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Alloying promotion of Pd-based metallenes in electrocatalytic hydrogenation of functionalized nitroarenes

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Electrocatalytic hydrogenation (ECH) provides a controllable and sustainable reduction of organic compounds via multi-electron-transfer processes at ambient conditions, which urgently demands high-performance electrocatalysts with satisfactory activity and selectivity. Here, two-dimensional Pd-based metallenes are for the first time introduced as efficient electrocatalysts for the ECH of nitroarenes, showing the intrinsic promotion of active sites by alloying effects. Thereinto, a Pd-Mo metallene with highly exposed active surface and strong electronic interactions between Pd and Mo atoms, affords the chemoselective hydrogenation of 4-nitrostyrene (4-NS) toward value-added 4-vinylaniline (4-VA). At -0.25 V vs RHE, it reaches the high selectivity (> 90.0%) and Faradic efficiency (78.3%) of 4-VA, outperforming the counterparts of home-made Pd metallene and commercial Pd/C. The consistent alloying promotion is further verified on a series of Pd-M (M = Cr, Mo and W) metallenes, with the specific activity sequence (Pd-Mo > Pd-W > Pd-Cr > Pd) that can be theoretically interpreted by the gradually strengthened chemisorption of 4-NS after alloying Pd with M. Moreover, the good efficiency within a broad substrate scope highlights the promise of Pd-based metallenes in electrochemical refinery.

Introduction

Avoiding harsh operations associated with high temperature and H₂ pressure, electrocatalytic hydrogenation (ECH) guarantees the hydrogenation of functional groups unsaturated (e.g., carbonyl, nitro, alkenyl, etc.) at ambient conditions with sustainable electricity as the driving energy and water as the hydrogen source.¹⁻⁴ For example, the hydrogenation of nitroarenes to aniline derivatives, a key process for manufacturing medicine, dyes, spices and other chemicals,⁵⁻⁷ is challenged by the trade-off between activity and selectivity in thermo-catalysis owing to the difficult control over pathways at heated and pressurized conditions.^{8,9} ECH enables a more controllable alternative to accommodate such multi-electron transfer processes via the convenient and accurate modulation of potential or current on working electrodes.^{8,10,11} Thereinto, electrocatalysts with elaborately designed surface configurations usually play a paramount role to promote an efficient transformation via target routes.¹²⁻¹⁵

Palladium (Pd) based electrocatalysts capable of adsorbing/activating protons and water are highly active for cathodic hydrogenation.¹⁶⁻²⁰ Unfortunately, they are also active for hydrogen evolution reaction (HER) that consumes chemisorbed H (H*, *

denotes an active site) and reduces the Faradaic efficiencies (FEs) of target aniline products.²¹ Moreover, the target reduction of nitro to amido in a complete manner, which avoids the formation of nitrosobenzene, phenylhydroxylamine, azoxybenzene, and hydrazobenzene, but well retains other reducible groups (e.g., C=C, C≡C, -F/Cl/Br/I, etc.),^{14,22,23} highly desires the atomic-level modulation on nanostructured Pd to optimize the chemisorption of substrates and intermediates. Recently, two-dimensional (2D) metallenes have attracted extensive interest in a variety of electrocatalysis (e.g., oxygen/nitrogen/water reduction, alcohol oxidation, CO₂ reduction, etc.) due to the largely exposed active surface and more importantly the tunable intrinsic activity after alloying with foreign elements.²⁴⁻³³ These features would not only ensure the feasible manipulation of reactant/intermediate chemisorption toward target ECH, but also provide a reliable platform with well-defined atomic arrangements and electronic configurations to unravel electrocatalytic mechanism.^{30,34} However, the relevant knowledge is still absent in the ECH of nitroarenes.

In this work, Pd-based metallenes are for the first time introduced as efficient electrocatalysts for the ECH of nitroarenes. Featuring highly exposed surface and strong electronic interactions between Pd and Mo atoms, ultrathin Pd-Mo (thickness ~ 3 nm) affords the chemoselective hydrogenation of 4-nitrostyrene (4-NS) to value-added 4-vinylaniline (4-VA) in a wide potential range of -0.05 ~ -0.45 V vs. RHE. At -0.25 V vs RHE, it reaches the high selectivity (>90.0%) and Faradic efficiency (78.3%) of 4-VA, superior to Pd metallene and commercial Pd/C counterparts. The consistent alloying promotion is further verified on a series of Pd-M (M = Cr, Mo and W) metallenes, whose specific activity for hydrogenating 4-NS follows the sequence of Pd-Mo > Pd-W >

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Pd-Cr > Pd. Accordingly, density functional theory (DFT) calculations show that alloying with foreign M atoms can effectively ameliorate electronic configurations to strengthen the chemisorption of 4-NS, which is conducive to the electrochemical hydrogenation toward anilines via the facilitated H* transfer to activated nitro groups, rather than gaseous H₂ evolution. This calculation gives coincident correlation between the specific activity and surface binding energy on Pd-based metallenes, confirming the alloying promotion of ECH within a broad substrate scope.

Experimental Section

Chemicals. 4-Nitrostyrene (4-NS, 97%), 4-vinylaniline (4-VA, 99%), and 4-ethylnitrobenzene (4-EA, 99%), molybdenum hexacarbonyl (Mo(CO)₆, 98%) and oleylamine (80-90%) were purchased from Macklin Inc. Shanghai. Ascorbic acid (AR) and LiClO₄ (AR) were provided by Aladdin Inc. Shanghai, and palladium acetyl acetonate (Pd(ac)₂, 95%) was bought from Meryer Co., LTD. All reagents were used directly without any treatments.

Synthesis of Pd-based metallenes. In the typical synthesis of Pd-Mo metallene,²⁴ 5 mL of oleylamine was used to dissolve Pd(ac)₂ (12 mg), Mo(CO)₆ (4 mg) and ascorbic acid (30 mg) in a 25 mL glass round-bottom flask immediately followed by ultrasonication for 30 min. The obtained homogeneous solution was then sealed and heated in an oil bath at 80 °C for 12 h with stirring, and then naturally cooled to room temperature. Residual oleylamine was washed by an ethanol-cyclohexane mixture. The colloidal material was stored in cyclohexane for later use. The synthesis of Pd-W and the Pd-Cr samples were conducted in the same manner except that Mo(CO)₆ was replaced by W(CO)₆ and Cr(CO)₆, respectively.

The Pd metallene was synthesized through the above wet-chemical method replacing Mo(CO)₆ with CO gas. 5 mL of oleylamine was used to dissolve Pd(ac)₂ (12 mg) and ascorbic acid (30 mg), followed by the ultrasonication until homogeneous solution was acquired. The solution was then placed into a Teflon high-pressure vessel saturated with CO gas and then heated at 80 °C for 12 h. Products were collected by centrifugation and washed with a mixture of ethanol-cyclohexane, which was then stored in cyclohexane (10 mg mL⁻¹) for use.

Physical characterization. X-ray diffraction (XRD) patterns were collected on Bruker D8 Advance diffractometer (Cu K α radiation, λ = 0.154 nm). Transmission electron microscopy (TEM) and high-angle annular dark-field scanning TEM (HAADF-STEM) images were acquired on JEOL JEM-2100F electron microscope. Scanning electron microscopy (SEM) was performed on ZEISS ULTRA 55. X-ray photoelectron spectroscopy (XPS) was processed on ThermoFisher scientific (Escalab 250Xi) using C 1s (284.6 eV) as a reference. The contents of metal elements in metallenes were detected by inductively coupled plasma-optical emission spectrometer (ICP-OES, OPTIMA 2000DV). Atomic-force microscopy (AFM, Bruker Innova) was recruited to explore the morphologies of the surface with tapping mode.

Electrochemical test. Pd-based metallene colloid kept in cyclohexane (10 mg mL⁻¹, 100 μ L) was loaded onto a carbon cloth (1 cm \times 2 cm) and dried naturally to reach a mass loading of 0.25 mg cm⁻². Afterwards, 10 μ L nafion 115 (5 wt%) solution was transferred

onto the electrode surface. To access the reliable electrolysis on the clean surface of Pd-based alloys free-from interference by adsorbed surfactants, the metallene was at first electrochemically cleaned by repeated cyclic voltammograms (CVs) in 1 M KOH.^{35,36} Typically, a metallene-loading working electrode was swept at 50 mV s⁻¹ in N₂-saturated solution (1.0 M KOH) for 40 cycles (-0.8 to 0.3 V vs. SCE), with a standard calomel electrode (SCE) and a Pt foil as the reference and counter electrodes, respectively. Next, the electrode was removed out and washed by ultrapure water and ethanol for later tests.

The ECH of 4-NS to 4-VA was tested in an airtight two-compartment electrochemical cell separated by a proton exchange membrane (Nafion 117, Sigma-Aldrich). The electrolyte was 45 mL LiClO₄ solution (pH 6.8) containing 15 mmol L⁻¹ of 4-NS in cathodic cell. Each compartment contained approximate 10 mL headspace. N₂ gas was passed into the cathodic compartment electrolyte for at least 30 min to stripped the dissolved air before test. During the test, a N₂ gas flow (35 mL min⁻¹) was delivered into the cathodic chamber and then vented into the gas-sampling loop of a gas chromatograph (GC). Linear sweep voltammetry (5 mV s⁻¹) was conducted on a potentiostat of CHI 660e (CH Instruments), using a SCE and a graphite rod as the reference and counter electrodes, respectively. The working potentials in ECH were calibrated to the reversible hydrogen electrode (RHE), according to Nernst equations.

Product analysis. The H₂ and the liquid products were measured by GC and high-performance liquid chromatography (HPLC), respectively. GC (FULI 9790) equipped with a gas sample loop was employed to quantify the H₂ gas produced by HER every 30 min, and N₂ (99.99%) was the carrier gas. The FE of H₂ production were calculated from the GC results as below:

$$FE_{(H_2)} = \frac{\text{peak area of } H_2 \times \text{flow rate} \times z \times F \times t}{\alpha \times V_m \times Q}$$

where α is the conversion factor for H₂ based on calibration of GC with a standard sample, $z = 2$ (transferred electrons), t is the total reaction time, Q is the total charge passed, $V_m = 22.4$ L mol⁻¹ and $F = 96485$ C mol⁻¹.

Liquid products in the cathode electrochemical cell were analysed by HPLC (SHIMADZU LC-20AT) equipped with a UV detector. The column (INERTSUSTAIN C18) was operated at 40 °C and the binary gradient method containing H₂O and CH₃OH (CH₃OH: 60 vol.%) was adopted at a flow rate of 0.8 mL min⁻¹. The conversion (%) of reactants, the selectivity (%) and yield (%) of products, and the efficiency (%) of hydrogenation products were calculated based on the following equations:

$$\text{Conversion (\%)} = \frac{\text{Mole of product}}{\text{Mole of initial substrate}} \times 100\%$$

$$\text{Selectivity (\%)} = \frac{\text{Mole of target product}}{\text{Mole of total products}} \times 100\%$$

$$\text{Yield (\%)} = \frac{\text{Mole of product}}{\text{Mole of theoretical product}} \times 100\%$$

$$FE (\%) = \frac{\text{Mole of product} \times z \times F}{\text{Total charge used}} \times 100\%$$

where z , the number of transferred electrons, was 6 for 4-VA and 8 for 4-ethylaniline (4-EA) products.

Theoretical calculations. DFT calculations were performed at the GGA level within the Perdew–Burke–Ernzerhof (PBE) functional using the CASTEP software implemented in Materials Studio. The total

energy calculation were performed using a kinetic energy cutoff of 450.0 eV assigned to the plane-wave basis set for calculating the density of state. The self-consistent field (SCF) tolerance was 1×10^{-6} eV. The Brillouin zone was sampled by $5 \times 5 \times 1$ k-points. The core electrons were replaced with ultrasoft pseudo-potentials. All Pd-M structures for calculation were the commonly observed (111) facet of face-centred cubic (*fcc*) structure materials, and were modeled with vacuum widths of 12 Å, using a five-layer 2×2 surface slab. Pd-M (M = Mo, W, and Cr) structures were replaced one of the *hcp*-Pd atoms by M.

The binding energy (BE) of H and 4-NS was obtained by:³⁷

$$BE_{(adsorbate)} = E_{(slab+adsorbate)} - E_{(slab)} - E_{(adsorbate)}$$

in which $E_{(slab+adsorbate)}$, $E_{(slab)}$ and $E_{(adsorbate)}$ are the total energy of Pd-M surface with adsorbates, the energy of pure surface/facet and the energy of gaseous adsorbates, respectively. The $E_{(H)}$ was taken as a half the total energy of H₂ molecule during the calculation of hydrogen binding energy.

Results and discussion

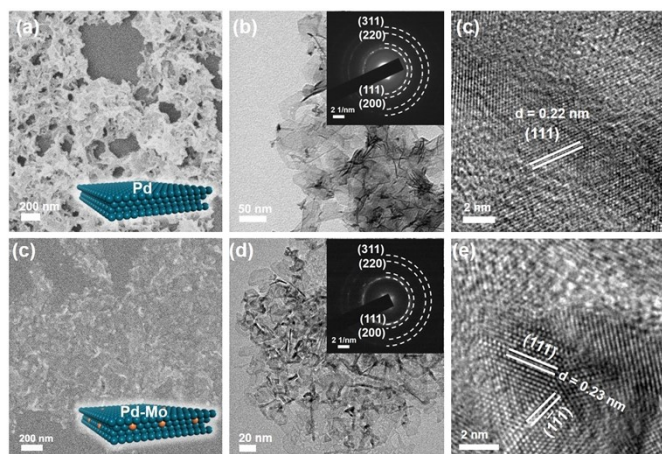


Fig. 1 (a, d) SEM, (b, e) TEM and (c, f) HR-TEM images of (a ~ c) Pd and (d ~ f) Pd-Mo metallenes. Insets of b and d displayed the SAED images.

Pd-Mo metallene was synthesized via a one-pot wet-chemical approach,²⁴ as mentioned in the experimental section. For reference, monometallic Pd metallene was obtained via the consistent procedure except replacing Mo(CO)₆ by CO. Their SEM images (Fig. 1a and d) showed the flower-like products composed of 2D nanosheets, which was further confirmed by the corresponding TEM images in Fig. 1b and e. The selective area electronic diffraction (SAED) patterns suggested the polycrystal nature of both Pd-Mo and Pd metallenes (insets of Fig. 1b and e). The high resolution TEM (HR-TEM) image of Pd-Mo metallene clearly depicted a lattice spacing of 0.23 nm (Fig. 1f), slightly larger than the Pd(111) (0.22 nm) observed in Pd counterparts (Fig. 1c). This should be ascribed to the lattice expansion after alloying Pd with relatively larger Mo atoms. Accordingly, HAADF-STEM and the elemental mapping confirmed the homogenous distribution of Pd and Mo throughout the nanosheets (Fig. S1, ESI[†]), and the atomic ratio of Mo/Pd was 0.03. The further quantification by ICP-OES showed the Mo content of 3.1 wt.% in Pd-Mo, suggesting a

consistent Mo/Pd molar ratio of 0.04 (Table S1, ESI[†]). Interestingly, the Mo/Pd ratio was remained at the same level (0.03 ~ 0.04) in a series of 2D nanostructured Pd-Mo samples received after varying the feeding content of Mo(CO)₆ from 2 to 15 mg along with the fixed one of Pd(ac)₂ (12 mg) (Fig. S2 and Table S2, ESI[†]). This should be associated with the crystalline nature of Pd-Mo alloys, and excessive Mo during preparation is residual in reaction solution.

XRD investigation identified the same *fcc* structure of both Pd and Pd-Mo metallenes (Fig. 2a). But the diffraction peaks of Pd-Mo were negatively shifted to lower 2θ compared to those of Pd metallene and commercial Pd/C, indicating the formation of alloys with expanded lattices. XPS further revealed that Pd in the metallenes and Pd/C was dominant in its metallic state, along with a few Pd²⁺ species due to slight surface oxidation (Fig. 2b). Of note is that Pd-Mo afforded the visible blue-shift of Pd 3d_{5/2} and 3d_{3/2} to higher binding energies in comparison with Pd metallene and Pd/C, associated with the strong electronic interactions between Mo and Pd after alloying. Accordingly, the XPS profile of Mo 3d (Fig. S3, ESI[†]) showed the presence of Mo⁰ in nanosheets, which increased along with reaction time. The binding energies of 227.6 eV (3d_{5/2}) and 229.8 eV (3d_{3/2}) were obviously lower than the typical values of Mo metal (228.0 and 231.0 eV).³⁸ As indicated, Mo is negatively charged after alloying due to the electron donation by Pd, in accordance with the XPS profile of Pd (Fig. 2b) and the follow-up DFT calculation. In addition, AFM measurement was conducted to evaluate the ultrathin 2D nanostructure. As shown in Fig. 2c and d, Pd and Pd-Mo metallenes possessed the consistent thickness of 3 ~ 4 nm, which implied the negligible influences on morphology by alloying Pd with Mo atoms.

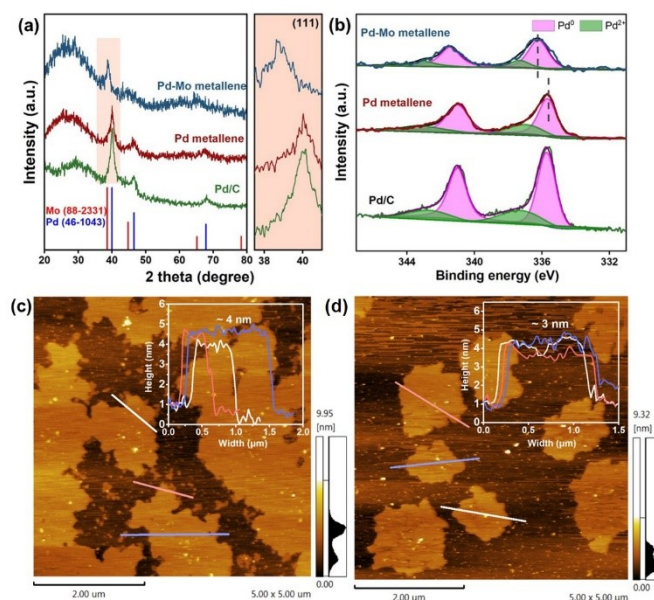


Fig. 2 (a) XRD patterns and (b) Pd core-level XPS profiles of commercial Pd/C, Pd metallene and Pd-Mo metallene. AFM images and the corresponding height profiles of (c) Pd and (d) Pd-Mo metallenes.

Prior to electrocatalytic tests, Pd-based metallenes were electrochemically cleaned by repeated CVs. The significantly improved current densities on Pd and Pd-Mo suggested the successful removal of adsorbed surfactants (Fig. S4, ESI[†]).³⁶ Then, the

CVs of Pd-Mo were measured in 0.1 M LiClO₄ (pH 6.8) containing 10 mmol L⁻¹ of 4-NS (Fig. S5, ESI[†]), which showed a new cathodic peak at 0.05 V vs. RHE corresponding to the stepwise reduction of nitro.^{39,40} Such cathodic reduction of 4-NS before HER confirms its thermodynamic priority, in which electrons can be used to reduce nitroarenes with chemisorbed H* or via a proton-coupled-electron transfer (PCET) process.^{18,41} The reduction of 4-NS can produce 4-VA and 4-ethylnitrobenzene (4-EN) via selectively hydrogenating nitro and vinyl groups, respectively, both of which would be further reduced to 4-EA.⁴² Because of the more thermodynamically preferred reduction of nitro to vinyl, the production of 4-EN is usually prohibited.⁴³ Fig. 3a presents the linear sweep voltammetry curves of Pd-Mo and Pd metallenes, along with the reference of commercial Pd/C. The cathodic currents of all the three catalysts increased after introducing 4-NS, confirming again the favourable reduction in comparison with HER. Among these electrocatalysts, Pd-Mo delivered the highest current with 4-NS, implying the best activity for hydrogenation.

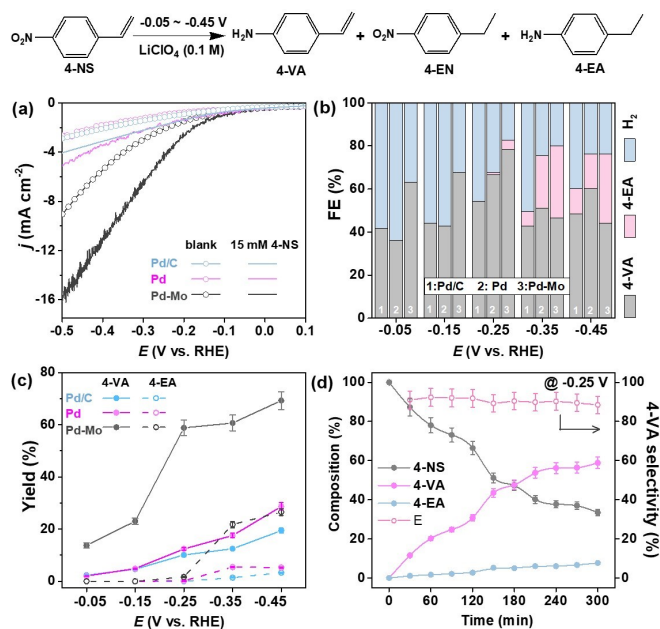


Fig. 3 ECH performance of 4-NS over Pd-based metallenes. (a) Polarization curves of Pd-Mo and Pd metallenes and commercial Pd/C in 0.1 M LiClO₄ with and without 15 mM of 4-NS at a scan rate of 10 mV s⁻¹. (b) FEs and (c) yields of products for the ECH of 4-NS over Pd-based metallenes and commercial Pd/C in a wide potential range of -0.05 ~ -0.45 V vs. RHE (4-NS: 15 mM, reaction time: 5 h). (d) Time curves of 4-NS, 4-VA and 4-EA on Pd-Mo metallene at -0.25 V vs. RHE.

Afterwards, electrocatalytic tests were carried out at -0.05 ~ -0.45 V vs. RHE for 5 h, within a 0.1 M LiClO₄ solution containing 15 wt.% methanol to improve the solubility of 4-NS (15 mM). HPLC clearly identified the conversion of 4-NS to target 4-VA and 4-EA by-product (Fig. S6, ESI[†]). As shown in Fig. 3b, Pd-Mo metallene gained the FE of 4-VA > 60.0% at -0.05 V and -0.15 V vs. RHE, obviously higher than those on Pd and Pd/C counterparts (~ 40.0%), which identified the more favourable ECH of 4-NS than HER over Pd-Mo. The FE of 4-VA on Pd-Mo increased to 78.3% at -0.25 V vs. RHE, with a low FE of 4-EA (4.5%). At more negative potentials (e.g., -0.35 and -0.45 V vs. RHE), Pd-Mo delivered the visibly decreased FE of 4-VA owing to the over-hydrogenation, but it still remained the high FE (~ 80.0%) for 4-NS reduction. As indicated, the hydrogenation of vinyl in 4-VA is

favored at more negative potentials, where the reduction of either nitro or vinyl exceeds H₂ evolution. Remarkably, the control of ECH pathways can be achieved by easily controlling working potentials,⁴⁴ and to produce more valuable 4-VA, the electrolysis should be proceeded above -0.25 V vs. RHE. Fig. 3c further summarizes the yields of 4-VA and 4-EA over these electrocatalysts at -0.05 ~ -0.45 V vs. RHE. Visibly, Pd-Mo presented the higher yield of 4-VA in comparison with Pd metallene and commercial Pd/C, confirming its superiority in ECH. Although the yield of 4-EA increased at -0.35 and -0.45 V vs. RHE, the yield of target 4-VA remained at a high level. The above results clearly pointed out the advantages of Pd-Mo metallene with highly exposed active surface. More importantly, the alloying promotion in ECH was underscored by directly comparing the performance of Pd-Mo and Pd metallenes that possess the consistent nanostructures. In further comparison with recently reported electrocatalysts used for 4-NS reduction (Table S3), Pd-Mo metallene performed among the best, and featured its mild operation with near-neutral electrolytes, avoiding the use of corrosive acids and alkalis.

Fig. 3d displays the electrocatalytic conversion of 4-NS to 4-VA and 4-EA on Pd-Mo metallene at -0.25 V vs. RHE as a function of time. The concentration of 4-NS decreased rapidly during electrolysis, and the target product of 4-VA accordingly increased, while the by-product of 4-EA remained at a low level, resulting in a high selectivity (> 90.0%) of 4-VA. This indicated the highly selective hydrogenation of nitro rather than vinyl groups at this moderately negative potential, owing to the preferred activation of nitro groups on Pd sites via perpendicular chemisorption.⁴⁵ Moreover, the robust service life of Pd-Mo electrocatalysts could be confirmed by 5 successive tests at -0.25 V vs. RHE (Fig. S7, ESI[†]), which showed the well-remained FE and yield of 4-VA. Accordingly, the spent Pd-Mo metallene verified the structural and chemical stability satisfactory for the ECH, according to TEM, XRD and XPS results (Fig. S8 and 9, ESI[†]).

Quasi *in situ* EPR measurement coupled with the electrochemical test was conducted to detect the active species during reduction. 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) as a trapping agent was introduced into the electrolyte. As shown in Fig. 4a, the characteristic EPR signals of DMPO-H adducts (nine peaks, $a_N = 16.5$ G and $a_H = 22.6$ G) were visible at -0.25 V vs. RHE, which suggested that the active H* species for 4-NS hydrogenation was produced via water reduction.^{46,47} Pd-based electrocatalysts are capable of reducing the free-energy barrier of a Volmer step in neutral aqueous solution due to their strong binding with H₂O, leading to the rapid generation of H* species on surface.⁴⁸ The successful trapping of hydrogen radicals is associated with the spillover and diffusion of H* on Pd-Mo surface, consistent with the larger H region and the more negative potential of H₂O reduction on Pd-Mo compared with Pd metallene (Fig. S10, ESI[†]).

We carried out DFT calculation to analyse the electronic configurations and binding energies of H* and 4-NS* on crystal models. The facets of Pd(111) and Pd-Mo(111) were adopted as the calculation models, because they were commonly observed in TEM. Fig. 4b depicts the projected density of state (PDOS) for the *d* bands of Pd(111) and Pd-Mo(111). The *d*-band of Pd-Mo was visibly broadened as compared with pristine Pd, suggesting electron redistribution after alloying with Mo. Accordingly, the *d*-band centre

(ϵ_d) slightly downshifted away from the E_F from -2.20 eV (Pd) to -2.34 eV (Pd-Mo). In the meanwhile, the electron density difference diagram showed that electrons on (111) facet were concentrated around Mo atoms in Pd-Mo, while the distribution was uniform in Pd(111) (Fig. 4c). This can be used to explain the shift of Pd 3d and Mo 3d binding energies in the XPS profile of Pd-Mo metallene (Fig. 2b and Fig. S3, ESI[†]). As highlighted in previous reports,^{49,50} tuning electron distribution is feasible to engineer the energetics of reaction intermediates in electrocatalysis. Fig. 4d and 4e show the binding energies of H* (BE_H) and 4-NS* (BE_{4-NS}) on Pd(111) and Pd-Mo(111), whose adsorption configurations were accordingly summarized in Fig. S11, ESI[†]. A linear relationship of binding energies with ϵ_d has been previously proved on metal surface,^{51,52} however, BE_H is still correlated with adsorption sites, in particular on an alloy surface with multiple metal atoms. Such difference associated with adsorption sites has been examined in this work. Of note, the charge redistribution in Pd-Mo results in positively charged Pd, which enables the Pd site close to Mo (Pd1 in Fig. 4d) with the relatively higher BE_H compared to metallic Pd, and another site (Pd2) with a similar value. By contrast, the negatively charged Mo sites exhibit the weak BE_H . The alloying of Mo would strengthen the chemisorption of H* on adjacent Pd sites, which is conducive to stabilizing reactive H* for subsequent hydrogenation. Moreover, the BE_{4-NS} on the Pd1 and Pd2 sites was obviously increased on Pd-Mo in comparison with Pd, and reached the maximum at the Mo site (Fig. 4e). The Mo with relatively stronger oxyphilicity than Pd favours the strong binding with a nitro group, which is of great importance for its activation toward efficient reduction. Taking both BE_H and BE_{4-NS} into account, we can assume that the adjacent atoms of Pd and Mo would sever as the active-sites to chemisorb H* and 4-NS* intermediates, respectively, which subsequently proceed the surface steps of consecutive hydrogenation via a typical Langmuir-Hinshelwood mechanism.

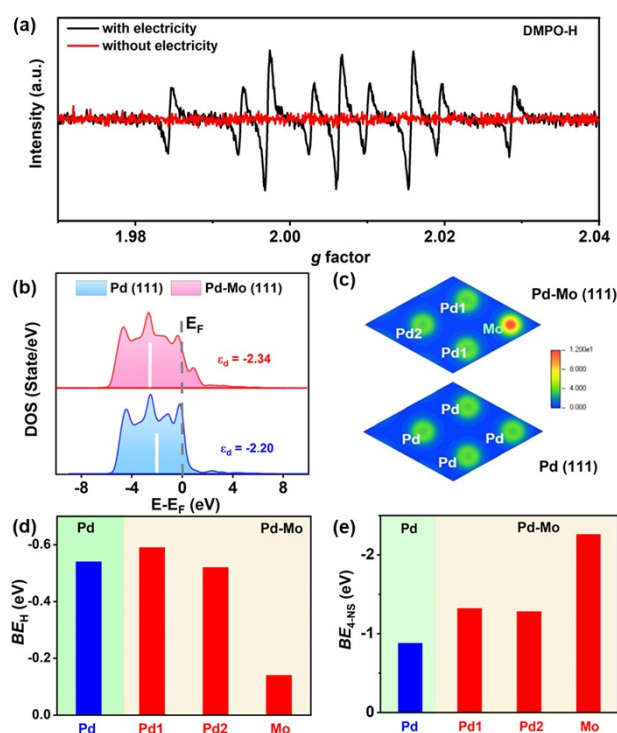


Fig. 4 (a) Quasi *in situ* EPR trapping for hydrogen radicals over Pd-Mo metallene. (b) PDOS for the d band of Pd and PdMo, and (c) electron density difference with Pd (111) and Pd-Mo (111). (d) BE_H and (e) BE_{4-NS} on Pd (111) and Pd-Mo (111).

Via the same synthetic approach with $Cr(CO)_6$, $Mo(CO)_6$ or $W(CO)_6$ as reactants, a family of Pd-M (M = Cr, Mo and W) metallenes can be successfully achieved, which serves as a reliable platform to acquire further insights into the alloying promotion of ECH. Their XRD patterns were summarized in Fig. 5a. In comparison with Pd, Pd-W and Pd-Mo showed the obvious shift of (111) peak to lower 2θ , but Pd-Cr presented the opposite move to higher degree, associated with the order of atomic radius, i.e., $Cr(1.29 \text{ \AA}) < Pd < (1.37 \text{ \AA}) < Mo(1.40 \text{ \AA}) < W(1.41 \text{ \AA})$. The alloying of Pd with secondary metals (Cr, Mo and W) leads to the lattice contraction or expansion relying on their different atomic sizes. It's further identified by TEM that 2D nanostructures with varied sizes were harvested in these Pd-M samples (Fig. S12, ESI[†]). To evaluate the exposure of surface active-sites, the electrochemical surface area (ECSA) of Pd-M was taken into comparison. The ECSA values of Pd, Pd-Cr, Pd-Mo and Pd-W metallene were 111.60, 100.41, 123.46 and 129.71 $cm^2 mg^{-1}$, respectively, calculated from the cathodic peak of PdO reduction in CVs (Fig. S13 and Table S4, ESI[†]).

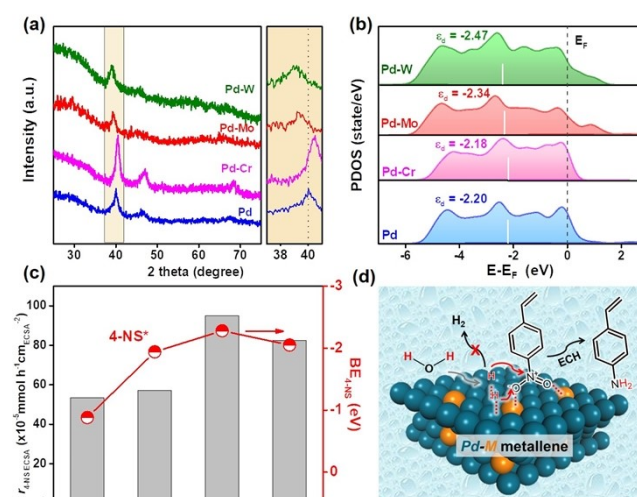
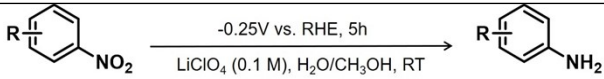
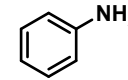
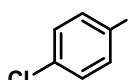
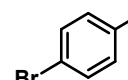
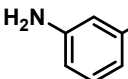
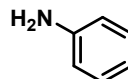
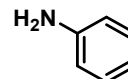
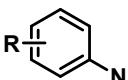


Fig. 5 (a) XRD patterns of Pd, Pd-Cr, Pd-Mo and Pd-W metallenes. (b) PDOS for the d band of Pd and Pd-M (M = Cr, Mo, and W). (c) Specific reaction rate of 4-NS on Pd and Pd-M metallenes plotted against BE_{4-NS} . (d) Schematic illustration for the ECH mechanism of 4-NS.

DFT calculations on Pd-M showed that the PDOS near the E_F increased after introducing Mo or W atoms, but decreased with Cr (Fig. 4b). The ϵ_d downshifted away from the E_F in the order of Pd-W (-2.47 eV) < Pd-Mo (-2.34 eV) < Pd (-2.20 eV) < Pd-Cr (-2.18 eV). Accordingly, the BE_{4-NS} increased with the alloying of Cr, Mo and W, in the order of Pd-Mo > Pd-W > Pd-Cr > Pd (Fig. 5c and Fig. S12, ESI[†]), indicating that the oxygen-philic elements of Cr, Mo and W would enhance the adsorption/activation of nitro substrates.¹⁴ It's more interesting that the specific rate ($r_{4-NS,ECSA}$) of 4-NS hydrogenation in 1 h electrolysis normalized by the ECSA was closely correlated with the order of BE_{4-NS} on Pd-M, pointing out the dominant contribution of nitro activation due to its high energy barrier.^{9,45} Therefore, the alloying promotion of Pd-M metallenes can be intrinsically ascribed to the strengthened chemisorption of 4-NS*.²³ As schematically

illustrated in Fig. 5d, the strong adsorption of 4-NS on oxygenphilic M centres helps to the activation of nitro groups, and in the meantime the available H* on the neighbour Pd sites is conducive to attacking the activated nitro group for further hydrogenation, leading to the facilitated ECH kinetics. The vertical chemisorption of 4-NS on Pd-M via bonding nitro with M sites would enable the highly selective reduction towards 4-VA with a well-remained vinyl.

Table 1 ECH of various functionalized nitroarenes over Pd-Mo metallene.

	
	FE 90.0%, Yield 64.1%
	FE 78.1%, Yield 56.1%
	FE 72.0%, Yield 60.8%
	FE 74.9%, Yield 50.3%
	FE 88.2%, Yield 55.4%
	FE 81.0%, Yield 59.6%
	R=OCH ₃ (p), FE 88.1% Yield 54.5%
	R=OCH ₃ (m), FE 92.2% Yield 58.0%
	R=OCH ₂ CH ₃ (p), FE 93.0% Yield 58.3%
	R=OCH ₂ CH ₃ (m), FE 90.6% Yield 67.8%

Finally, we examined the efficacy of Pd-Mo metallene for the electrochemical reduction of a series of nitro compounds (Table 1). For nitrobenzene, the FE and yield of aniline were 90.0% and 64.1% on Pd-Mo metallene, respectively, in which the byproducts of phenylhydroxylamine and H₂ were rarely detected. In comparison, the yield (50.3–60.8%) and FE (72.0–88.2%) of target aniline derives were decreased for halogenated nitrobenzenes, due to the weakened π coupling between nitro and benzene ring by electron-withdrawing halogens. Accordingly, the electron-donating alkoxy groups favoured the ECH of nitro with high FE. These results verify Pd-Mo metallene as a promising catalyst for the ECH of nitroarenes.

Conclusions

In this work, a series of Pd-based metallenes are for the first time introduced as efficient electrocatalysts for the ECH of nitro compounds, in which the alloying promotion has been well identified. Thanks to highly exposed surface and strong electronic interactions between Pd and Mo atoms, ultrathin Pd-Mo metallene enables the chemoselective hydrogenation of 4-NS to value-added 4-VA in a wide potential range of -0.05 ~ -0.45 V vs. RHE, superior to Pd metallene and commercial Pd/C. The consistent alloying promotion is further verified on Pd-M (M = Cr, Mo and W) metallenes, with a specific activity sequence of Pd-Mo > Pd-W > Pd-Cr > Pd, which is highly correlated to the strengthened chemisorption of 4-NS* after alloying Pd with M. It is expectable that a precise control over the alloying effects on binary, ternary, quaternary, and even high-entropy metallene platforms could further boost electrocatalytic applications.

Author Contributions

Wenbiao Zhang: synthesis, investigations, methodology, DFT calculation, data curation, writing – original draft. Wanling Zhang: synthesis, data validation. Jingwen Tan: EPR testing. Di Pan: experimental analysis. Yi Tang: conceptualization, supervision, funding acquisition. Qingsheng Gao: conceptualization, supervision, writing – review and editing, funding acquisition.

Conflicts of interest

The authors declare no competing financial interest.

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