Molybdenum-doped ordered L1\textsubscript{0}-PdZn nanosheets for enhanced oxygen reduction electrocatalysis

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Abstract
Ultrathin Pd-based two-dimensional (2D) nanosheets (NSs) with tunable physicochemical properties have emerged as promising candidate for oxygen reduction reaction (ORR). Unfortunately, structurally ordered Pd-based NSs can be hardly prepared as high temperature annealing (>600° C) is necessary for disorder to order phase transition, making it a considerable challenge for morphology control. Herein, a new class of ultrathin structurally ordered Mo-doped L1\textsubscript{0}-PdZn NSs with curved geometry and abundant defects/lattice distortions is reported as an efficient oxygen reduction electrocatalyst in alkaline solution. It is found that Mo(CO)\textsubscript{6} serves as reducing agent and Mo source to generate the unique ordered 2D morphology, which leads to the significantly modified electronic structure. The developed L1\textsubscript{0}-Mo-PdZn NSs exhibit excellent ORR mass activity of 2.6 A mg\textsubscript{Pd}^{-1} at 0.9 V versus reversible hydrogen electrode, 31.5 and 17.6 times higher than those of Pd/C and Pt/C, respectively, outperforming most of the reported Pd-based ORR electrocatalysts. Impressively, L1\textsubscript{0}-Mo-PdZn NSs is extremely stable for ORR, with only 2.3% activity loss after 10 000 potential cycles. Density functional theory study suggests that ordered L1\textsubscript{0} structure and Mo doping can raise the vacancy formation energy of Pd atom and thus promote the ORR stability.

KEYWORDS
electrocatalysis, fuel cell, nanosheets, oxygen reduction, Pd-based intermetallics
1 | INTRODUCTION

The sluggish kinetics of oxygen reduction reaction (ORR) is the key bottleneck limiting the performance of fuel cells or metal-air batteries.\textsuperscript{1–3} To enhance the performance and advance the practical applications of these energy conversion devices, numerous efforts have been devoted to developing efficient ORR electrocatalysts. To date, platinum (Pt) and its alloy (Pt-M, M = Fe, Co, Ni, etc.) nanocrystals (NCs) are the most active ORR electrocatalysts.\textsuperscript{4–6} Yet, the limit reserve, high cost, and unsatisfactory stability of Pt and Pt-M NCs arise as other concerns for widespread commercializations.\textsuperscript{7–9} It is necessary to develop alternative electrocatalysts with respectable ORR activity and stability.

Owing to the similar electronic structure with Pt, and relatively higher abundance of Palladium (Pd) on earth, Pd-M NCs have recently attracted much research interest as ORR electrocatalysts.\textsuperscript{10–13} Pd-based two-dimensional (2D) structures, with the advantages of high atomic utilization efficiency and larger interfacial areas contacting with support compared to 0D nanoparticles (NPs),\textsuperscript{14–16} have become promising candidate electrocatalysts for ORR. For instance, PdMo metallenes,\textsuperscript{14} and porous Pd metallenes,\textsuperscript{17} have displayed much enhanced ORR activity in both half-cell and Zn-air battery tests. Nevertheless, another obstacle is the durability issue of these Pd-M NCs, which can be ascribed to the less stabilized M in disordered Pd-M alloy, and the M atoms will be etched away during electrochemical tests.\textsuperscript{18} By contrast, structurally ordered intermetallic PtM and PdM NCs, due to the high cohesive energy and negative structural formation energy ($E_f$), display much improve electrochemical stability and thus have attracted a broad range of research interest.\textsuperscript{19,20} In principle, the more negative $E_f$ would lead to the higher vacancy formation energy ($E_{\text{vac}}$). For instance, our recent work demonstrates that the $E_{\text{vac}}$ of M atom in L1$_0$-ordered structure, that is, Pt/M = 1/1, is much increased compared to that in disordered A1 counterpart.\textsuperscript{21} Therefore, designing ultrathin 2D Pd-based nanosheets (NSs) together with ordered L1$_0$ structure would be of significance to improve the ORR activity and stability simultaneously. Unfortunately, the preparation of L1$_0$ structure usually requires high temperature annealing (>600°C), which will lead to agglomeration of the NCs and make it difficult for morphology control. As a result, the reports on Pt- or Pd-based 2D NSs with ordered L1$_0$ structure are much limited. Meanwhile, it has proven that doping Pt- or Pd-based NCs with a third metal can not only improve the ORR activity by tuning the local strain and electronic structure but also stabilize the structure and enhance the stability. For example, Mo-doped PtNi NCs show impressive ORR activity and stability because of the stabilization of Pt/Ni atoms against dissolution.\textsuperscript{22,23} Besides, the cohesive energy of Mo is as large as 6.82 eV/atom, much higher than Pd (3.89 eV/atom) and Zn (1.35 eV/atom), which may improve the stability from the perspective of thermodynamics.

Herein, 2D Mo-doped L1$_0$-ordered PdZn (L1$_0$-Mo-PdZn) NSs with ultrathin thickness (∼2.1 nm) are developed as ORR electrocatalysts. Compared to Fe and Cu ions, which may catalyze Fenton reaction to generate reactive oxygenate species,\textsuperscript{24,25} Zn is an antioxidative element and can restrain Fenton reaction.\textsuperscript{21} Meanwhile, the $E_f$ of L1$_0$-PdZn intermetallics is as large as −0.575 eV/atom (compared to −0.066 eV/atom for L1$_0$-PdFe and −0.124 eV/atom for B2-PdCu), which may render much improved stability. The developed L1$_0$-Mo-PdZn NSs demonstrate promising ORR activity and stability in alkaline electrolyte, with a high mass activity (MA) of 2.6 A mg$_{\text{Pd}}$$^{-1}$ at 0.9 V versus reversible hydrogen electrode (RHE), nearly 17.6 times higher than that of commercial Pt/C. Meanwhile, negligible activity loss and structural change are observed after 10 000 potential cycles. The enhanced ORR activity is ascribed to the modified electronic structure of Pd and high electrochemical active surface area (ECSA), while the stability is attributed to the increased $E_{\text{vac}}$ of Pd as a result of L1$_0$-ordering and Mo doping.

2 | RESULTS AND DISCUSSION

Mo-doped L1$_0$-PdZn (denoted as L1$_0$-Mo-PdZn) NSs were prepared by a wet-chemical co-reduction approach (for details see Supporting Information, SI). Briefly, the L1$_0$-Mo-PdZn NSs were produced in oleylamime (OAm) at 300°C in the presence of Mo(CO)$_6$. Mo(CO)$_6$ can decompose into carbon monoxide (CO) gas and Mo atoms, where CO serves as a capping agent for the controlled growth of 2D morphology, and Mo atoms can dope into PdZn lattice. Under high temperature (300°C), Pd and Zn atoms can diffuse and rearrange into L1$_0$ intermetallic structure. As a comparison, disordered A1-PdZn NSs and ordered L1$_0$-PdZn NSs were prepared at 280 and 300°C in the presence of CO gas, respectively. The as-prepared NSs were loaded onto carbon (Vulcan XC-72, denoted as A1-PdZn/C, L1$_0$-PdZn/C, and L1$_0$-Mo-PdZn/C NSs) and washed with acetate acid to remove the residual OAm for further use.

The morphology of L1$_0$-Mo-PdZn NSs was characterized by transmission electron microscopy (TEM) and high-angle annular dark-field-scanning TEM (HAADF-STEM). 2D sheets with lengths up to several hundred nanometers are the dominant product (Figure 1A and Figure S1). Some wrinkles can be clearly observed within L1$_0$-Mo-PdZn NSs (Figure 1B), indicating the high flexibility similar to graphene, which may generate strain as a result of curved geometry (Figure S2).\textsuperscript{14,16,17} Besides, the contrast of
L10-Mo-PdZn NSs in flat region is quite low compared to the background, implying the ultrathin nature. Indeed, the thickness of L10-Mo-PdZn NSs is measured to be ∼2.1 nm from the folded edge (Figure 1C), with only 7–10 atomic-layer. Meanwhile, the lateral size is estimated in the range of 45–200 nm. Atomic force microscopy was employed to further measure the thickness of L10-Mo-PdZn NSs. As shown in Figure 1D, the height profile is about 2.7 nm, slight higher than that measured in STEM results, which may be ascribed to the residual capping agent on the NSs.26,27

Figure 1E shows the high resolution TEM (HRTEM) image of the lateral region of L10-Mo-PdZn NSs. The spacing lattice fringe is measured to be 0.219 nm, corresponding to (111) facet of L10-PdZn. Meanwhile, several grain boundaries in L10-Mo-PdZn NSs can be clearly observed (Figure 1E). The corresponding fast Fourier transform (FFT) pattern also confirms the plly-crystalline nature of
L1₀-Mo-PdZn NSs. In addition, the curved geometry is further evidenced in the HRTEM image of folded edge region (Figure 1F), where the distortion of lattice fringes along the curved edge is clearly observed. Noteworthy, these grain boundaries and lattice distortions can provide plenty of defect sites, which have been proven to benefit the catalytic activity.28,29

The atomic-scale structure of L1₀-Mo-PdZn NSs was further characterized by spherical aberration (Cs)-corrected HAADF-STEM (Figure 2). Figure 2A shows the atomic arrangement of L1₀-Mo-PdZn NSs viewed along (11–2) zone axis. The ordered structure is clearly indicated by the bright (Pd) and dark (Zn) atoms and their periodic arrangement along <1–10> direction. The atomic arrangements are in good agreement with the standard L1₀ structure along (11–2) projection (Figure 2B). Interestingly, the lattice distortion, with a twisted angle of ca. 4.4°, can be identified as a result of curved geometry and is in accordance with HRTEM results (Figure 1F). The inset of Figure 2A is the corresponding FFT pattern of this area, and the presence of (110) superlattice spots is observed. The spacings of lattice fringes are measured to be 0.309 and 0.220 nm, corresponding to (110) and (111) facets, respectively. Besides, the periodic L1₀ structure is further confirmed by HAADF line-scan profile (Figure 2C). The alternating intensity profile of line 2 reveals the ordered arrangement of Pd and Zn atoms, while line 1 shows the presence of Pd atom only. These results confirm the presence of L1₀ ordered structure with some lattice distortion. HAADF-STEM energy-dispersive X-ray spectroscopy (EDX) elemental mappings of L1₀-Mo-PdZn NSs demonstrate the uniform distribution of Pd/Zn/Mo elements throughout the nanosheet (Figure 2D). The molar ratio of Pd/Zn/Mo in L1₀-Mo-PdZn NSs is measured to be 52/42/6 by the TEM-EDX analysis (Figure S3), in line with the result obtained by the inductively coupled plasma optical emission spectrometer (ICP-OES, 57/41/2).

Figures S4 and S5 show the morphology of A1-PdZn NSs and L1₀-PdZn NS. Unlike L1₀-Mo-PdZn NSs, the thickness of A1-PdZn NSs and L1₀-PdZn NSs becomes thicker, and some aggregations are observed, which can be ascribed to the low CO concentration in the OAm solution. Therefore, the in situ generated CO molecule via the decomposition of Mo(CO)₆ is vital to prepare ultrathin 2D NSs. The Pd/Zn...
FIGURE 3 (A) X-ray diffraction (XRD) patterns of Al-PdZn/C, L10-PdZn/C, and L10-Mo-PdZn/C nanosheets (NSs). (B and C) High resolution Pd 3d X-ray photoelectron spectroscopy (XPS) spectra of Pd/C, Al-PdZn/C, L10-PdZn/C, and L10-Mo-PdZn/C NSs. (D) Pd (0) and Pd (II) content in Pd/C, Al-PdZn/C, L10-PdZn/C, and L10-Mo-PdZn/C NSs show the high resolution Pd 3d XPS spectra, where the binding energies at around 336 eV and 341 eV can be assigned to 3d_{5/2} and 3d_{3/2} orbitals of metallic Pd. Meanwhile, the peaks at around 338 eV and 343 eV are associated with Pd (II). These results indicate the coexistence of metallic Pd (0) and oxidative Pd (II) in Pd/C, Al-PdZn/C, L10-PdZn/C, and L10-Mo-PdZn/C NSs. Specifically, the ratio of Pd (0) to Pd (II) in L10-Mo-PdZn/C NSs is calculated to be 76.5/23.5, much higher than those in Pd/C (43/57), Al-PdZn/C NSs (60.5/39.5), and L10-PdZn/C NSs (67/33) (Figure 3D). Such results demonstrate that phase transition from Al to L10 as well as Mo doping can improve the antioxidant capability of L10-Mo-PdZn/C NSs. In addition, the Pd 3d_{5/2} binding energies of Al-PdZn/C (336.2 eV), L10-PdZn/C (336.1 eV), and L10-Mo-PdZn/C (336.2 eV) NSs are higher than that in Pd/C (335.7 eV), which indicates a downshift of the d-band center of Pd can weaken the adsorption of oxygenated species, thus enhancing the ORR activity. 31 Figure S9 shows the high resolution Mo 3d XPS spectrum of L10-Mo-PdZn/C NSs. Both of metallic state (Mo (0)) and oxidative state (Mo (VI)) are observed in XPS spectrum, in consistency with previous ratios of Al-PdZn NSs and L10-PdZn NSs are 75/25 and 55/45, respectively, as determined by ICP-OES. The NSs are well dispersed after loading onto the carbon support (Figures S6–S8).

X-ray diffraction (XRD) was performed to characterize the crystal structure of the obtained NSs. As shown in Figure 3A, after reacting at 280 °C, the Al-PdZn/C NSs show similar diffraction peaks with standard face-centered cubic Pd (PDF#65-2867), which can be attributed to the insufficient reduction and diffusion of Zn element at 280 °C. The diffraction peaks reveal a slight right-shift as a result of the incorporation of smaller Zn atom. By contrast, when reacted at 300 °C, the diffraction patterns become different, where the peak at around 68° disappears, while other peaks at 63° and 73° appear, suggesting the transition from disordered Al1 structure to ordered L10 structure. Indeed, the diffraction peaks of L10-Mo-PdZn/C and L10-PdZn/C can be well indexed to the L10-PdZn structure (PDF#65-9523). Importantly, the ultrathin 2D morphology of Pd-Zn NSs is well maintained after phase transition (Figure 1A), which makes it possible to take the advantages of ultrathin 2D architecture and ordered structure for electrocatalysis.

X-ray photoelectron spectroscopy (XPS) was carried out to analyze the valence state and electronic structures of Pd in the studied samples. All the binding energies were calibrated with C 1s at 284.8 eV as a reference. Figure 3B,C X-ray diffraction (XRD) patterns of Al-PdZn/C, L10-PdZn/C, and L10-Mo-PdZn/C nanosheets (NSs). (B and C) High resolution Pd 3d X-ray photoelectron spectroscopy (XPS) spectra of Pd/C, Al-PdZn/C, L10-PdZn/C, and L10-Mo-PdZn/C NSs. (D) Pd (0) and Pd (II) content in Pd/C, Al-PdZn/C, L10-PdZn/C, and L10-Mo-PdZn/C NSs.
We then evaluated the electrocatalytic performance of the prepared catalysts in 0.1 M KOH electrolyte. Commercial Pt/C (JM, 40 wt.%), homemade Pd/C (HM, 10 wt.%), and Pd NSs are employed as references. Figure S10 shows the TEM image of Pd/C. The Pd nanoparticles distribute uniformly on the carbon support, with an average diameter of only 1.9 ± 0.2 nm. Pd NSs can also be prepared in the presence of CO gas. TEM images show that Pd NSs is the major product, while some aggregates are observed as well (Figure S11), similar to A1-PdZn NSs. The studied samples were first subjected to 50–100 cyclic voltammetry (CV) cycles between 0.0 and 1.0 V (vs. RHE) in N₂-saturated 0.1 M KOH for activation. Figure 4A and Figure S12 show the stable CV curves of the studied electrocatalysts. The Pd-containing electrocatalysts display similar electrochemical behavior in 0.1 M KOH solution (Figure 4A), where the redox peaks at the potential range of 0–0.4 V are associated with the underpotential adsorption and desorption of hydrogen (H\textsubscript{upd}). At the potential range of 0.65–0.75 V, cathodic peaks associated with Pd reduction (reduction of Pd-OH\textsubscript{ad}) can be clearly observed. Notably, the Pd-OH\textsubscript{ad} reduction peak of L10-Mo-PdZn/C NSs positively shifts by 70 mV compared to Pd/C, which indicates a weak oxygen affinity and may be beneficial to ORR by reducing the adsorption of oxygenated species.\textsuperscript{31–33} By contrast, Pt/C reveals different electrochemical behaviors with more symmetric redox peaks of H\textsubscript{upd} and Pt-OH (Figure S12).

CO stripping voltammetry was also carried out to study the surface electronic structures. Compared to Pd/C, L10-Mo-PdZn/C NSs display a more negative CO
stripping peak (Figure 4B), which suggests a down-shifted \textit{d}-band center of surface Pd atoms and the weakened Pd-O binding energy.\textsuperscript{34} Meanwhile, the CO stripping peaks of Al-PdZn/C and L\textsubscript{10}-PdZn/C NSs are similar with that of L\textsubscript{10}-Mo-PdZn/C NSs, implying a similar electronic structure, in accordance with CV and XPS results. The electrochemical active surface areas (ECSAs) of Pd/C, Pd/C NSs, Al-PdZn/C NSs, L\textsubscript{10}-PdZn/C NSs, and L\textsubscript{10}-Mo-PdZn/C NSs, calculated by CO stripping voltammetry, are 80.9, 31.6, 27.5, 21.3, and 60.4 m\textsuperscript{2} g\textsubscript{Pd}\textsuperscript{-1}, respectively. The higher ECSA of L\textsubscript{10}-Mo-PdZn/C NSs is ascribed to the thinnest thickness compared to Al-PdZn/C and L\textsubscript{10}-PdZn/C NSs.

Figure 4C shows the positive-going ORR polarization curves of the studied electrocatalysts in O\textsubscript{2}-saturated 0.1 M KOH. L\textsubscript{10}-Mo-PdZn/C NSs demonstrate the highest half-wave (\(E_{1/2}\)) of 0.894 V, much higher than those of Pd/C (0.837 V), Pt/C (0.84 V), Pd/C NSs (0.85 V), Al-PdZn/C NSs (0.876 V), and Al-PdZn/C NSs (0.869 V). The ORR activity of each electrocatalysts is further quantified by calculating the kinetic current at 0.9 V and normalizing with Pd loading and ECSA (Figure 4D). Impressively, the L\textsubscript{10}-Mo-PdZn/C NSs deliver MA and specific activity (SA) of 2.6 A mg\textsubscript{Pd}\textsuperscript{-1} and 4.31 mA cm\textsuperscript{-2}, respectively. The MA of L\textsubscript{10}-Mo-PdZn/C NSs is about 31.5 and 17.6 times higher than those of Pd/C (0.08 A mg\textsubscript{Pd}\textsuperscript{-1}) and Pt/C (0.14 A mg\textsubscript{Pt}\textsuperscript{-1}), respectively, representing one of the most active Pd-based electrocatalysts in alkaline electrolyte (Table S1). In addition, the MA of L\textsubscript{10}-Mo-PdZn/C NSs is much superior to those of Pd/C NSs (0.465 A mg\textsubscript{Pt}\textsuperscript{-1}), Al-PdZn/C NSs (0.96 A mg\textsubscript{Pt}\textsuperscript{-1}), and L\textsubscript{10}-PdZn/C NSs (0.65 A mg\textsubscript{Pt}\textsuperscript{-1}), while the difference in SA of these three electrocatalysts is not as noticeable as the difference in MA (Figure 4D). In this regard, the higher MA of L\textsubscript{10}-Mo-PdZn/C NSs may originate from the ultrathin 2D structure and higher ECSA.

The ORR Tafel slopes of the studied electrocatalysts are calculated (Figure 4E). The obtained Tafel slope of
Li$_{10}$-Mo-PdZn/C NSs is 58 mV dec$^{-1}$, closed to those of Pd/C (70 mV dec$^{-1}$), A1-PdZn/C (67 mV dec$^{-1}$), and Li$_{10}$-PdZn/C (72 mV dec$^{-1}$) NSs. The similar Tafel slopes of Pd-containing electrocatalysts suggest the similar reaction mechanism that the migration of reaction intermediates is the rate-determining step (RDS). As for Pt/C, the Tafel slope is 92 mV dec$^{-1}$, which implies the different RDS for Pt/C and Pd-containing electrocatalysts. The electron transfer numbers as well as H$_2$O$_2$ production rate of Li$_{10}$-Mo-PdZn/C NSs during ORR process were evaluated by rotating ring-disk electrode, as shown in Figure 4F. Li$_{10}$-Mo-PdZn/C NSs demonstrate an H$_2$O$_2$ yield below 5% and an electron transfer number of 3.9 in the range of 0.4–0.9 V, verifying the high selectivity of Li$_{10}$-Mo-PdZn/C NSs for ORR. Noteworthy, Li$_{10}$-Mo-PdZn/C NSs also shows comparable ORR activity to commercial Pt/C with a similar loading in 0.1 M HClO$_4$ (Figure S13). The enhanced ORR catalytic activity of Li$_{10}$-Mo-PdZn/C NSs could be ascribed to the weakened Pd-O binding strength, ultrathin 2D architecture with abundant grain boundaries/defect sites.

Stability tests were performed in O$_2$-saturated 0.1 M KOH by cycling between 0.6–1.0 V versus RHE at a scan rate of 100 mV s$^{-1}$. All of Pd/C, Pt/C, and A1-PdZn/C NSs show noticeable activity loss after 10 000 potential cycles, with 12 mV, 27 mV, and 16 mV loss in $E_{1/2}$, respectively (Figure 5A and Figure S14). After A1 to Li$_{10}$ transition, the stability of Li$_{10}$-PdZn/C NSs is much improved, and only 5 mV loss in $E_{1/2}$ is observed (Figure 5B). Impressively, Mo doping can further enhance the stability, and negligible change in ORR polarization curves is observed after potential cycles (Figure 5C). To be more quantified, we calculated the change in MA after potential cycles. Li$_{10}$-Mo-PdZn/C NSs retain a MA of 2.54 A mg$^{-1}$ after stability test, while Pd/C NSs, A1-PdZn/C NSs, and Pt/C suffer from 26.7%, 58.4%, and 50% activity loss, respectively (Figure 5D and Figure S15), further confirming the excellent stability of Li$_{10}$-Mo-PdZn/C NSs. After potential cycles, Li$_{10}$-Mo-PdZn/C NSs can maintain the 2D architecture, and the composition is nearly unchanged (Figure S16).

We performed Density functional theory (DFT) calculation to elucidate insights into the excellent stability of Li$_{10}$-Mo-PdZn/C NSs. Vacancy formation energy (E$_{vac}$) of Pd atom is employed as stability descriptor, where a higher E$_{vac}$ suggests better stability. As shown in Figure 5E, the E$_{vac}$ of Pd in A1-PdZn is 1.2 eV. After A1 to Li$_{10}$ transition, the E$_{vac}$ of Pd increases by 0.084 eV, suggesting improved antioxidative capability of Pd atoms due to the strong Pd-Zn interatomic interaction in Li$_{10}$ structure. Mo doping can further increase the E$_{vac}$ of Pd to 1.423 eV, rendering a much improve stability by inhibiting the oxidation and dissolution of Pd atoms. In addition, the ratio of Pd (0) to Pd (II), obtained by XPS results, is in good agreement with E$_{vac}$ of Pd in A1-PdZn, Li$_{10}$-PdZn, and Li$_{10}$-Mo-PdZn that Li$_{10}$-Mo-PdZn shows the most antioxidative tendency. Besides, the 2D anisotropic architecture also helps improve the stability by reinforcing the interaction between PdZn NSs and carbon support. Taking these factors together, the excellent stability of Li$_{10}$-Mo-PdZn/C NSs is attributed to the unique Li$_{10}$ structure, Mo doping, and 2D architecture.

3 CONCLUSIONS

In summary, we have demonstrated the construction of Mo-doped, ultrathin, and defect-rich Li$_{10}$-PdZn NSs as efficient ORR electrocatalysts in alkaline electrolyte. It is found that the in situ generated CO via the decomposition of Mo(CO)$_6$ is the key for the preparation of ultrathin 2D morphology. The developed Li$_{10}$-Mo-PdZn NSs exhibit high ORR MA of 2.6 A mg$^{-1}$ at 0.9 V versus RHE, 31.5 and 17.6 times higher than those of Pd/C (0.08 A mg$^{-1}$) and Pt/C (0.14 A mg$^{-1}$), respectively. Notably, Li$_{10}$-Mo-PdZn NSs display an excellent stability, and only 2.3% activity loss is observed after 10 000 potential cycles. The impressive ORR activity and stability make our Li$_{10}$-Mo-PdZn NSs one of the best Pd-based ORR catalysts. According to XPS and CO stripping voltammetry, the outstanding catalytic activity can be attributed to the modified electronic structure of Pd atom that optimizes oxygen adsorption energy on Pd. DFT results demonstrate that the ordered Li$_{10}$ structure and Mo doping can simultaneously increase the vacancy formation energy of Pd atom, thereby inhibiting the oxidation and dissolution of Pd atoms and improving the stability. This work demonstrates a promising strategy for shape and structure controlled electrocatalysts with advanced activity and durability, which will be of great significance for energy conversion applications and beyond.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.
DATA AVAILABILITY STATEMENT
All data supporting the findings of this study are available within the article and the Supplementary Information file.

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**SUPPORTING INFORMATION**

Additional supporting information can be found online in the Supporting Information section at the end of this article.

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