Atomically ordered non-precious Co$_3$Ta intermetallic nanoparticles as high-performance catalysts for hydrazine electrooxidation

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Nano-ordered intermetallic compounds have generated great interest in fuel cell applications. However, the synthesis of non-preciousearly transition metal intermetallic nanoparticles remains a formidable challenge owing to the extremely oxyphilic nature and very negative reduction potentials. Here, we have successfully synthesized non-precious Co$_3$Ta intermetallic nanoparticles, with uniform size of 5 nm. Atomic structural characterizations and X-ray absorption fine structure measurements confirm the atomically ordered intermetallic structure. As electrocatalysts for the hydrazine oxidation reaction, Co$_3$Ta nanoparticles exhibit an onset potential of $-0.086$ V (vs. reversible hydrogen electrode) and two times higher specific activity relative to commercial Pt/C (+0.06 V), demonstrating the top-level performance among reported electrocatalysts. The Co-Ta bridge sites are identified as the location of the most active sites thanks to density functional theory calculations. The activation energy of the hydrogen dissociation step decreases significantly upon N$_2$H$_4$ adsorption on the Co-Ta bridge active sites, contributing to the significantly enhanced activity.
Highly efficient, low cost, and stable electrocatalysts are crucial for commercial applications of fuel cells. Considering the high cost, scarcity, and low operational stability of Pt catalysts, hindering the large-scale commercialization of fuel cell technology, some alternatives catalysts based on non-precious metals have been investigated, including the use of transition metals, perovskites, carbon-based materials, and metal carbides. These alternatives are from naturally abundant resources and are attractive due to their low cost and favorable catalytic performance. While these catalysts appear promising, their relatively low activity and poor long-term stability still cannot meet the requirements necessary for long-term use. Major challenges remain for research efforts focused on non-precious metal catalysts with high performance in fuel cells.

Compared with disordered alloys and monometallic nanocrystals, structurally ordered intermetallic nanomaterials can perform better as fuel cell electrocatalysts in terms of catalytic activity, long-term stability, and poison tolerance due to their definite composition, exceptional structural, and electronic properties. Early investigations of ordered intermetallics as efficient fuel cell electrocatalysts focused on Pt-based late transition metal intermetallic nanoparticles (NPs) (e.g., PtCu, PtFe, PtCo, PtNi, PtZr, and PtAg), which reduced the platinum catalyst consumption and showed significant enhancement in catalytic activity and stability compared with Pt NPs. Recently, early transition metal (the group IIIB, IVB, and VB) intermetallic compounds have shown great potential as efficient fuel cell electrocatalysts. For instance, Dirsalvo and co-workers reported that atomically ordered Pt3Ti nanoparticles prepared with sodium naphthalide exhibited higher electrocatalytic current densities and much lower affinity for CO adsorption than atomically disordered Pt3Ti, pure Pt, or Pt-Ru NPs for both formic acid and methanol oxidation reactions.

Hideki et al. found that both 150-nm NbPt3 and 100-nm TaPt3 intermetallic particles showed significant enhancement in catalytic activity and stability compared with Pt NPs. Despite these obvious advantages, the works of the related early transition metal nano-intermetallic compounds are preliminary (e.g., Pt3Ti, Pt3V, ZrPt3, NbPt3, TaPt3, and Pt3Y) due to higher melting points, more oxophilic nature and much more negative reduction potentials of these metals compared with late transition metals. Furthermore, non-precious early transition metal nano-intermetallics, to the best of our knowledge, have not yet been reported.

Herein, we report an ordered Co3Ta intermetallic compound with an average particle size of 5 nm and uniform distribution on carbon supports. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) imaging and X-ray absorption fine structure (XAFS) measurements reveal the ordered intermetallic crystal structure of Co3Ta. As an electrocatalyst for hydrazine oxidation reaction (H2O2), Co3Ta/C NPs exhibit outstanding performance for both activity and stability, including an ultralow onset potential ($E_{onset}$) of $-0.086$ V (vs the reversible hydrogen electrode, RHE) and twofold improvement of specific activity relative to commercial Pt/C (+0.06V). To the best of our knowledge, the superior catalytic activity for H2O2 is the top-level performance among the reported electrocatalysts. XAFS measurements and density functional theory (DFT) theoretical calculations identify that the Co-Ta bond bridge sites are the location of the most active sites of H2O2 in the ordered Co3Ta. The tuning of the electronic structure of the ordered Co3Ta leads to the superior electrocatalytic hydrazine oxidation activity. The excellent performances on H2O2 provide a potential application for Co3Ta NPs to be an anode catalyst in direct hydrazine fuel cells.

**Results**

**Synthesis and characterization of Co3Ta intermetallic NPs.** To prepare early transition metal intermetallic compounds, extremely strong reductants and high temperatures are usually adopted, which leads to significant agglomeration and unwanted particle growth. With this in mind, we instead added surface treated carbon supports to the reaction solution before the co-reduction of metal salts (details can be found in the Methods section). Supplementary Fig. 1 shows the powder X-ray diffraction patterns of the precursors and products. After the precursors were treated at 400 °C for 3 h, the diffraction peaks were identified but appeared broad, allowing for assignment of Co3Ta as a face-centered cubic (fcc) structure in the Pm-3m space group (JCPDS, No. 15–0028). Broad diffraction peaks are indicative of small particles size. A representative HAADF-STEM overview image of the Co3Ta NPs is shown in Fig. 1a. The Co3Ta NPs are well dispersed on the carbon supports, with an average diameter of 5 nm, which is much smaller than that of other reported Pt-based early transition metal intermetallic compounds (Supplementary Table 1). The high-resolution transmission electron microscope (HRTEM) image of Co3Ta NPs is shown in Fig. 1b, with lattice spacing 2.10 Å corresponding to the (111) plane of intermetallic Co3Ta. The same lattice spacing measured for other NPs (Supplementary Fig. 2) suggests that Co3Ta NPs have (111) basal planes. Energy-dispersive spectroscopy (EDS) mapping and line scanning profiles of a single Co3Ta NP are presented in Fig. 1c–e and Supplementary Fig. 3, respectively, revealing that both Co and Ta are homogeneously dispersed. Combined with the result of inductively coupled plasma (ICP) analysis, the molar ratio of these two elements is 75.95:24.05 (Fig. 1f), that is 3:1 ratio of Co3Ta.

High-magnification HAADF-STEM imaging was employed to reveal the ordered intermetallic crystal structure of Co3Ta. From the ordered arrangement of atoms, we can identify the ordered intermetallic structure of Co3Ta. Figure 2a shows a representative atomic resolution image of Co3Ta along the [111] zone axis, with lattice spacing of 2.56 Å corresponding to the (110) plane. Because of the ‘Z-contrast’ of Ta and Co, the Ta columns display a higher intensity than that of the Co columns in HAADF-STEM images. It can be seen that each Ta atom is surrounded by six Co atoms in a periodic hexagonal array. The corresponding fast Fourier transformation (FFT) pattern (Fig. 2b) is matched with the simulated image in Fig. 2c, further demonstrating the crystallinity and ordered intermetallic phase of Co3Ta. This ordered intermetallic structure also presents along the [211] zone axes. In Fig. 2d, a HAADF-STEM image of Co3Ta NP is viewed along the [211] zone axis with lattice spacings of 2.09 and 2.56 Å, which are assigned to (111) and (110) lattice fringes of the Co3Ta intermetallic structure. Due to the overlap of Ta and Co atoms in some positions along the [211] zone axis, the ‘Z-contrast’ of Ta and Co is small. The FFT pattern is shown in Fig. 2e. To further confirm the ordered structure, we have simulated the diffraction patterns of an ideal Co3Ta crystal along its [211] zone axis (Fig. 2f), which matches the experimental result. This is conclusive evidence that the atomically ordered Co3Ta intermetallic nanostructures have been successfully synthesized. To further determine the entire ordered intermetallic structure of the Co3Ta NPs, we carried out X-ray absorption fine structure (XAFS) measurements for the Co3Ta NPs and other possible phases. Comparisons between the calculated and experimental absorption patterns of Co and Ta in the ordered intermetallic structure of Co3Ta and other potential samples (i.e., CoO, Co3O4, Co foil, Ta2O5, and Ta powder) are shown in Fig. 2g. h. The Computational Methods show how to obtain the theoretical spectrum. The experimental spectrum of the sample has been successfully reproduced, both for the peak positions and...
intensities, by using the theoretical Co$_3$Ta configuration. Using the “fingerprint” of the Co K-edge and Ta L$_3$-edge XAFS, we can easily determine the dominant existence of the ordered intermetallic Co$_3$Ta phase structure. As to the small difference observed in the A peak site (Fig. 2g), this may be attributed to oxidation of the Co$_3$Ta surface upon exposure of sample in air for relatively long period during the measurements. X-ray photoelectron spectroscopy (XPS) (Supplementary Fig. 4) also confirms the presence of a slight oxidation, which is in agreement with previous metal nanocrystal studies. The XAFS results strongly suggest that the as-prepared product is an ordered intermetallic Co$_3$Ta phase structure as a whole.

To characterize the intrinsic activity of the Co$_3$Ta catalyst, the kinetic currents shown in this work are all normalized to the electrochemically active surface area (ECSA) for a quantitative and more convincing comparison. According to the previous reports, the ECSA was determined by measurement of the electrochemical double-layer capacitance (EDLC) (Supplementary Fig. 5). The electrocatalytic HzOR activities of Co$_3$Ta/C NPs measured in different concentrations of hydrazine with scan rates of 5 mV s$^{-1}$ are displayed in Fig. 3a. From the linear sweep voltammetry (LSV) curve for the solution without hydrazine, we can see that no obvious anodic current appears in the potential window. However, when placed in a 0.1 M hydrazine solution, a significantly rising anodic current appears. Furthermore, the current density increases with increasing hydrazine concentration, indicating that the Co$_3$Ta/C NPs are highly efficient for the HzOR.

In order to further evaluate the intrinsic superior catalytic performance of Co$_3$Ta/C NPs, several samples (including the precursors, Co/C, XC-72, commercial Ir/C, and commercial Pt/C) were employed as control samples in a solution containing 0.2 M hydrazine and 3 M KOH at a scan rate of 5 mV s$^{-1}$, as shown in Fig. 3b. The onset potential is usually regarded as a very important evaluation criterion to determine the catalytic performance of catalysts. It can be seen that the $E_{on}$ of Co$_3$Ta/C NPs is $-0.086$ V (vs RHE; i.e., $-1.175$ V vs SCE), which is 16, 35, and 141 mV lower than that of Co/C, commercial Pt/C, and commercial Ir/C, respectively (Supplementary Fig. 6). Compared with that of other catalysts reported in the recent literatures (Supplementary Table 2), the onset potential of the ordered intermetallic Co$_3$Ta/C catalyst is the lowest, indicating that Co$_3$Ta/C NPs have an ultrahigh intrinsic activity toward HzOR. In addition, the Tafel slope of Co$_3$Ta/C NPs (56.9 mV dec$^{-1}$) is...
lower than those of Co/C NPs (60.6 mV dec$^{-1}$) and commercial Pt/C (73.7 mV dec$^{-1}$) (Fig. 3c), demonstrating that Co$_3$Ta/C NPs increase the current density more quickly than other samples during the HzOR. Notably, at a potential of $+0.06$ V (vs RHE) shown in Fig. 3d, Co$_3$Ta/C NPs produced a praiseworthy current ($25.2$ mA cm$^{-2}$), which is 1.67 and 2.02 times higher than that of Co/C NPs ($15.1$ mA cm$^{-2}$) and commercial Pt/C ($12.5$ mA cm$^{-2}$), respectively. Furthermore, compared with our previous studies (e.g., ultrathin nickel nanosheet arrays ($68$ mA mg$^{-1}$) and ultrathin nickel–cobalt alloy nanosheet arrays ($92$ mA mg$^{-1}$)), the ordered intermetallic Co$_3$Ta shows a considerably high mass activity of $534$ mA mg$^{-1}$ at a potential of $+0.05$ V (vs RHE) in $0.5$ M hydrazine solution. The above results demonstrate that Co$_3$Ta/C NPs show ultrahigh electrocatalytic activity for the HzOR.

Stability is another important parameter to evaluate the practical performance of a catalyst. As shown in Supplementary Fig. 7, long-term stability of the Co$_3$Ta/C NPs for $12,000$ s under a constant potential ($+0.1$ V vs RHE) in $0.2$ M hydrazine solution was investigated. After this harsh $12,000$ s test, Co$_3$Ta/C NPs show a loss of only $12.8\%$ of the initial current density (Fig. 3e). In contrast, Co/C NPs and commercial Pt/C exhibit a serious current density loss of $40.8\%$ and $38.4\%$, respectively. Moreover, after $12,000$ s, the $E_{on}$ of the Co$_3$Ta/C catalyst shows a positive shift of only $10$ mV (Supplementary Fig. 8), electrochemical impedance spectroscopy (EIS) displays negligible changes (Supplementary Fig. 9), and the structure remains intact with no particle agglomerations (Supplementary Fig. 10). The above results demonstrate that Co$_3$Ta/C NPs are remarkably stable. The excellent stability and ultrahigh electrocatalytic activity of Co$_3$Ta/C NPs may be ascribed to its atomically ordered structure and electronic effect of Co$_3$Ta.

X-ray absorption near-edge structure (XANES) analysis. Figure 4a, b show the K-edge and L$_3$-edge X-ray absorption near-edge of Co and Ta elements in the ordered intermetallic structure of Co$_3$Ta and other potential phases (i.e., bulk Co foil, CoO, Co$_3$O$_4$, bulk Ta powder, and Ta$_2$O$_5$). It can be seen that the Co K-edge and Ta L$_3$-edge X-ray absorption edge energy is arranged in

Fig. 2 Atomic structural characterization and X-ray absorption fine structure spectrum measurement of Co$_3$Ta intermetallic nanoparticles. a Atomically resolved HAADF-STEM image of Co$_3$Ta intermetallic NPs. b The corresponding FFT of (a). c The simulated diffraction pattern from the [111] zone axis in (a). d Atomic HAADF-STEM image. e FFT pattern and corresponding simulated diffraction pattern (f) from the [211] zone axis in (d). g The absorption pattern comparisons at the Co K-edge of the experimental Co$_3$Ta nanoparticles (Co$_3$Ta-Exp), calculated Co$_3$Ta nanoparticles (Co$_3$Ta-Cal), Co foil, CoO, and Co$_3$O$_4$. h The absorption pattern comparisons at the Ta L$_3$-edge of the Co$_3$Ta-Exp, Co$_3$Ta-Cal, Ta powder, and Ta$_2$O$_5$.
the order of Co$_3$O$_4$ > CoO > Co$_3$Ta = Co foil and Ta$_2$O$_5$ > Co$_3$Ta = bulk Ta powder. The bader charge calculation$^{47,48}$ by using DFT method also confirms the slight charge transfer between Co and Ta in Co$_3$Ta, as shown in Supplementary Table 3. Despite the net gain of charge in the electron count from Ta due to the difference in electronegativity between Ta and Co, the Co absorption edge energy in Co$_3$Ta exhibits no significant negative shift with respect to that of bulk metallic Co, which is consistent with the previous works$^{49,50}$, and the Ta absorption edge energy in Co$_3$Ta also exhibits a small positive shift with respect to that of bulk metallic Ta. Both are related with the size effect and the tuning of electronic structure of the Ta atom by Co, suggesting that the 5d hole in Ta atom increases$^{51,52}$. An increase in the 5d hole will promote donation of electrons from the reactant orbital to the Ta 5d orbital. Thus, the tuning of electronic structure of Co and Ta likely facilitates the adsorption of N$_2$H$_4$ through

**Fig. 3** Electrochemical performance of Co$_3$Ta/C electrocatalyst for hydrazine oxidation reaction. **a** HzOR polarization curves of Co$_3$Ta/C intermetallic NPs at different hydrazine concentrations. **b** LSV curves of Co$_3$Ta/C, the precursors, Co/C, XC-72, commercial Ir/C, and commercial Pt/C in 3 M KOH solution with 0.2 M hydrazine. The Tafel slopes of Co$_3$Ta/C NPs, Co/C NPs, and commercial Pt/C; Co$_3$Ta/C NPs quickly increase the current density for the HzOR. **d** HzOR performance comparisons of Co$_3$Ta/C, Co/C, commercial Pt/C, and commercial Ir/C at different potentials. **e** Quantitative comparison of the current densities of Co$_3$Ta/C NPs, Co/C NPs, and commercial Pt/C before and after constant applied potential for 12,000 s; Co$_3$Ta/C NPs are remarkably stable.
A schematic illustration for the stepwise N2H4 molecular dehydrogenation process on the Pt (111) surface. Navy blue, orange, and yellow balls represent Pt, N, and H atoms, respectively. Purple and cyan balls represent Co and Ta atoms, respectively. Density functional theory (DFT) calculations. Identifying the location of the active sites in an intermetallic is conducive to the design of optimal catalysts. Generally, there are several forms of hydrazine adsorption on Co3Ta catalyst surface. As shown in Supplementary Fig. 11, the Ta-Co-cis conformation has the lowest adsorption energy (Supplementary Table 4), indicating the most stable adsorption configuration. It is preferable for the N–N molecular axis projection onto the surface be parallel with the Ta-Co bridge. That means the Co-Ta bridge sites can be identified as the location of the most active sites of HzOR in the ordered Co3Ta intermetallic. DFT calculations were carried out to further reveal the origin of the superior intrinsic activity of ordered intermetallic Co3Ta toward hydrazine oxidation. The surface structure plays an important role about the computations of adsorption of hydrazine on metal surface. Based on the HRTEM, XRD results, and the analysis of surface energies (Supplementary Table 5), the dehydrogenation process of hydrazine was analyzed over the Co3Ta (111) surface, with the dehydrogenation process of hydrazine over the (111) surface of Pt used as a control, as shown in Supplementary Fig. 12. Because both the Ta-Co-cis and Pt-anti conformations have the lowest adsorption energies (Supplementary Tables 4, 6), these conformations were selected as the adsorption configurations for DFT calculations. The density of states (DOS) of the Co3Ta (111) surface indicated that the electron structure of the surface is similar to bulk metal, and the surface DOS distribution crosses over the Fermi level, which benefits electron transport during the HzOR process (Supplementary Figs. 13 and 14). Because of the magnetic properties of Co, the spin down parts are larger than the spin up parts near the Fermi energy level. Figure 4c, d illustrate the stepwise N2H4 molecular dehydrogenation process on the Pt (111) and the Co3Ta (111) surface, respectively, which consist of four intramolecular dehydrogenation steps (N2H4 → N2H3 → N2H2 → N2H → N2)41,55. Figure 4d shows the free energy profiles of the HzOR on the Pt (111) and Co3Ta (111) surfaces accordingly. The first dehydrogenation step (N2H4 → N2H3) is exothermic on the Co3Ta surface (0.65 eV), which is much higher than on the Pt surface (0.37 eV). This demonstrates that the first dehydrogenation step is more readily carried out on the surface of Co3Ta than that of Pt. Though the second dehydrogenation step (N2H3 → N2H2) is endothermic on both surfaces, the activation energy is much easier to overcome on the Co3Ta surface (0.03 eV) than on the Pt surface (0.31 eV). Overall, from the state of adsorbed N2H4 to the state of adsorbed N2, the exothermic energy on the Co3Ta surface (1.83 eV) is much larger than that on the Pt surface (1.25 eV), indicating a more thermodynamically favorable catalytic process over the ordered intermetallic Co3Ta. Based on the discussion above, ordered intermetallic Co3Ta exhibits ultrahigh electrocatalytic activity toward hydrazine electrooxidation, including an ultralow onset potential, low Tafel slope, and high current density. The origin of the ultrahigh hydrazine oxidation activity can be explained as follows. First, the electronic structure of the Ta atom is tuned by Co and there is a synergistic effect between Co and Ta in Co3Ta. Second, the activation energy of the hydrogen dissociation step decreases significantly during HzOR. Both will intrinsically contribute to the superior electrocatalytic activity of non-precious ordered nano-intermetallic Co3Ta toward hydrazine oxidation.
Discussion
In summary, we have demonstrated the excellent performance and stability of novel Co3Ta NPs as an intermetallic electro-catalyst that contains non-precious metals and only early transition metals. The use of air-free synthetic conditions and subsequent annealing leads to the formation of atomically ordered Co3Ta NPs with a uniform particle size of 5 nm. As an electrolyte for hydrazine oxidation reaction (H2OR), Co3Ta/C NPs exhibit high stability and a higher electrocatalytic performance than conventional electrocatalysts in terms of their low onset potentials (−0.086 V vs RHE) for fuel oxidation. Theoretical calculations reveal that the activation energy of hydrogen dissociation decreases significantly upon N2H4 adsorption on the Co-Ta bridge active sites, which not only increases the number but also enhances the activity of the active sites, contributing to the considerably enhanced H2OR activity. The extraordinarily high performance of the supported ordered Co3Ta intermetallic nanocrystals provides a very promising alternative to the conventional Pt/C catalyst for the H2OR in direct liquid fuel cells.

Methods

Synthesis of Co3Ta intermetallic nanoparticles. Co3Ta intermetallic NPs were synthesized by co-reduction of tantalum and cobalt salts under anhydrous and anaerobic conditions, followed by annealing. In a typical procedure, CoCl2 and 0.065 mmol TaCl5 were dissolved in 35 mL of rigorously dried and degassed tetrahydrofuran (THF) and diglyme solution in an argon-filled glovebox. The obtained product was quickly transferred to a glovebox, then the mixture was transferred to a 150 mL round-bottom flask and heated to 120 °C with stirring overnight. Next, sodium triethylborohydride (NaEt3BH, 1 M in THF, Sigma-Aldrich) was injected into the mixture under vigorous stirring and left to stir for 8 h to form a homogeneous catalyst ink. A 15 mL aliquot of the dispersion was collected on an X-ray diffractometer (Bruker D8, Cu Kα) for powder X-ray diffraction (XRD) measurements. The XRD patterns were obtained by using the Vienna Ab-initio Simulation Package (VASP)59,60 with Perdew-Burke-Ernzerhof (PBE) functional. The plane-wave basis (kinetic energy cutoff values Ecut = 520 eV) and projector-augmented wave (PAW) pseudopotential62,63 were employed. The atomic positions were fully optimized until the Hellmann-Feynman force was <0.05 eV/Å and total energy convergence criterion was set to 1 × 10−5 eV. The two Pt (111) and Co3Ta (111) surfaces were employed in our calculations. The adsorption energies were calculated using the 441 supercell, which includes four atomic layers, with the atomic position of the two top layers optimized, while the two bottom layers were fixed. The adsorption energies $E_{\text{ads}}$ which one N2H4 molecule adsorbed on Co3Ta (111) surface with different layers were shown in Supplementary Table 7. The results indicated that four layers surface model in our calculation was workable. To avoid the interaction of neighboring images, a 15 Å vacuum layer was set to the direction of the c axis. The Monkhorst-Pack64 k-point grid 3 × 3 × 1 was set in all calculations. The calculation of the Gibbs free energy of the intermediates followed the Norskov method65.

The calculation of the theoretical XAFS spectra of Co3Ta; the calculation of the theoretical spectra was performed by the software Artemis based on a standard model of Co3Ta with a Pm-3m space group (ICPDS, No. 15-0028). The core of the calculation was based on the framework of FEFF’s multiple scattering path expansion, where the simulated spectra is the summation of one or more scattering paths computed by FEFF. To obtain the theoretical spectra, the ATOF module was ran with a cluster size of 5.5 Å and longest scattering path of 5.0 Å. The calculation was done in the R space within an R range of 1.05–3.78 Å during which the Fourier transformation was conducted. Finally, the theoretical XAFS spectra were acquired by inverse Fourier transformation from R space and compared with experimental results.

The Gibbs free energy change $\Delta G$ is defined as follows: $\Delta G = \Delta E + \Delta ZPE = \Delta E + \Delta G_{\text{us}} + \Delta G_{\text{inh}}$, where $\Delta E$ is the change of electronic energy obtained from DFT calculations, $\Delta ZPE$ is the change of zero-point energy, and $\Delta S$ is the entropy difference (see the values in Supplementary Table 8). $\Delta G_{\text{us}}$ is the free energy contributed by the electrode potential ($\Delta G_{\text{us}} = -nF \Delta U$ ($n$ represents the number of electrons transferred in the corresponding elementary steps and $U$ is the electrode potential, respectively)). $\Delta G_{\text{inh}}$ is the free energy related to the H+ concentration. The $\Delta G_{\text{us}}$ and $\Delta G_{\text{inh}}$ are set to zero in our calculation. The contribution of vibration of all adsorbed species was considered in our calculation.

Data availability
The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Author contributions
G.F. and D.X. conceived the idea. G.F., L.A., and B.L. carried out the sample synthesis, characterization and performance measurement. L.A., F.N., and N.J. performed the DFT simulation and theoretical analyses. B.L., Y.Z., and J.S. helped with the XAFS measurements and discussion. X.C. and Y.Z. helped with the HAADF-STEM measurements and discussion. The paper was written by G.F. and D.X., and D.X. edited the paper. All authors contributed to discussing and revising the paper.

Competing interests
The authors declare no competing interests.

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