

A Defect-enriched PdMo Bimetallic for ethanol oxidation reaction and 4-nitrophenol reduction

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1. Experimental Section

1.1. Chemicals and materials.

All chemicals and materials utilized in this investigation were sourced from reputable commercial suppliers, and their application required no further purification. Specifically, Palladium (II) acetylacetonate ($\text{Pd}(\text{acac})_2$, purity 99.00%), ammonium bromide (NH_4Br , purity 99.99%), oleylamine (OAm, purity >80%), cyclohexane (C_6H_{12} , purity 99.99%), isopropyl alcohol ($\text{C}_3\text{H}_8\text{O}$, purity 99.90%), and Pt/C catalyst (20 wt% Pt nanoparticles on graphitized carbon, purchased from Macklin Biochemical Technology Co., Ltd.) were part of the materials procured. Molybdenum hexacarbonyl ($\text{Mo}(\text{CO})_6$, purity 99.90%), Ascorbic acid (AC, purity 99.90%), and potassium hydroxide (KOH, purity 95.00%) were acquired from Aladdin Reagent Co., Ltd. Ethanol ($\text{C}_2\text{H}_5\text{OH}$, purity 99.90%) was sourced from Hangzhou Gaojing Fine Chemical Industry Co., Ltd., and Nafion dispersion (5 wt.%) was obtained from Suzhou Sinero Technology Co., Ltd. All solutions were meticulously prepared using ultrapure water ($18.3 \text{ M}\Omega \text{ cm}^{-1}$).

1.2. Synthesis of original PdMo bimetallic.

8 mg of $\text{Pd}(\text{acac})_2$, 28 mg of ascorbic acid, and 4 mg of $\text{Mo}(\text{CO})_6$ was dissolved in 5 mL of OAm through ultrasonication for approximately 30 minutes, resulting in a yellow solution. Subsequently, the obtained solution was transferred into a 50 mL stirred batch reactor and then heated at 80 °C for 12 hours. After reaction, a black colloid was formed, and the powder was collected by centrifugation with ethanol followed by dried in a vacuum oven.

1.3. Synthesis of defective PdMo bimetallic.

The original PdMo bimetallic was then re-dispersed in 5 mL C_6H_{12} and then transferred into a 10 mL tetrafluoroethylene hydrolysis tube, with an additional 5 mg of NH_4Br and 5 μL of OAm. After ultrasonication for about 15 minutes, the tube was sealed tightly and heated at 45 °C for 6 hours. Subsequently, a black colloid product was obtained,

and the powder precipitate was collected through ethanol centrifugation. Finally, the powder underwent further drying in a vacuum oven.

1.4. The preparation of ink.

A 5 mg portion of the electrocatalyst was added to a 1 mL mixed solution containing 750 μL of water, 250 μL of isopropanol, and 50 μL of Nafion (0.5 wt%). The resulting solution was transformed into ink after 15 minutes of ultrasonication. Subsequently, a 5 μL droplet of the ink was applied to a polished glassy carbon electrode (GCE, 3 mm in diameter).

1.5. Characterizations.

SEM imaging was conducted on an S4800 scanning electron microscope, employing an accelerating voltage of 10 kV. TEM analysis was performed using a JEM 2100 Plus transmission electron microscope at an acceleration voltage of 120 kV. AFM measurements were carried out with a Bruker Dimension Icon. XRD analysis was performed on a D8A8 Advance instrument with Cu K radiation ($\lambda=0.1541$ nm) at 40 kV voltage and 30 mA current. XPS spectra were acquired on a Thermo Scientific XPS instrument (ESCALAB 250 XI) using Al K α radiation (1486.6 eV). The metal concentrations of the catalysts were quantitatively determined through ICP-AES using an Agilent 8800 instrument. The samples for ICP-AES underwent pretreatment in a microwave digestion and extraction system (MARS Xpress).

1.6. Evaluation of ethanol oxidation reaction.

Electrochemical analyses, encompassing cyclic voltammetry (CV), and chronopotentiometry (V-t) curves were conducted using a CHI760E electrochemical workstation. The three-electrode system was employed with a glass carbon electrode as the working electrode, Hg/HgO electrode as the reference electrode, and Pt foil as the counter electrode. For ethanol oxidation reaction (EOR), the electrolyte solution was N₂-saturated 1 M C₂H₅OH + 1M KOH, respectively. Following stabilization of cyclic voltammograms

at a sweep rate of 500 mV s^{-1} , slow CVs were recorded at 50 mV s^{-1} . The electrochemical active surface areas (ECSAs) were calculated using the underpotentially deposited H (Hupd) method. ECSAs of catalysts were determined based on the charge of Hupd desorption peak, assuming a charge density of $210 \mu\text{C cm}^{-2}$ for one monolayer of hydrogen desorption on Pd.

1.7. Evaluation of catalytic performance of 4-NP reduction.

Using NaBH_4 as the reducing agent, a template reaction was employed to convert 4-nitrophenol (4-NP) to 4-aminophenol (4-AP), and the catalytic performance of defective PdMo catalyst was investigated using UV-vis spectroscopy. Initially, a mixture was prepared by combining 0.70 mL of 4-NP aqueous solution (0.10 mmol L^{-1}) with 0.30 mL of NaBH_4 solution (0.50 mol L^{-1}). The mixture immediately transferred from pale yellow to bright yellow. Subsequently, 2 mL of defective PdMo suspension ($2.0 \text{ mg mL}^{-1} \text{ Pd}$) was added, initiating an immediate reaction, and the solution color rapidly faded. Simultaneously, the reduction process was monitored using UV-vis spectroscopy. The absorption peak intensity at 400 nm decreased with reaction time, corresponding to the reduction of 4-NP. Under identical conditions, PdMo bimetallic and commercial Pd/C catalysts were used as control catalysts.

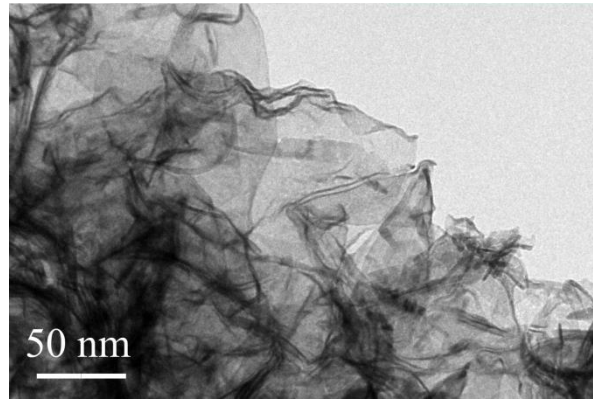


Figure S1 The HRTEM images of original PdMo bimetallic.

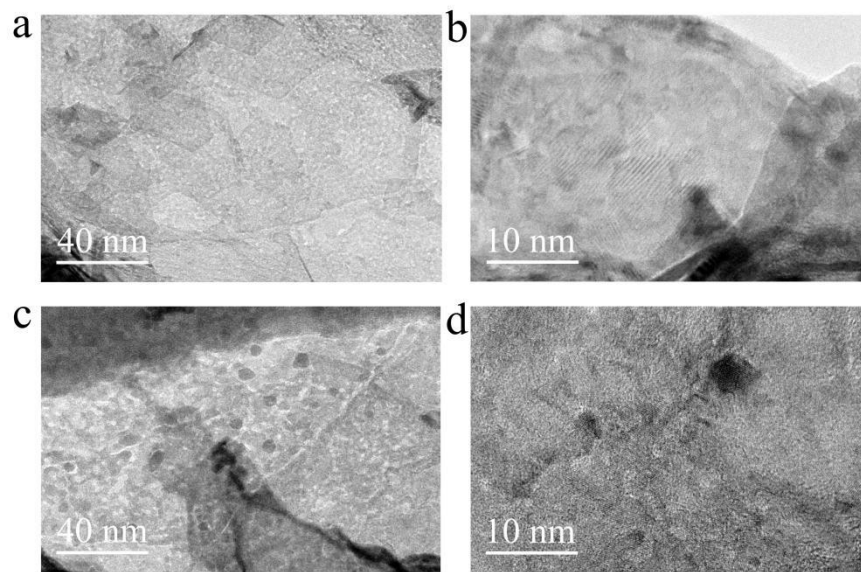


Figure S2 SEM images of PdMo bimetallic etched in (a-b) 3 mg NH_4Br and (c-d) 7 mg NH_4Br .

When the amount of NH_4Br is 3 mg, there are less defects on the surface of PdMo bimetallic (Figure S2a and b). However, there are many nanoparticles distributed on the surface after adding 7 mg NH_4Br due to the formation of stable $[\text{PdBr}_4]^{2-}$ under the condition of excess Br^- , resulting a lower reduction of rate[1] (Figure S2c and d). The nanoparticles distributed on the surface of PdMo bimetallic will form some grain boundaries. The synthesis results under different amount of NH_4Br etchant confirmed the crucial role of the etchant on the formation of defective PdMo bimetallic.

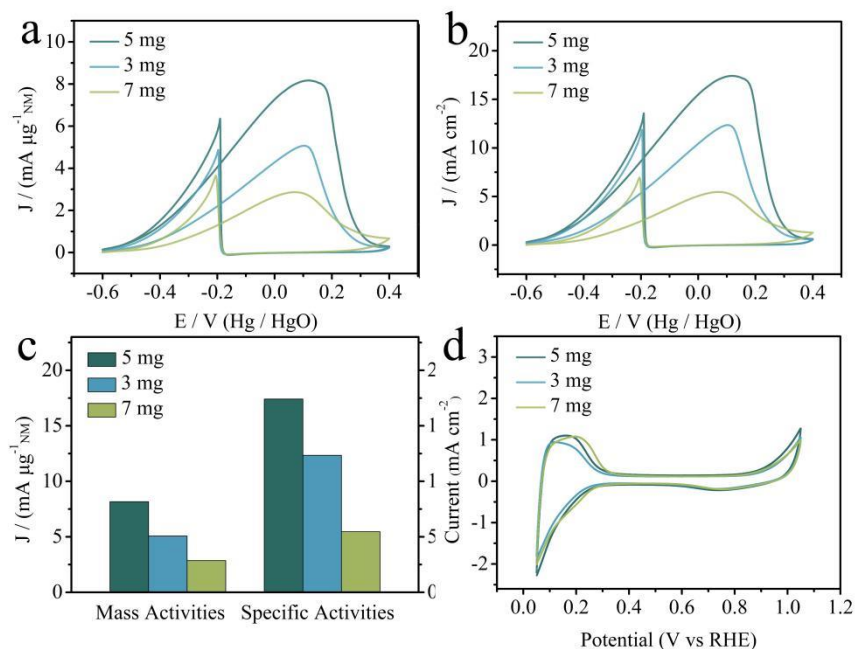


Figure S3 The catalytic performances of PdMo bimetallic etched by different NH_4Br amounts for ethanol oxidation reaction (EOR). (a) mass activity (MA), (b) specific activity (SA), (c) the comparison of mass activity and specific activity, (d) CV curves recorded in 0.1 M HClO_4 solution.

The CV curves for EOR activity were recorded in a solution of 1.0 M $\text{KOH} + 1.0$ $\text{CH}_3\text{CH}_2\text{OH}$. The corresponding mass activity (MA) and specific activity (SA) are determined by normalizing CV curves using mass of Pd and specific surface area (Figure S3a and b), respectively. As observed from Figure S3c, the PdMo bimetallic etched by 5 mg NH_4Br exhibits a high MA (8.17 $\text{mA } \mu\text{g}_{\text{Pd}}^{-1}$), which is higher than that etched by 3 mg NH_4Br (5.07 $\text{mA } \mu\text{g}_{\text{Pd}}^{-1}$) and 7 mg NH_4Br (2.86 $\text{mA } \mu\text{g}_{\text{Pd}}^{-1}$). Moreover, the catalyst produced in 5 mg NH_4Br demonstrates a SA (17.41 mA cm^{-2}) than that produced in 3 mg NH_4Br (12.79 mA cm^{-2}) and 7 mg NH_4Br (5.46 mA cm^{-2}), respectively. This reveals that the 5 mg of NH_4Br etchant is the optimum amount for realizing the maximum catalytic performance of etched PdMo bimetallic toward EOR.

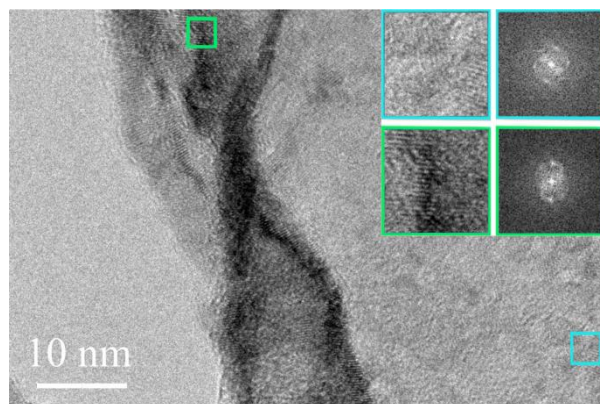


Figure S4 The HRTEM image of edges at *d*-PdMo bimetallic.

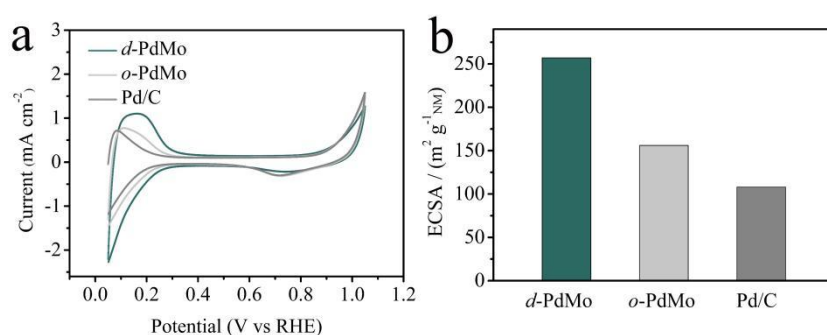


Figure S5 (a) the CV curves recorded in 0.1 M HClO₄ solution and (b) the corresponding ECSA.

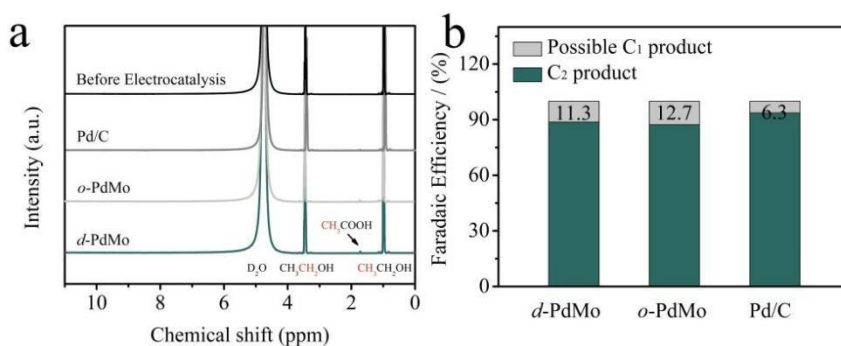


Figure S6 (a) The ¹H NMR spectra of electrolytes after EOR and (b) Faradaic efficiency of *d*-PdMo, *o*-PdMo, and Pd/C for different reaction pathways.

To further explore the EOR selectivity of PdMo bimetallic catalysts, the generated products after Chronoamperometry measurements carried out at -0.2 V vs. Hg/HgO for 1 hour were analyzed by ¹H NMR. The faradaic efficiency (FE) of the acetate was calculated ($FE = 4nF/Q$), where 4 is the number of electrons transferred, F is the Faraday

constant, n is moles of acetate, and Q is the total charge passed.[2] Meanwhile, FE (C1 pathway) = $1 - \text{FE (C2 pathway)}$.

Notably, acetate is the only liquid product (Figure S6a). Furthermore, as shown in Figure S6b, the Faradic efficiency of the C2 product for d -PdMo is 88.7%, which outperforms that of o -PdMo (87.3%), respectively. This indicates that the ultrathin thickness of Pd-based metal will improve the C2 pathway selectivity and the introduction of defects will further enhance the C2 pathway selectivity.

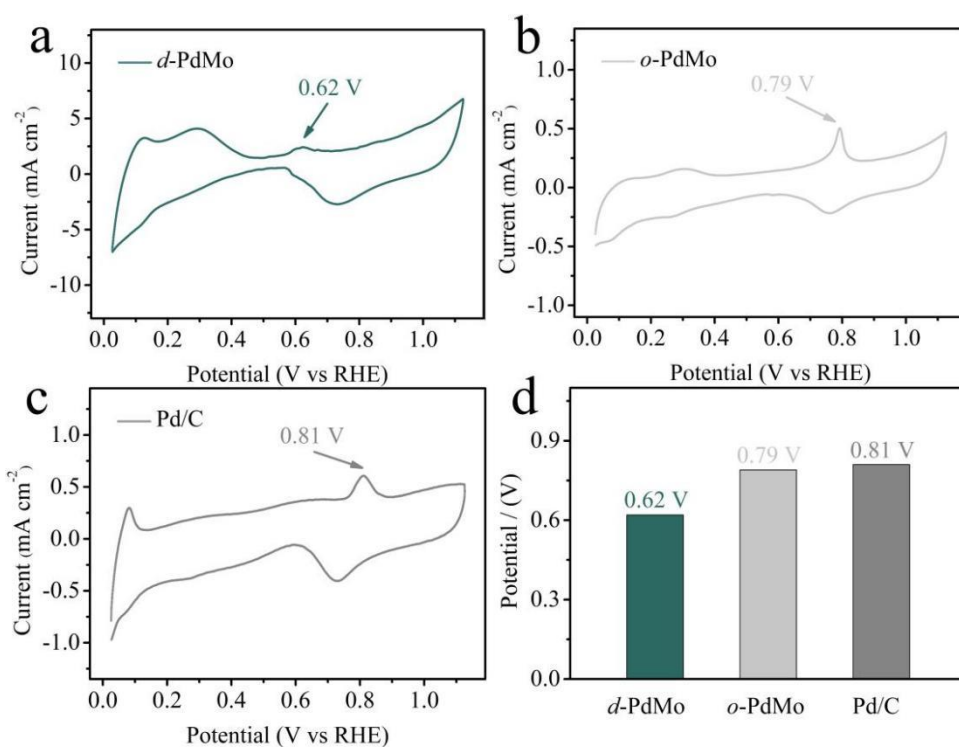


Figure S7. The CO stripping curve for (a) d -PdMo, (b) o -PdMo and (c) Pd/C. (d) the oxidation voltage of CO.

CO stripping experiments were carried out in 0.1 M NaOH solution. High-purity gaseous CO was bubbled into the electrolyte for 10 min. Subsequently, to remove the dissolved CO in the solution, gaseous Ar was bubbled into the above electrolyte for 20 min. Finally, two complete cycles of CO-stripping CV curves were obtained at a scan rate of 50 mV s⁻¹. The CO stripping curves are shown in Figure S7a-c and the comparison of

oxidation peak of CO is shown in Figure S7d. As observed, the oxidation voltages of CO for *d*-PdMo, *o*-PdMo, and Pd/C are 0.62 V, 0.79 V, and 0.81 V, respectively. This indicates the *d*-PdMo possesses a high performance of CO tolerance, which accounts for its excellent performance for EOR.

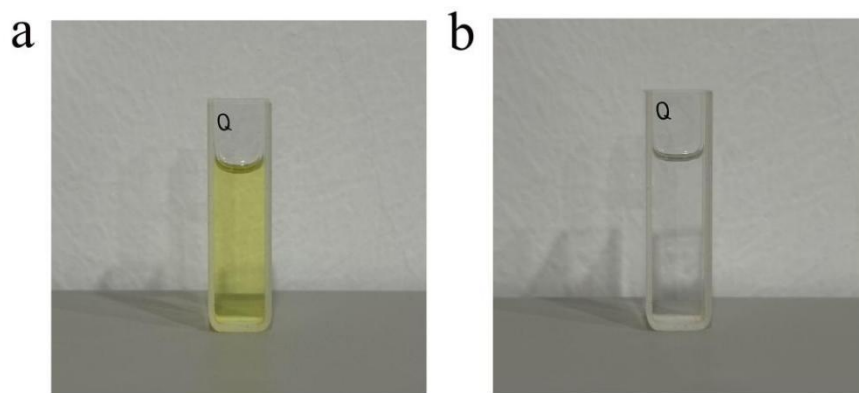


Figure S8 The mix solution of 4-NP and NaBH₄ at initial time (a) and after reaction (b).

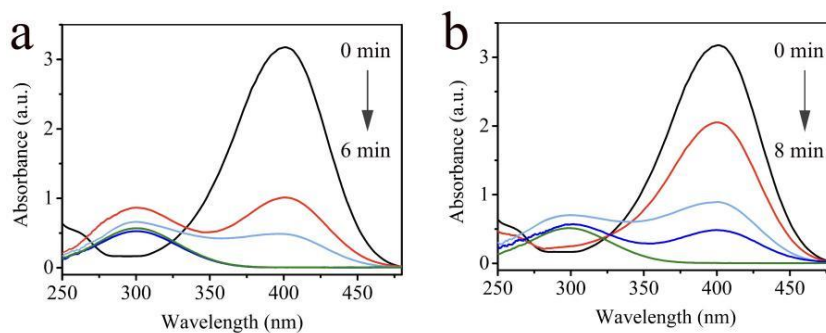


Figure S9 The UV-vis spectra of 4-NP hydrogenation at a certain time interval catalyzed by PdMo bimetallic (a) and Pd/C (b).

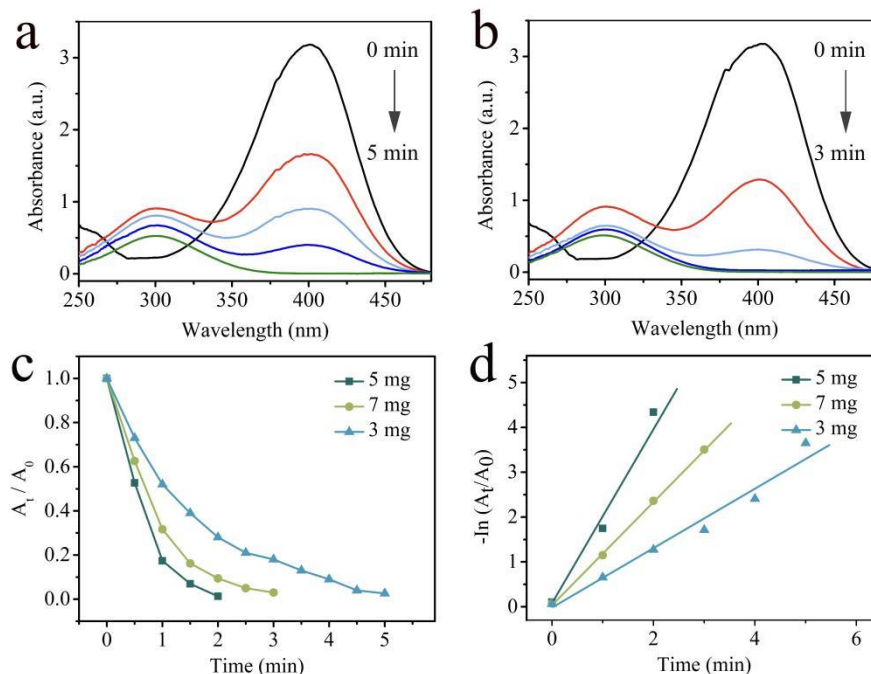


Figure S10 The catalytic performances of PdMo bimetallic catalysts etched by different NH_4Br amounts for 4-nitrophenol reduction. UV-vis spectra of PdMo bimetallic catalysts etched by (a) 3 mg NH_4Br and (b) 7 mg NH_4Br . (c) A_t/A_0 at different time and (d) simulated apparent rate constants.

It can be found that the 4-NP solution can be degraded in a few minutes. The catalysts can degrade 4-NP solution in a few minutes. The catalysts etched by 3 mg and 7 mg NH_4Br requires about 5 minutes (Figure S10a) and 3 minutes (Figure S10b), which are longer than that etched by 5 mg NH_4Br . Meanwhile, the catalyst produced in 5 mg NH_4Br also exhibits a high apparent rate constant with 1.98 min^{-1} , which is higher than that etched by 3 mg NH_4Br (0.65 min^{-1}) and 7 mg NH_4Br (1.15 min^{-1}).

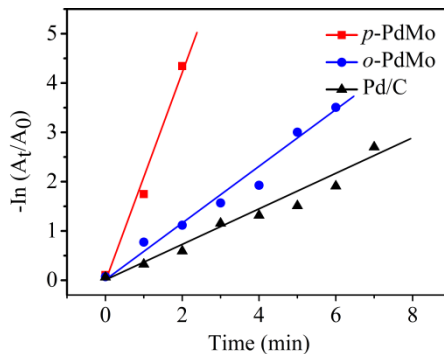


Figure S11 The plots of $-\ln(A_t/A_0)$ against reaction time of the catalysts.

Table S1 The atomic ratio of Mo/Pd of d-PdMo detected by XPS and ICP-OS

	Mo (%)	Pd (%)	Mo/Pd
XPS	0.14	3.38	0.02
ICP-OS	9.24	90.76	0.10

Reference

1. H.-C. Peng, S. Xie, J. Park, X. Xia, and Y. Xia, *J. Am. Chem. Soc.*, 2013. **135**: p. 3780-3.
2. S. He, Y. Liu, H. Li, Q. Wu, D. Ma, D. Gao, J. Bi, Y. Yang, and C. Cui, *ACS Appl. Mater. Interfaces*, 2021. **13**: p. 13311-13318.