammonia, a critical industrial chemical and key fertilizer component with an annual market size of 175 million tons, is predominantly produced via the Haber-Bosch process[7]. However, this method consumes 1–2% of global energy annually (5.5 EJ) and contributes 1.5% of global greenhouse gas emissions (450 million metric tons) due to the associated energy-intensive steam-reforming process for hydrogen production[8]. In addition to its environmental benefit, eNO_3RR to ammonia offers a sustainable alternative to the Haber-Bosch process, enabling potential energy-efficient, low-carbon production while supporting decentralized chemical manufacturing[9].

Cu is a representative catalyst for eNO_3RR with a reasonable efficiency[10-15]. Alloying Cu with other metals (e.g., Pd, Pt, Ni) can improve ammonia selectivity[16-21], either by enhancing NO_3^- adsorption or by leveraging favorable hydrogen adsorption through ligand or ensemble effects[22-24]. Among these bimetallic catalysts, ordered intermetallic nanocrystals have garnered particular interest for their high chemical and structural stability, which confers excellent durability in catalysis[25-27]. More importantly, the well-defined crystal structure and composition of intermetallics facilitate mechanistic studies that can guide catalyst optimization. For example, using machine learning-assisted design, CuPd (100) surface has been reported to disrupt scaling relationship between $*NO_3$ and *N (*: adsorbed) to improve eNO_3RR efficiency—strengthening NO_3 adsorption on surface Cu while weakening N adsorption on hollow sites by subsurface Pd[21]. However, such effects have only been demonstrated in CuPd nanocrystals larger than 50 nm, as synthesizing smaller, ordered intermetallic nanocrystals remains challenging. The high reaction temperatures required for forming ordered structures at smaller scales often hinder size control[25, 28-30], while the elevated surface energy of smaller nanocrystals complicates shape and facet engineering. Consequently, a comprehensive investigation into the size and surface effects of intermetallic nanocrystals for eNO_3RR has been lacking.

In this study, we present the synthesis of ordered B2-phase CuPd nanocrystals with monodisperse and tunable sizes ranging from 6 to 46 nm and investigate their eNO_3RR performance (Figure 1). By employing bromide ions (Br^-) to modulate the reduction rate of Pd and colloidal nanocrystal growth, we achieved synchronized reduction and nucleation of Cu and Pd, facilitating the

formation of the B2 phase. Without Br^-, disordered A1-phase CuPd was obtained. Notably, direct wet-chemical colloidal synthesis produced a mix of B2 and A1 phases in nanocrystals smaller than 33 nm, but mild thermal annealing at 300 °C successfully yielded phase-pure B2 CuPd across the full-size range. The catalytic performance of B2-phase CuPd nanocrystals revealed a volcano-like trend with respect to size, peaking at 33 nm. This optimal size balances the increased surface area of smaller particles with the enhanced catalytic activity of the (100) facet, which are more prevalent in larger nanocrystals. The higher activity over the CuPd (100) facet results from upshifted d orbitals of surface Cu and shorter Cu-Cu distances that reduce the energy cost for NO_3 adsorption. At 33 nm, the B2-phase CuPd catalyst achieved a maximum ammonia yield rate of 6.97 mol h^{-1} g^{-1} at −0.6 V vs. RHE in a diluted nitrate solution (0.143 M NO_3^-, 2000 ppm N), highlighting the critical interplay between size and surface properties in optimizing eNO_3RR performance.

Results

Formation of intermetallic structure

A1-phase CuPd nanocrystals were synthesized using Cu acetylacetonate ($Cu(acac)_2$) and $Pd(acac)_2$ as precursors, which underwent co-reduction by oleylamine (OAM) with tributylphosphine (TBP) as a surfactant, following a previously reported colloidal approach[31]. Although the B2 phase is thermodynamically favored, the faster reduction rate of Pd compared to Cu under this wet-chemical condition results in a kinetically controlled growth, leading to the formation of A1-phase CuPd[32, 33]. To achieve the ordered intermetallic B2-phase nanocrystals, we hypothesized that the reduction rate of Pd should be slowed to match that of Cu. Previous studies have shown that bromide ions (Br^-) are effective modulators in reducing the growth rate of Pd nanoparticles[34]. Therefore, to synthesize B2-phase CuPd, $PdBr_2$ was used as a precursor in place of $Pd(acac)_2$ (Figure 1). By maintaining all other reaction parameters constant, the introduction of Br^- significantly reduced the reaction rate (as suggested by the retarded color change of reaction solution), promoting the formation of the thermodynamically stable B2 phase. Inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis confirmed that the Cu:Pd composition ratios of both the A1 and B2 samples were approximately 1:1 (Table S1), consistent with the precursor ratio of Cu and Pd.

Transmission electron microscopy (TEM) images revealed that both A1- and B2-phase CuPd nanocrystals, with an average size of 6 nm, were successfully synthesized using this approach (Figure 2a and 2b). The crystal structures of A1 and B2 phases were further confirmed through powder X-ray diffraction (XRD) patterns (Figure 2c). The A1-phase CuPd displayed a characteristic face-centered cubic (fcc) diffraction pattern, while B2-phase CuPd exhibited distinct peaks at $2\theta = 30.3°$, 62.5°, and 79.1°, which are characteristic of the body-centered cubic (bcc) structure[21]. Additionally, the peak with the highest intensity, located around 43°, showed a positive shift for the B2 phase compared to the A1 phase, further differentiating the two structures[35]. However, the peak exhibited a slight asymmetry, suggesting the potential presence of residual A1 phase within the B2 CuPd sample.

Size modulation of intermetallic nanocrystals

By substituting TBP with the bulkier surfactant trioctylphosphine (TOP), nanocrystals of increased size were successfully synthesized. The bulkier TOP reduces the concentration of nuclei more effectively, allowing a larger proportion of metal atoms to contribute to nanocrystal growth[36]. Specifically, varying the volume of TOP (0.4 mL, 0.6 mL, 1.0 mL, and 1.1 mL) produced CuPd nanocrystals with average sizes of 8.5±0.8 nm, 11±1.0 nm, 33±2.9 nm, and 46±4.2 nm, respectively (Figure S1). As shown in Figure 3, these nanocrystals exhibit highly uniform size distributions. Interestingly, the nanocrystals display a clear trend of shape evolution as their size increases. At 6±0.6 nm, B2-phase CuPd adopts a polyhedral shape with a spherical appearance. As the size increases, nanocubes begin to emerge, with a higher proportion observed in 11 nm B2-phase CuPd compared to the 8.5 nm counterpart. When the size reaches 33 nm, a significant conversion to nanocubes is achieved, and a similar morphology, albeit larger, is observed in 46 nm B2-phase CuPd. This size-dependent shape evolution suggests that the (100) surface becomes more stable and increasingly exposed relative to the (111) surface as nanocrystals grow[37, 38].

Size-dependent phase evolution

The XRD patterns of as-synthesized B2-phase CuPd nanocrystals (Figure 4a) confirm the formation of the B2 structure through direct synthesis, while revealing differences in the degree of structural order across various nanocrystal sizes. For 8.5 nm and 11 nm CuPd, a shoulder peak preceding the B2 (110) peak at $2\theta = 43.0°$, corresponding to the A1 (111) spacing, and a small A1

(200) peak at 2θ = 49.2° indicate the presence of residual A1-phase grains. However, when the size increases further to 33 nm and 46 nm, fully ordered B2-phase CuPd nanocrystals are obtained, with no detectable diffraction peaks corresponding to the A1 phase.

To quantify the A1 residual content in the as-synthesized B2-phase CuPd nanocrystals and elucidate its size-dependent variation, peaks around 43° were deconvoluted into subpeaks representing A1 (111) and B2 (110) (Figure S2). Their full width at half maximum (FWHM) was used to calculate the estimated sizes of domain for both A1 and B2 based on the Scherrer equation (Table S2). The A1 content was defined as the ratio of A1 domain size to total domain size, serving as a measure of size-related disorder degree. The results (Figure 4b) reveal a volcano-like trend: the A1 content increases with particle size, peaking at 11 nm, and then diminishes completely as the size reaches 33 nm.

To achieve fully ordered B2-phase CuPd nanocrystals, as-synthesized nanocrystals were loaded onto Vulcan carbon support and annealed at 300℃ under forming gas (5% H_2 balanced in Ar). The XRD patterns of post-annealed CuPd samples confirm the exclusive formation of the B2 structure, with no peaks corresponding to the A1 phase observed (Figure 5a). TEM images of the annealed B2 CuPd nanocrystals (Figure S3) reveal that the nanocrystals retained their uniform size and morphology, consistent with the pre-annealing samples. This thermal treatment was also applied to 33 nm and 46 nm B2-phase CuPd nanocrystals. While these larger sizes already exhibited a fully ordered structure directly after synthesis, annealing was performed to remove organic ligands, facilitating their use in subsequent electrocatalysis applications[39]. In contrast, thermal treatment of A1-phase CuPd nanocrystals under the same conditions did not result in complete conversion to the ordered B2 structure[35]. XRD analysis revealed residual A1 (111) peaks, indicating that a significant fraction of the A1 phase remained (Figure S4). This suggests that the presence of as-synthesized B2 domains plays a critical role in facilitating the A1-to-B2 phase conversion, enabling the structural transformation at relatively mild temperatures.

Size-dependent surface facets of nanocrystals

High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images of 11 nm and 33 nm B2 CuPd nanocrystals reveal more information on their atomic structures. A 11 nm B2 CuPd particle was observed along the [100] zone axis (ZA), and a 33 nm

B2 CuPd cube was observed along the [110] ZA, corresponding to the atomic models shown in the insets of Figure 5c and 5e, respectively. The distinct Z-contrast images reveal atom-alternating periodicity between Cu and Pd, confirming the intermetallic structure (Figure 5c, e). The measured lattice spacings of 3.07 Å and 3.04 Å correspond to the d-spacing of the B2 (100) plane. Additionally, the prominent (100) facet was observed on the surface of the 33 nm nanocube (Figure 5d). In contrast, the 11 nm polyhedral nanocrystal exhibited a mixture of exposed facets (Figure 5b). Energy-dispersive spectroscopy (EDS) elemental mapping demonstrated that Cu and Pd are homogeneously distributed across the 33 nm nanocube, which aligns with the expected B2 structure (Figures 5f-i).

The electronic interaction between Cu and Pd was elucidated through X-ray absorption near-edge structure (XANES) spectroscopy of the Pd and Cu K-edge (Figure 6a and Figure S5a). A positive shift in the Pd K-edge absorption edge relative to Pd foil indicates electron transfer from Pd to Cu (Figure 6a). To further investigate the local atomic structure, Fourier-transformed extended X-ray absorption fine structure (EXAFS) spectra of the 33 nm B2 CuPd nanocrystals were compared to those of Pd and Cu foil references. As shown in Figure 6b and S5b, the Cu–Pd distance is shorter than the Pd–Pd bond in Pd foil but slightly longer than the Cu–Cu bond in Cu foil. Quantitative EXAFS fitting was performed for both Pd and Cu K-edges (Figures 6c, 6d and Figure S6, S7), with the results summarized in Tables S3 and S4. The coordination numbers of Cu and Pd in the first shell were determined to be 7.96 and 8.10, respectively, which are lower than the value of 12 expected for bulk fcc Cu or Pd and are consistent with the theoretical value of 8 for the intermetallic B2 CuPd structure.[21] In the second shell, the coordination numbers were found to be 6.85 for Cu and 7.18 for Pd, in agreement with the theoretical value of 6 for the B2 CuPd structure. Furthermore, the fitted Cu–Pd bond distance of 2.57 Å lies between those of Pd–Pd in Pd foil (2.74 Å) and Cu–Cu in Cu foil (2.54 Å), corroborating the formation of the ordered B2 CuPd structure. And the fitted second-shell scattering distances for Cu-Cu and Pd-Pd were 3.01Å and 2.99Å, respectively, aligning with the theoretical value of 2.99Å for B2 CuPd.[40]

Catalytic performance for eNO_3RR

All CuPd samples were supported on Vulcan carbon with a ~20% metal loading, as determined by ICP-OES, for the subsequent electrocatalysis study. An industry-relevant nitrate solution (0.143 M NO_3^- in 1 M KOH) containing 2000 ppm nitrogen was utilized as the electrolyte to

evaluate eNO_3RR performance.[41-43] Chronoamperometry (CA) measurements were performed in a nitrate solution for 30 minutes under various applied potentials with continuous Ar bubbling (Figure S8). The concentrations of NH_3 were determined using the colorimetric method with Nessler's reagent (Figure S9). Produced nitrite was quantified using ion chromatography (Figure S10-S12). Fully ordered B2 CuPd samples after forming gas treatment were tested to compare their electrochemical performance with A1 6 nm CuPd sample. With the same size of 6 nm, B2-phase CuPd catalyst exhibited a higher ammonia Faradaic efficiency (FE) of 81.1% at a potential of −0.6 V vs RHE (Figure 7a), surpassing the 74.2% NH_3 FE achieved by the A1 CuPd (Figure S13). At the same potential, the NH_3 yield rate of 6 nm B2-phase CuPd reached 5.11 mol h^{-1} g^{-1} significantly higher than the 3.31 mol h^{-1} g^{-1} yield rate of A1-phase CuPd. These results suggest that the intermetallic CuPd structure is more catalytically active for nitrate reduction than the disordered structure.

As shown in Figure 7a, the NH_3 FE increased with more negative potentials for all B2-phase catalysts, reflecting suppression of the hydrogen evolution reaction (HER). Most B2-phase CuPd samples achieved peak FE at −0.6 V vs. RHE, with no significant change observed at −0.7 V vs. RHE. Additionally, NH_3 yield rates increased with more negative potentials (Figure S14), and yield rates at −0.6 V vs. RHE were used to evaluate eNO_3RR activity across all B2 CuPd samples (Figures 7b). A volcano-shaped trend was observed for NH_3 yield rate with particle size variation. Higher production rates were obtained with larger CuPd nanocrystals up to 33 nm, which exhibited optimal performance. Beyond this size, the yield declined, with 46 nm CuPd showing reduced activity compared to the 33 nm samples. Linear sweep voltammetry (LSV) results reveal a consistent activity trend, with the 33 nm CuPd exhibiting the highest current density (Figure S15).

Among all B2 CuPd catalysts, the 33 nm sample demonstrated the highest NH_3 production rate of 6.97 mol h^{-1} g^{-1} and an 84.1% FE at −0.6 V vs. RHE, outperforming most of the reported catalysts (Table S6). At −0.7 V vs. RHE, the NH_3 yield rate further increased to 10.1 mol h^{-1} g^{-1} with an FE of 84.0%. Stability testing over ten consecutive electrolysis cycles at −0.6 V vs. RHE showed no noticeable decline in catalytic performance, highlighting the high durability of the 33 nm B2 CuPd catalyst (Figure 7c). After the stability test, the cubic morphology was retained without observable aggregation, as confirmed by TEM and HAADF-STEM imaging (Figure S16a, b). The alternating arrangement of Cu and Pd atoms indicates that the intermetallic structure remained intact, with the

(100) facet still predominantly exposed (Figure S16c). EDS elemental mapping further confirmed the uniform distribution of Cu and Pd (Figure S16d-g). Additionally, ICP-OES analysis showed that the Cu:Pd atomic ratio remained close to 1:1, demonstrating the structural integrity and electrochemical stability of the catalyst. To investigate the nitrogen source in the NH_3 product, control experiments were conducted using 1 M KOH with and without NO_3^- as the electrolytes. Electrochemical testing revealed that almost no NH_3 was detected in the absence of NO_3^-, confirming nitrate as the nitrogen source (Figure 7d).

The intrinsic activity of CuPd nanocrystals with varying sizes was evaluated by normalizing the NH_3 yield rate to the electrochemically active surface area (ECSA). The ECSA was determined from the reduction peak of PdO in cyclic voltammetry (CV)[44-46], measured in 1 M KOH under Ar at a scan rate of 100 $mV \cdot s^{-1}$. As expected, the intensity of this peak significantly decreased with increasing nanocrystal size (Figure S17), indicating a smaller ECSA (Table S5). The intrinsic properties of these B2 CuPd catalysts are summarized in Figure 7e. Unlike the volcano-shaped trend observed when normalizing activity per unit mass of catalyst, the intrinsic activity increased with nanocrystal size, reaching a plateau at approximately 33 nm. This trend aligns with the structural evolution of the nanocrystals, where larger sizes promote the exposure of the (100) surface. A notable enhancement factor of ~ 6 was observed when comparing the intrinsic activity of 33 nm and 6 nm nanocrystals with the same B2 phase, indicating the substantially higher activity of the (100) surface. Besides, the 33 nm and 46 nm CuPd nanocubes exhibited comparable intrinsic catalytic activities due to their similar morphology, further confirming the dominant role of the (100) facet in promoting NH_3 production. The combination of intrinsic active site properties and ECSA collectively determines the overall volcano-shaped performance observed in Figure 7b. The 33 nm CuPd nanocrystals exhibit optimal performance by balancing a reasonably high surface area with a high proportion of (100) surface facets.

Computational studies of eNO_3RR

To understand the enhanced performance of eNO_3RR to ammonia on B2 CuPd (100) facet, the reaction mechanisms on CuPd (100) and (111) facets were investigated using DFT calculations. The computational catalyst model was constructed based on experimental observations from STEM results. The computationally optimized catalyst with the CuPd (100) facet shows the Cu-

Cu distance is in the range of 2.98 to 3.01 Å, in agreement with the experimentally measured distances of 3.07 Å and 3.04 Å (Figure 5c and 5e). These observations validate the computational models for the following thermodynamics calculations.

The possible reaction pathways for eNO_3RR to ammonia are presented in Figure 8a. The eNO_3RR to ammonia is a multi-step electrochemical process, involving several key intermediates and multiple possible pathways. The pathway starts from the adsorption of NO_3^- on the surface, followed by deoxygenation steps, $*NO_3 \rightarrow *NO_2 \rightarrow *NO$. Each deoxygenation step consists of two electron-proton transfer with the elimination of water (indicated by black arrows). From *NO, a few reaction branches are possible, and they are different in the sequences of N-O bond cleavage and hydrogenation steps: (1) $*NO \rightarrow *NHO \rightarrow *NH_2O \rightarrow *NH_2OH \rightarrow *NH_2 \rightarrow NH_{3(g)}$, (2) $*NO \rightarrow *NHO \rightarrow *NHOH \rightarrow *NH \rightarrow *NH_2 \rightarrow NH_{3(g)}$, (3) $*NO \rightarrow *NHO \rightarrow *NHOH \rightarrow *NH_2OH \rightarrow *NH_2 \rightarrow NH_{3(g)}$, and (4) $*NO \rightarrow *NOH \rightarrow *NHOH \rightarrow *N \rightarrow *NH \rightarrow *NH_2 \rightarrow NH_{3(g)}$. The free energy profiles based on reaction network shown in Figure 8a are presented in Figure S18a and S18b on CuPd (100) and CuPd (111) surfaces, respectively.

The most favorable pathways on CuPd (100) and CuPd (111) surfaces are presented in Figure 8b. On both surfaces, the most favorable reaction pathway proceeds as follows: $NO_3^- \rightarrow *NO_3 \rightarrow *NO_2 \rightarrow *NO \rightarrow *NHO \rightarrow *NHOH \rightarrow *NH(*NH_2OH) \rightarrow *NH_2 \rightarrow NH_{3(g)}$. On CuPd (100), the $*NH_2OH$ intermediate is more favorable, whereas on CuPd(111), *NH is slightly preferred. The key difference in the free energy profile originates from the adsorption of NO_3^- on the two catalysts surfaces. Particularly, the adsorption of NO_3^- is exergonic on CuPd (100), with an adsorption energy of -0.35 eV, while it is endergonic on the CuPd (111) surface, with a free energy change of 0.48 eV. The notable observation is that formation of CuPd intermetallic structure enhances the adsorption of NO_3^- species. Previously reported nitrate adsorption energies are 0.4 and 0.6 eV on Cu (100) and Cu (111) surfaces, respectively[21].

To understand the origin of the difference in nitrate adsorption, both geometric and electronic structure analyses of $*NO_3$ were carried out. The projected density of states (PDOS) analysis was conducted for the O atom in NO_3 and the Cu atom on the surface of both CuPd (100) and CuPd (111), as shown in Figure S18c and S18d, respectively. The increased overlap of the DOS between O and Cu in CuPd (100), particularly in the energy range of 0 to -1 eV relative to the Fermi energy, indicates stronger orbital hybridization, which contributes to the increased adsorption of $*NO_3$ on

CuPd (100). Additionally, comparison of DOS of the surface Cu atom in CuPd (100) and (111), presented in Figure 8c, shows upshifted d orbitals to the Fermi energy of CuPd(100), further supporting its stronger capability of $*NO_3$ adsorption. The optimized structures of $*NO_3$ (insets in Figure 8b) and surface geometries (Figures 8d and 8e) were analyzed by examining the O-N-O bond angles and the Cu–Cu distances. The O-N-O bond angle in $*NO_3$ on CuPd (100) is 116.7°, very close to that in a gas-phase HNO_3 molecule (113.6°, Figure 8f), indicating minimal molecular distortion upon adsorption. In contrast, the O-N-O angle in $*NO_3$ on CuPd (111) is significantly larger, 133.5°, suggesting substantial distortion of the $*NO_3$ due to adsorption. To quantify this distortion, the distortion energies were also calculated to be 0.18 eV for $*NO_3$ on CuPd (100) and 1.98 eV on CuPd (111). This higher distortion energy of $*NO_3$ on CuPd (111) is attributed to the longer Cu–Cu distances on the surface, which hinders optimal binding geometry for $*NO_3$.

Discussion

This work highlights the critical structural factors influencing the catalytic properties of intermetallic B2 phase CuPd nanocrystals in the eNO_3RR. By controlling the growth rate of CuPd nanocrystals through colloidal synthesis, we successfully obtained size-adjustable B2 CuPd nanocrystals ranging from 6 nm to 46 nm. A direct comparison between B2 CuPd and disordered A1 CuPd revealed the superior catalytic performance of intermetallic CuPd. Our investigation into size-dependent catalytic properties demonstrated that the (100) surface of B2 CuPd plays a pivotal role in enhancing activity, outperforming other surface facets. DFT calculations revealed that the superior catalytic performance of CuPd (100) compared to (111) arises from its stronger NO_3 adsorption, attributed to more pronounced Cu-O orbitals hybridization near the Fermi level and minimal structural distortion of NO_3 upon adsorption on the (100) surface. To maximize (100) surface exposure, precise size modulation is required, as smaller nanocrystals with high surface energy disfavor the formation of this surface. As a result, 33 nm CuPd exhibited the highest catalytic performance, achieving an NH_3 production rate of 6.97 mol h^{-1} g^{-1} at −0.6 V and 10.1 mol h^{-1} g^{-1} at −0.7 V vs. RHE. The combined effects of surface facet exposure and size optimization present a general design principle for developing high-performance electrocatalysts for various catalytic applications.

Methods

Synthesis of A1 CuPd nanocrystals

A mixture containing 95.7 mg of copper (II) acetylacetonate $Cu(acac)_2$, 92.7 mg of palladium (II) acetylacetonate $Pd(acac)_2$, and 18 mL of oleylamine (OAM) was added to a 125 mL three-necked flask under vigorous stirring. The mixture was heated to 90 °C under vacuum and maintained for 1 hour to eliminate impurities and moisture, yielding a transparent blue solution. Subsequently, the vacuum environment was replaced with nitrogen (N_2) using a Schlenk line, and 0.05 mL of tributylphosphine (TBP) was injected into the reaction mixture. The temperature was then raised to 230 °C at a heating rate of 10 °C/min and maintained for 2 hours. After the reaction mixture cooled to room temperature, nanocrystals were precipitated by introducing 40 mL of isopropanol, followed by centrifugation at 8,500 rpm for 8 minutes. The resulting nanocrystals were further purified through a dispersion step in hexane, followed by precipitation with isopropanol and subsequent centrifugation. Finally, the purified nanocrystals were dispersed in hexane for storage or further use.

Synthesis of intermetallic B2 CuPd nanocrystals

For the preparation of 6 nm B2 CuPd nanocrystals, a mixture containing 149.2 mg $Cu(acac)_2$, 81 mg palladium (II) bromide ($PdBr_2$), and 18 mL of OAM was introduced into a 125 mL three-necked flask under continuous vigorous stirring. The flask was then heated to 90 °C under vacuum conditions for 1 hour to remove residual moisture and impurities, forming a clear blue solution. Afterwards, the vacuum atmosphere was switched to N_2 via a Schlenk line, and 0.2 mL of TBP was added to the reaction mixture. The solution temperature was gradually increased to 230 °C at a heating rate of 10 °C/min and maintained at this level for 2 hours. Once cooled to room temperature, nanocrystals were precipitated by adding 40 mL of isopropanol and isolated by centrifugation at 8,500 rpm for 8 minutes. Further purification involved dispersing the nanocrystals in hexane, precipitating with isopropanol, and another centrifugation step. The purified nanocrystals were finally dispersed in hexane for subsequent use or storage.

Similarly, as-synthesized B2 CuPd nanocrystals with sizes of 8.5 nm, 11 nm, 33 nm, and 46 nm were obtained by utilizing 0.4 mL of trioctylphosphine (TOP), 0.6 mL of TOP, 1.0 mL of TOP, and 1.1 mL of TOP, respectively.

Preparation of Catalysts

All synthesized B2 nanocrystals were deposited onto carbon black (Vulcan XC-72R) with 20% weight loading amount by using sonication. The resulting powder samples were then annealed under a forming gas atmosphere (5% H_2 in Ar) at 300 °C for 2 hours to remove residual ligands and achieve full structural ordering in some of the nanocrystals.

Characterizations

Transmission electron microscopy (TEM) images were obtained on a FEI Tecnai Spirit (120 kV). STEM-EDS was performed at 200 kV on a Titan Themis. High-angle annular-dark-field (HAADF) STEM images were acquired with a scattering angle of 74 to 200 mrad. Powder X-ray diffraction (XRD) was conducted on a Bruker D8A25 diffractometer with Cu Kα radiation (λ = 1.54184 Å). Inductively coupled plasma-optical emission spectrometry (ICP-OES) analyses were performed on a PerkinElmer Avio-200 ICP optical emission spectrometer. The colorimetric experiment using Nessler's reagent was carried out on a UV-vis spectrophotometer (Agilent 3500) to quantify the produced ammonia. The concentration of nitrite was determined using ion chromatography (Metrohm Eco IC). X-ray absorption spectroscopy (XAS) measurements for the Pd and Cu K-edges were conducted at the beamline 7-BM of the National Synchrotron Light Source II at the Brookhaven National Laboratory. Both XANES and EXAFS were collected under fluorescence mode with a Passivated Implanted Planar Silicon detector. All XAS data processing were performed using the Athena software.

Electrochemical measurements

Electrochemical evaluations were carried out in a gas-tight H-cell separated by an ion-exchange membrane (Nafion 117). A three-electrode configuration connected to a BioLogic electrochemical potentiostat was employed. Prior to use, the Nafion 117 membrane was pretreated by immersion in a 5% H_2O_2 solution at 80 °C for 1 hour, followed by soaking in a 0.5 M H_2SO_4 solution at 80 °C for another hour, and subsequently rinsed with deionized water. In the three-electrode system, a platinum foil was used as the counter electrode, and a Hg/HgO electrode (4.0 M KOH) served as the reference electrode. The working electrode comprised carbon-supported catalysts deposited on carbon paper, prepared as follows: 5 mg of catalyst (20% metal loading) was mixed with 1 mL of isopropanol and 20 μL of Nafion solution, and sonicated for 1 hour to form a homogeneous ink. Subsequently, 200 μL of this ink was drop-casted onto a 1 cm^2 carbon paper substrate. A 1 M KOH

+ 0.143 M KNO_3 electrolyte solution was prepared, and prior to testing, Ar gas (20 sccm) was bubbled through the solution for 30 minutes to eliminate dissolved oxygen. The potential difference between the Hg/HgO electrode and the reversible hydrogen electrode (RHE) was calibrated by open-circuit potential measurements in the electrolyte solution. Chronoamperometry (CA) experiments were performed for 30 minutes at potentials ranging from -0.4 V to -0.7 V vs. RHE. Linear sweep voltammetry (LSV) tests were conducted over a potential range of +0.3 V to -0.8 V vs. RHE at a scan rate of 10 $mV \cdot s^{-1}$. To evaluate the electrochemically active surface area (ECSA), cyclic voltammetry (CV) was performed within a potential window of +1.2 V to +0.06 V vs. RHE at a scan rate of 100 $mV \cdot s^{-1}$. The ECSA was determined by integrating the charge associated with the PdO reduction peak located between +0.6 V and +0.7 V vs. RHE. The ECSA values (m^2/g_{Pd}) were calculated using the following equation:

$$\mathrm{ECSA} = \mathrm{Q}/(0.405 \times \mathrm{W_{Pd}})$$

Where Q is the columbic charge obtained from the integrated reduction peak; W_{Pd} is the mass loading of Pd on the electrode; 0.405 represents the charge required to reduce a monolayer of PdO (mC per $\mathrm{cm^2_{Pd}}$).

Detection and quantification of ammonia

A colorimetric experiment with Nessler's reagent was carried out to detect the ammonia in electrolyte after electrolysis on an ultraviolet–visible spectrophotometer and absorbance at 420 nm was measured. A calibration curve was plotted by preparing a series of NH_4Cl solutions with varied concentrations. The concentrations of ammonia in the electrolyte can be obtained from the calibration curves.

Following equation was used to calculate the faradic efficiency (FE) of NH_3:

$$\mathrm{FE} = (\frac{\mathrm{ncVF}}{\mathrm{it}})$$

Production of yield of NH_3 was described as:

$$\mathrm{Production\ yield} = (\frac{\mathrm{cV}}{\mathrm{mt}})$$

where c is the moles of NH_3 detected from the electrolyte, n is the number of electrons transferred with 1 mol of NH_3 produced, V is the volume of electrolyte used in the electrolysis, F

is the Faraday constant (96485 C · mol^{-1}), i is the current, t is the electrolysis time and m is the mass of catalysts.

Computational details

All calculations were performed using the Vienna Ab-initio Simulation Package (VASP) [47], employing the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional and projector augmented wave (PAW) potentials. [48-50] The B2-phase CuPd intermetallic primitive cell was taken from Materials Project database and optimized at the same level of theory, which reproduced a lattice constant of 2.98 Å. CuPd (100) and (111) surfaces were cleaved from bulk-optimized unit cell. The (111) and (100) slabs consisted of 6 and 5 atomic layers, respectively, constructed from 5 × 3 supercells. A vacuum layer of 15Å was added along the z-direction to prevent inter-slab interactions, resulting in supercell dimensions of 12.64Å × 12.64Å × 20.16Å for (111) and 8.94Å × 8.94Å × 20.16Å for (100). The Brillouin zone sampling was performed using a Γ-centered k-point mesh of 3 × 3 × 1 for (111) and 4 × 4 × 1 for (100), with a plane-wave energy cutoff of 400 eV. During geometry optimization, the top three atomic layers were relaxed while the bottom layers were fixed at their bulk positions. Optimizations were carried out using the quasi-Newton or conjugate gradient algorithm until the forces on each atom were below 0.02 eV/Å and the total energy converged to less than 10^{-6} eV. Methfessel-Paxton smearing with a σ value of 0.2 eV was applied. Van der Waals interactions were accounted for using the DFT-D3 dispersion correction with zero damping.[51, 52] The implicit continuum solvation model implemented in VASPsol was used in all calculations.[53, 54]

The free energies of all intermediates were calculated using the equation

$$\Delta G^{o} = E^{o}_{elect} + ZPE - TS$$

Here, E°_{elect} was taken from the DFT calculations, while zero-point energy (ZPE) and entropy (TS) terms were taken from a previous study.[55] The chemical potential of each proton-electron pair was determined using the Computational Hydrogen Electrode (CHE) model introduced by Nørskov et al., where $\mu[H^+ + e^-]$ is equated to $0.5\mu[H_2(g)]$ under standard conditions with no applied potential (U = 0).[56] Free energy of nitrate adsorption was calculated using the same approaches used in previous studies.[21, 57-58]

$$\begin{aligned}\Delta G_{*NO_3} &= G_{ads}(*NO_3) + 0.075 + 0.317 \\ &= G_{*NO_3} + {}^{1}/_{2}\, G(H_2) - E_{sur} - G_{gas}(HNO_3) + 0.392eV \\ &= E_{*NO_3} + {}^{1}/_{2}\, E(H_2) - E_{sur} - E_{gas}(HNO_3) + 0.75eV\end{aligned}$$

The 0.75 is sum of 0.392 and correction (ZPE -TS) for $*NO_3$, H_2 and HNO_3.The Gibbs free energy change for the vaporization of HNO_3(l) was determined by calculating the difference in standard Gibbs free energies of formation between its liquid and gaseous phases, yielding a value of 0.075 eV. Additionally, the Gibbs free energy for the formation of HNO_3 (l) from aqueous NO_3^- was found to be 0.317 eV. All these values were taken from the CRC Handbook of Chemistry and Physics.[59] This correction on DFT-calculated total energy to obtain the Gibbs free energy change of NO_3 adsorption has been taken from a previous work.[57]

Distortion energy of nitrate upon adsorption on CuPd(100) and CuPd(111) surfaces was also calculated. Nitrate structure (NO_3) was optimized in vacuum as a reference energy ($NO_{3(g)}$, $E_{NO_3(g)}$). In the next step, the slab atoms were removed from the $*NO_3$ structure, and the position of NO_3 was fixed. A single-point energy calculation was then performed on the fixed NO_3 structure without the slab atoms, yielding E_{*NO_3}. The distortion energy was calculated using the equation:

$$E_{distortion} = E_{NO_3(g)} - E_{*NO_3}$$

Resource availability

Lead contact

The lead contact of this work is Prof. Sen Zhang (sz3t@virginia.edu).

Materials availability

All the preparation procedures of materials are provided in supplemental information. Further information is available from the lead contact upon request.

Data and code availability

Full experimental results and procedures are provided in supplemental information.

ACKNOWLEDGMENTS

L.Z. and S.Z. acknowledge support from the U.S. National Science Foundation (CHE-2404265) for catalyst synthesis and electrocatalysis studies. Y. C. acknowledges support from the U.S. Department of Energy, Office of Basic Energy Sciences, Chemical Sciences, Geosciences, and Biosciences Division (DE-SC00234430) for XAS analysis. M.K. and L.Z. acknowledge faculty startup funding provided by Iowa State University supporting STEM characterization. The DFT calculations were performed at the OU Supercomputing Center for Education & Research (OSCER) and the National Energy Research Scientific Computing Center (NERSC), a U.S. Department of Energy Office of Science User Facility. B.W. acknowledges support from the U.S. Department of Energy, Basic Energy Sciences, Chemical Sciences, Geosciences, and Biosciences (CSGB) Division, Catalysis Science (Grant DE-SC0018284) for computational work. This research used resources 7-BM of the National Synchrotron Light Source II, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Brookhaven National Laboratory under Contract No. DE-SC0012704.

AUTHOR CONTRIBUTIONS

L.Z.: conceptualization, methodology, investigation, data curation, formal analysis, validation, writing—original draft, writing—reviewing and editing; Z.M.: methodology, investigation, data curation, formal analysis, validation, writing—original draft, writing—reviewing and editing; Q.G.: investigation, data curation, writing—reviewing and editing; M.K.: investigation, data curation, writing—reviewing and editing; X.W.: data curation, writing—reviewing and editing; Y.Z.: data curation, writing—reviewing and editing; Z.G.: data curation, writing—reviewing and editing; Y.C.: data curation, writing—reviewing and editing; L.M.: methodology, investigation, writing—reviewing and editing; H.Z.: methodology, resources, writing—reviewing and editing; L.Z.: methodology, writing—reviewing and editing; B.W.: supervision, methodology, resources, writing, reviewing and editing; S.Z.: supervision, conceptualization, methodology, resources, writing, reviewing and editing

All authors have read and given approval to the final version of the manuscript.

DECLARATION OF INTERESTS

The authors declare no competing interests.

Reference

1. Gruber, N.; and Galloway, J.N. (2008). An Earth-system perspective of the global nitrogen cycle. Nature. *451*, 293-296. https://doi.org/10.1038/nature06592
2. Duca, M.; and Koper, M. T. M. (2012). Powering denitrification: the perspectives of electrocatalytic nitrate reduction. Energy Environ. Sci. *5*, 9726-9742. https://doi.org/10.1039/C2EE23062C
3. Galloway, J.N.; Townsend, A.R.; and Erisman, J. W. (2008). Transformation of the Nitrogen Cycle: Recent Trends, Questions, and Potential Solutions. Science. *320*, 889-892. https://www.science.org/doi/abs/10.1126/science.1136674
4. Canfield, D.E.; Glazer, A.N.; and Falkowski, P. G. (2010). The Evolution and Future of Earth's Nitrogen Cycle. Science. *330*,192-196. https://www.science.org/doi/abs/10.1126/science.1186120
5. Rosca, V.; Duca, M.; de Groot, M. T.; and Koper, M. T. M. (2009). Nitrogen Cycle Electrocatalysis. Chem. Rev. *109*, 2209-2244. https://doi.org/10.1021/cr8003696
6. van Langevelde, P. H.; Katsounaros, I.; and Koper, M. T. M. (2021). Electrocatalytic Nitrate Reduction for Sustainable Ammonia Production. Joule. *5*, 290-294. https://doi.org/10.1016/j.joule.2020.12.025
7. Lim, J,; Fernández, C. A.; Lee, S. W.; and Hatzell, M. C. (2021). Ammonia and Nitric Acid Demands for Fertilizer Use in 2050. ACS Energy Lett. *6*, 3676–3685. https://doi.org/10.1021/acsenergylett.1c01614
8. MacFarlane, D. R.; Cherepanov, P. V.; Choi, J.; Suryanto, B. H. R.; Hodgetts, R. Y.; Bakker, J. M.; Ferrero Vallana, F. M.; and Simonov, A. N. (2020). A Roadmap to the Ammonia Economy. Joule. *4,* 1186-1205. https://doi.org/10.1016/j.joule.2020.04.004
9. Soloveichik, G. (2019). Electrochemical synthesis of ammonia as a potential alternative to the Haber–Bosch process. Nat Catal. *2,* 377–380. https://doi.org/10.1038/s41929-019-0280-0
10. Hu, Q.; Qin, Y.; Wang, X.; Wang, Z.; Huang, X.; Zheng, H.; Gao, K.; Yang, H.; Zhang, P.; Shao, M. et al. (2021). Reaction intermediate-mediated electrocatalyst synthesis favors specified facet and defect exposure for efficient nitrate–ammonia conversion. Energy Environ. Sci. *14*, 4989-4997. https://doi.org/10.1039/D1EE01731D
11. Fu, Y.; Wang, S.; Wang, Y.; Wei, P.; Shao, J.; Liu, T.; Wang, G.; and Bao, X. (2023). Enhancing Electrochemical Nitrate Reduction to Ammonia over Cu Nanosheets via Facet Tandem Catalysis. Angew. Chem. Int. Ed. *62,* e202303327. https://doi.org/10.1002/anie.202303327
12. Wang, Y.; Zhou, W.; Jia, R.; Yu, Y.; and Zhang, B. (2020). Unveiling the Activity Origin of a Copper-based Electrocatalyst for Selective Nitrate Reduction to Ammonia. Angew. Chem. Int. Ed. *59,* 5350. https://doi.org/10.1002/anie.201915992
13. Zhu, T.; Chen, Q.; Liao, P.; Duan, W.; Liang, S.; Yan, Z.; and Feng, C. (2020). Single-Atom Cu Catalysts for Enhanced Electrocatalytic Nitrate Reduction with Significant Alleviation of Nitrite Production. Small. *16*, 2004526. https://doi.org/10.1002/smll.202004526

14. Yang, J.; Qi, H.; Li, A.; Liu, X.; Yang, X.; Zhang, S.; Zhao, Q.; Jiang, Q.; Su, Y.; Zhang, L. et al. (2022). Potential-Driven Restructuring of Cu Single Atoms to Nanoparticles for Boosting the Electrochemical Reduction of Nitrate to Ammonia. J. Am. Chem. Soc. *144,* 12062–12071. https://doi.org/10.1021/jacs.2c02262
15. Zhou, N.; Wang, Z.; Zhang, D.; Bao, H.; Zhong, H.; and Zhang, X. (2023). Potential-Induced Synthesis and Structural Identification of Oxide-Derived Cu Electrocatalysts for Selective Nitrate Reduction to Ammonia. ACS Catal. *13,* 7529–7537.
https://doi.org/10.1021/acscatal.3c01315
16. Gao, W.; Xie, K.; Xie, J.; Wang, X.; Zhang, H.; Chen, S.; Wang, H.; Li, Z.; and Li, C. (2023). Alloying of Cu with Ru Enabling the Relay Catalysis for Reduction of Nitrate to Ammonia. Adv. Mater. *35,* 2202952. https://doi.org/10.1002/adma.202202952
17. Wang, Y.; Xu, A.; Wang, Z.; Huang, L.; Li, J.; Li, F.; Wicks, J.; Luo, M.; Nam, D.-H.; Tan, C.-S. et. al. (2020). Enhanced Nitrate-to-Ammonia Activity on Copper–Nickel Alloys via Tuning of Intermediate Adsorption. J. Am. Chem. Soc. *142,* 5702–5708.
https://doi.org/10.1021/jacs.9b13347
18. He, W.; Zhang, J.; Dieckhöfer, S.; Varhade, S.; Brix, A. C.; Lielpetere, A.; Seisel, S.; Junqueira, J. R. C.; and Schuhmann, W. (2022). Splicing the active phases of copper/cobalt-based catalysts achieves high-rate tandem electroreduction of nitrate to ammonia. Nat Commun. *13,* 1129. https://doi.org/10.1038/s41467-022-28728-4.
19. Liu, H.; Lang, X.; Zhu, C.; Timoshenko, J.; Rüscher, M.; Bai, L.; Guijarro, N.; Yin, H.; Peng, Y.; Li, J. et al. (2022). Efficient Electrochemical Nitrate Reduction to Ammonia with Copper-Supported Rhodium Cluster and Single-Atom Catalysts. Angew. Chem. Int. Ed. *61,* e202202556. https://doi.org/10.1002/anie.202202556
20. Cerrón-Calle, G. A.; Fajardo, A. S.; Sánchez-Sánchez, C. M.; and Garcia-Segura, S. (2022). Highly reactive Cu-Pt bimetallic 3D-electrocatalyst for selective nitrate reduction to ammonia. Appl. Catal. B: Environ. *302.* 120844. https://doi.org/10.1016/j.apcatb.2021.120844.
21. Gao, Q.; Pillai, H. S.; Huang, Y.; Liu, S.; Mu, Q.; Han, X.; Yan, Z.; Zhou, H.; He, Q.; Xin, H. et al. (2022). Breaking adsorption-energy scaling limitations of electrocatalytic nitrate reduction on intermetallic CuPd nanocubes by machine-learned insights. Nat Commun. *13,* 2338.
https://doi.org/10.1038/s41467-022-29926-w
22. Liu, Y.; Huang, S.; Lu, J.; Niu, S.; Shen, P. K.; Hu, Z.; Tsiakaras, P.; and Gao, S. (2024). $Ni_{0.25}Cu_{0.5}Sn_{0.25}$ Nanometallic Glasses As Highly Efficient Catalyst for Electrochemical Nitrate Reduction to Ammonia. Adv. Funct. Mater. *34*, 2411325.
https://doi.org/10.1002/adfm.202411325
23. Liu, Y.; Niu, S.; Zou, Y.; Huang, S.; Shi, Y.; Gao, S.; and Tsiakaras, P. (2025).
Electrochemical production of ammonia: Nitrate reduction over novel Cu-Ni-Al metallic glass nanoparticles used as highly active and durable catalyst. Appl. Catal. B. 363, 124729.
https://doi.org/10.1016/j.apcatb.2024.124729
24. Yang, W.; Chang, Z.; Yu, X.; Shen, R.; Wang, L.; Cui, X.; and Shi, J. (2025). Triple Regulations via Fe Redox Boosting Nitrate Reduction to Ammonia at Industrial Current Densities. Angew. Chem. Int. Ed. *64*, e202415300. https://doi.org/10.1002/anie.202415300
25. Qiu, Y.; Xin, L.; Li, Y.; McCrum, I. T.; Guo, F.; Ma, T.; Ren, Y.; Liu, Q.; Zhou, L.; Gu, S. et al. (2018). BCC-Phased PdCu Alloy as a Highly Active Electrocatalyst for Hydrogen Oxidation in Alkaline Electrolytes. J. Am. Chem. Soc. *140,* 16580–16588.
https://doi.org/10.1021/jacs.8b08356

26. Kim, J.; Lee, Y.; and Sun, S. (2010). Structurally Ordered FePt Nanoparticles and Their Enhanced Catalysis for Oxygen Reduction Reaction. J. Am. Chem. Soc. *132,* 4996–4997. https://doi.org/10.1021/ja1009629
27. Pan, Y.-T.; Yan, Y.; Shao, Y.-T.; Zuo, J.-M.; and Yang, H. (2016). Ag–Pt Compositional Intermetallics Made from Alloy Nanoparticles. Nano Lett. *16,* 6599–6603. https://doi.org/10.1021/acs.nanolett.6b03302
28. Li, G.; Kobayashi, H.; Kusada, K.; Taylor, J. M.; Kubota, Y.; Kato, K.; Takata, M.; Yamamoto, T.; Matsumura, S.; and Kitagawa, H. (2014). An ordered bcc CuPd nanoalloy synthesised via the thermal decomposition of Pd nanoparticles covered with a metal–organic framework under hydrogen gas. Chem. Commun. *50,* 13750-13753. https://doi.org/10.1039/C4CC05941G
29. Wang, D.; Xin, H. L.; Hovden, R.; Wang, H.; Yu, Y.; Muller, D. A.; DiSalvo, F. J.; and Abruña, H. D. (2013). Structurally ordered intermetallic platinum–cobalt core–shell nanoparticles with enhanced activity and stability as oxygen reduction electrocatalysts. Nature Mater. *12*, 81-87. https://doi.org/10.1038/nmat3458
30. Cui, Z.; Chen, H.; Zhao, M.; and DiSalvo, F. J. (2016). High-Performance Pd3Pb Intermetallic Catalyst for Electrochemical Oxygen Reduction. Nano Lett. *16,* 2560–2566. https://doi.org/10.1021/acs.nanolett.6b00121
31. Wu, C. H.; Liu, C.; Su, D.; Xin, H. L.; Fang, H.-T.; Eren, B.; Zhang, S.; Murray, C. B.; and Salmeron, M. B. (2019). Bimetallic synergy in cobalt–palladium nanocatalysts for CO oxidation. Nat Catal. *2,* 78–85. https://doi.org/10.1038/s41929-018-0190-6
32. Li, J.; and Sun, S. (2019). Intermetallic Nanoparticles: Synthetic Control and Their Enhanced Electrocatalysis. Acc. Chem. Res. *52,* 2015–2025. https://doi.org/10.1021/acs.accounts.9b00172
33. Yan, Y.; Du, J. S.; Gilroy, K. D.; Yang, D.; Xia, Y.; and Zhang, H. (2017). Intermetallic Nanocrystals: Syntheses and Catalytic Applications. *Adv. Mater. 29,* 1605997. https://doi.org/10.1002/adma.201605997
34. Zhang, L.; Choi, S.-I.; Tao, J.; Peng, H.-C.; Xie, S.; Zhu, Y.; Xie, Z.; and Xia, Y. (2014). Pd–Cu Bimetallic Tripods: A Mechanistic Understanding of the Synthesis and Their Enhanced Electrocatalytic Activity for Formic Acid Oxidation. Adv. Funct. Mater. *24,* 7520-7529. https://doi.org/10.1002/adfm.201402350
35. Wang, C.; Chen, D. P.; Sang, X.; Unocic, R. R.; and Skrabalak, S. E. (2016). Size-Dependent Disorder–Order Transformation in the Synthesis of Monodisperse Intermetallic PdCu Nanocatalysts. ACS Nano. *10,* 6345–6353. https://doi.org/10.1021/acsnano.6b02669
36. Zhang, S.; Hao, Y.; Su, D.; Doan-Nguyen, V. V. T.; Wu, Y.; Li, J.; Sun, S.; and Murray, C. B. (2014). Monodisperse Core/Shell Ni/FePt Nanoparticles and Their Conversion to Ni/Pt to Catalyze Oxygen Reduction. J. Am. Chem. Soc. *136*, 15921–15924. https://doi.org/10.1021/ja5099066
37. Ling, T.; Zhu, J.; Yu, H.; and Xie, L. (2009). Size Effect on Crystal Morphology of Faceted Face-Centered Cubic Fe Nanoparticles. J. Phys. Chem. C. *113,* 9450–9453. https://doi.org/10.1021/jp903496c
38. Ding, R.; Padilla Espinosa, I. M.; Loevlie, D.; Azadehranjbar, S.; Baker, A. J.; Mpourmpakis, G.; Martini, A.; and Jacobs, T. D. B. (2022). Size-dependent shape distributions of platinum nanoparticles. Nanoscale Adv. *4,* 3978-3986. https://doi.org/10.1039/D2NA00326K

39. Li, D.; Wang, C.; Tripkovic, D.; Sun, S.; Markovic, N. M.; and Stamenkovic, V. R. (2012). Surfactant Removal for Colloidal Nanoparticles from Solution Synthesis: The Effect on Catalytic Performance. ACS Catal. *2,* 1358–1362. https://doi.org/10.1021/cs300219j
40. Liu, S.; Li, Y.; Yu, X.; Han, S.; Zhou, Y.; Yang, Y.; Zhang, H.; Jiang, Z.; Zhu, C.; Li, W.-X., et al. (2022). Tuning crystal-phase of bimetallic single-nanoparticle for catalytic hydrogenation. Nat Commun. *13*, 4559. https://doi.org/10.1038/s41467-022-32274-4
41. Glass, C.; and Silverstein, J. (1999). Denitrification of high-nitrate, high-salinity wastewater. Water Res. *33*, 223-229. https://doi.org/10.1016/S0043-1354(98)00177-8
42. Du, R.; Cao, S.; Peng, Y.; Zhang, H.; and Wang, S. (2019). Combined Partial Denitrification (PD)-Anammox: A method for high nitrate wastewater treatment. Environ. Int. *126*, 707-716. https://doi.org/10.1016/j.envint.2019.03.007
43. Fernández-Nava, Y.; Marañón, E.; Soons, J.; and Castrillón, L. (2008). Denitrification of wastewater containing high nitrate and calcium concentrations. Bioresour. Technol. *99*, 7976-7981. https://doi.org/10.1016/j.biortech.2008.03.048
44. Li Chen, L.; Lu, L.; Zhu, H.; Chen, Y.; Huang, Y.; Li, Y.; and Wang, L. (2017). Improved ethanol electrooxidation performance by shortening Pd–Ni active site distance in Pd–Ni–P nanocatalysts. Nat Commun. *8,* 14136. https://doi.org/10.1038/ncomms14136
45. Qiu, Z.; Martín-Yerga, D.; Lindén, P. A.; Henriksson, G.; and Cornell, A. (2022). Green hydrogen production via electrochemical conversion of components from alkaline carbohydrate degradation. Int. J. Hydrogen Energy. *47*, 3644-3654. https://doi.org/10.1016/j.ijhydene.2021.11.046
46. Ghosh, S.; Remita, H.; Kar, P.; Choudhury, S.; Sardar, S.; Beaunier, P.; Roy, P. S.; Bhattacharyea, S. K.; and Pala, S. K. (2015). Facile synthesis of Pd nanostructures in hexagonal mesophases as a promising electrocatalyst for ethanol oxidation. J. Mater. Chem. A. *3,* 9517-9527. https://doi.org/10.1039/C5TA00923E

47. Kresse, G.; and Furthmüller, J. (1996). Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. Phys. Rev. B. *54*, 11169. https://doi.org/10.1103/PhysRevB.54.11169
48. Perdew, J. P.; Burke, K.; and Ernzerhof, M. (1996). Generalized gradient approximation made simple. Phys. Rev. Lett. *77*, 3865. https://doi.org/10.1103/PhysRevLett.77.3865
49. Kresse, G.; and Joubert, D. (1999). From ultrasoft pseudopotentials to the projector augmented-wave method. Phys. Rev. B. *59*, 1758. https://doi.org/10.1103/PhysRevB.59.1758
50. Blöchl, P. E. (1994). Projector augmented-wave method. Phys. Rev. B. *50*, 17953. https://doi.org/10.1103/PhysRevB.50.17953
51. Grimme, S.; Antony, J.; Ehrlich, S.; and Krieg, H. (2010). A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. J. Chem. Phys. *132*, 154104. https://doi.org/10.1063/1.3382344
52. Grimme, S.; Ehrlich, S.; and Goerigk, L. (2011). Effect of the damping function in dispersion corrected density functional theory. J. Comput. Chem. *32*, 1456–1465. https://doi.org/10.1002/jcc.21759
53. Mathew, K.; Sundararaman, R.; Letchworth-Weaver, K.; Arias, T. A.; and Hennig, R. G. (2014). Implicit solvation model for density-functional study of nanocrystal surfaces and reaction pathways. J. Chem. Phys. *140*, 084106. https://doi.org/10.1063/1.4865107
54. Mathew, K.; Kolluru, V. S. C.; Mula, S.; Steinmann, S. N.; and Hennig, R. G. (2019). Implicit self-consistent electrolyte model in plane-wave density-functional theory. J. Chem. Phys. *151*, 234101. https://doi.org/10.1063/1.5132354

55. Hu, T.; Wang, C.; Wang, M.; Li, C. M.; and Guo, C. (2021). Theoretical insights into superior nitrate reduction to ammonia performance of copper catalysts. ACS Catal. *11*, 14417–14427. https://doi.org/10.1021/acscatal.1c03666
56. Nørskov, J. K.; Rossmeisl, J.; Logadottir, A.; Lindqvist, L.; Kitchin, J. R.; Bligaard, T.; and Jónsson, H. (2004). Origin of the overpotential for oxygen reduction at a fuel-cell cathode. J. Phys. Chem. B. *108*, 17886–17892. https://doi.org/10.1021/jp047349j
57. Liu, J.-X.; Richards, D.; Singh, N.; and Goldsmith, B. R. (2019). Activity and selectivity trends in electrocatalytic nitrate reduction on transition metals. ACS Catal. *9*, 7052–7064. https://doi.org/10.1021/acscatal.9b02179
58. Calle-Vallejo, F.; Huang, M.; Henry, J. B.; Koper, M. T. M.; and Bandarenka, A. S. (2013). Theoretical design and experimental implementation of Ag/Au electrodes for the electrochemical reduction of nitrate. Phys. Chem. Chem. Phys. *15*, 3196–3202. https://doi.org/10.1039/C2CP44620K
59. Lide, D. R. (2012). CRC Handbook of Chemistry and Physics; CRC Press: Boca Raton.

Figure 1. Schematic illustration of CuPd electrocatalysts optimization for NO_3RR.

Synthesis of CuPd nanocrystals with the control over crystal structure, size, morphology and surface facets via the designed reaction conditions, which leads to the optimization of electrocatalysts for the eNO_3RR.

Figure 2. Characterizations of 6 nm A1 and B2 CuPd nanocrystals.

TEM images of (a) as-synthesized 6 nm A1 CuPd and (b) as-synthesized 6 nm B2 CuPd. (c) XRD patterns for 6 nm A1 CuPd and 6 nm B2 CuPd in comparison to references.

Figure 3. **Morphology characterizations of B2 CuPd nanocrystals.**

(a)-(e) TEM images for 6 nm, 8.5 nm, 11 nm, 33 nm, 46 nm B2 as-synthesized CuPd.

Figure 4. **Crystal structure characterizations of B2 CuPd nanocrystals.**

(a) XRD patterns for as-synthesized B2 CuPd nanocrystals. (b) A1 content analysis for as-synthesized B2-phase CuPd with different sizes.

Figure 5. **Characterizations of B2 CuPd nanocrystals after annealing treatment.**

(a) XRD patterns for B2 CuPd after 300℃ forming gas treatment. HAADF -STEM results for (b), (c) 11 nm CuPd, and (d), (e) 33 nm CuPd. (f)-(i) EDS elemental mapping for 33 nm B2 CuPd.

Figure 6. XAS analysis for 33 nm B2 CuPd.

(a) Pd K-edge XANES spectra of 33 nm B2 CuPd nanocrystals and Pd foil reference, with a magnified view of the Pd K-edge as inset. (b) EXAFS Fourier-transformed k3-weighted χ(k) function spectra of 33 nm B2 CuPd nanocrystals and Pd foil reference. The EXAFS fitting results of the (c) Pd K-edge and (d) Cu K-edge for 33 nm B2 CuPd nanocrystals.

Figure 7. **Electrochemical NO_3RR performance of CuPd nanocrystals.**

(a) FE of NH_3 over B2 CuPd catalysts with different sizes. (b) NH_3 yield rates over B2 CuPd catalysts with different sizes at −0.6 V vs. RHE (c) Stability test by running 10 consecutive cycles of electrolysis with the 33 nm B2 CuPd catalyst under −0.6 V vs. RHE. (d) NH_3 yield rates with the 33 nm B2 CuPd catalyst at −0.6 V vs. RHE in 1M KOH with and without NO_3^-. (e) ECSA-normalized NH_3 yield rates obtained on B2 CuPd samples at −0.6 V vs. RHE.

Figure 8. **DFT calculations for B2 CuPd (100) and (111) facets.**

(a) Reaction scheme showing all possible pathways for eNO_3RR to ammonia. (b) Most favorable pathways for eNO_3RR to ammonia on CuPd (100) and (111) facets; insets show the optimized structure of $*NO_3$ on CuPd (100) and (111) surfaces. (c) Projected density of states (PDOS) of the Cu atom on the CuPd surface (binding with O from NO_3) for CuPd (100) and (111). (d)-(f) The atomic structures of the CuPd (100) and (111) as well as a gas-phase HNO_3 molecule (all distances are shown in Å).