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Nitrogen-doping induced oxygen divacancies in freestanding molybdenum trioxide single-layers boosting electrocatalytic hydrogen evolution

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ABSTRACT

High electrical conductivity and large amount of active sites are the two prerequisites for an efficient electrocatalyst. Doping engineering is widely utilized to tailor the electrical property, while investigation on the dopant-induced modification of active sites remains elusive. To address this issue, we construct an ideal model of atomically-thin layers and hence deliberately create element doping on their surface. As an example, freestanding N-doped MoO₃ single-layers are first synthesized by virtue of a lamellar intermediate. Positron annihilation spectrometry discloses that N-doping leads to increased $V_o^*V_o^-$ divacancies relative to intact MoO₃ single-layers, while the similar electrochemical active area implies that the increased $V_o^*V_o^-$ divacancies accounts for the former's 6 times higher H₂ evolution activity. In addition, density-functional calculations revealed that the presence of $V_o^*V_o^-$ divacancies results in increased states density near the valence band edge, which favors their improved electronic conductivity, verified by electrochemical impedance spectroscopy. This work demonstrates that N-doping confined in MoO₃ atomic-layers increase the concentration of $V_o^*V_o^-$ divacancies, which are first verified to be highly active sites for H₂ evolution. Thus, doping engineering in atomic-layers opens new opportunities for achieving efficient catalytic performances through tailoring the catalytically active sites.

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1. Introduction

Nowadays, fossil fuels comprise over 80% of global energy sources [1]; however, these limited resources can not last forever, which stimulates us to explore renewable green energy alternatives. In this regard, electrocatalytic water splitting into H_2 is regarded as one of the most promising pathways to produce the clean hydrogen energy [2]. Currently, precious metals, especially platinum, are still regarded as the best electrocatalysts for producing H_2 . However, the ultra-high prices, limited resource and easy deactivation of these noble metals impede their large-scale applications [2] and [3]. Recently, transition metal oxides are demonstrated to be attractive alternatives for these expensive and rare catalysts, benefiting from their low cost, earth abundance and chemical stability [4]. In spite of these several advantages, the

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http://dx.doi.org/10.1016/j.nanoen.2016.09.015 2211-2855/© 2016 Elsevier Ltd. All rights reserved. transition metal oxides still suffer from low energetic efficiency (i.e., high overpotential requirement), compared to the precious metals-based H₂ evolution electrocatalysts. This could be mainly ascribed to their inherently poor electrical conductivity as well as extremely low amount of active sites, which are actually the two prerequisites for a high-efficiency electrocatalyst. As is wellknown, doping engineering has been widely utilized to tailor the electronic structure of inorganic materials and hence improve the electrical conductivity [5]. However, to date, atomic level insights in the role of doping engineering in tailoring catalytically active sites are still not clear, which may be related to the large crystallite size associated with abundant microstructures in the previously fabricated HER electrocatalysts. The large size enables most dopants distribute on the interior of the catalysts, and hence the dopants could not effectively tailor the active sites on the surface. In addition, the presence of unintentional microstructures would inevitably obscure the effect of dopants on the catalytically active sites. Therefore, developing a suitable material model is imminently necessary for disclosing the role of dopants in tailoring catalytically active sites at the atomic level.







Scheme 1. Scheme illustration for the formation of freestanding pure MoO₃ single-layers and defective N-doped MoO₃ single-layers, with efforts to tailoring the active sites via doping engineering.

In this work, we initially built an ideal model of atomically-thin layers, in which the more exposed interior atoms would be easily escaped from the lattice to form abundant vacancy defects, which could serve as the catalytically active sites. Hence, we deliberately create element doping in the atomically-thin layers, in which the dopants mainly distribute on the surface and hence possess more opportunities for modulating the active sites. In this regard, ultrathin doped orthorhombic MoO₃ two-dimensional structure would be a promising candidate. In addition to possessing thermal stability, environmental friendliness, abundance of reserves, and low cost of raw materials [6], the orthorhombic MoO₃ also exhibits an anisotropic layered structure that involves stacking of MoO₆ octahedral bilayers along the [010] direction, in which the intrinsic structural anisotropy along with the weak van der Waals force makes the synthesis of MoO₃ single-layers to be theoretically feasible [7]. More importantly, as the thickness is down to atomicscale, the ultrahigh fraction of surface atoms in MoO₃ single-layers would be easily escaped to form surface oxygen vacancies [8], which could potentially act as the active sites for promoting catalytic performances. Inspired by the aforementioned concepts, the fabrication of N-doped orthorhombic MoO₃ single-layers is highly desirable, in which the N doping would not only help to improve the electrical conductivity but also have the possibility to increase the concentration of oxygen vacancies.

2. Experimental section

2.1. Synthesis of N-doped bulk MoO₃

In a typical procedure, 500 mg commercial MoO_3 was heated at 300 °C for 3 h in the atmosphere of NH_3 and then cooled to room temperature. The obtained powders were collected for further characterization.

2.2. Synthesis of lamellar hybrid MoO₃ or N-doped MoO₃-octylamine intermediate

In a typical procedure, 500 mg bulk MoO₃ or N-doped MoO₃ and 15 mL n-octylamine were added into a mixed solution of 20 mL octanol and 20 mL cyclohexane in order. Then the mixture was transferred into a 250 mL flask and hence refluxed at 60 °C for 24 h. The system was then allowed to cool down to room temperature naturally, the final product was collected by centrifuging the mixture, washed with ethanol and cyclohexane 5 times, and

then dried under vacuum overnight for further characterization.

2.3. Synthesis of freestanding MoO₃ or N-doped MoO₃ single layers

In a typical procedure, 200 mg lamellar hybrid MoO₃/N-doped MoO₃-octylamine intermediate was heated at 200 °C for 1 h in a quartz boat. The system was then allowed to cool down to room temperature naturally, and hence the product was transferred into 250 mL acetone and sonicated for 4 h. After 12 h standing, the supernatant of the resultant dispersions was centrifuged and washed with ethanol and cyclohexane 3 times. The final product was dried under vacuum overnight for further characterization.

2.4. Electrochemical measurements

All the electrochemical measurements were performed in a three-electrode system on an electrochemical workstation (CHI760E). Typically, 10 mg of catalyst and 30 µL Nafion solution (Sigma Aldrich, 5 wt%) were dispersed in 1 mL water-ethanol solution with volume ratio of 1:1 by sonicating for 1 h to form a homogeneous ink. Then 5 μ L of the dispersion (containing 50 μ g of catalyst) was loaded onto a glassy carbon electrode with 3 mm diameter (loading 0.694 mg cm^{-2}). Linear sweep voltammetry with a scan rate of 10 mV s⁻¹ was conducted in 0.5 M H₂SO₄ using Ag/AgCl (in 3 M KCl solution) electrode as the reference electrode, a graphite rod (Alfa Aesar, 99.9995%) as the counter electrode, and the glassy carbon electrode with various catalysts as the working electrode. All the potentials were calibrated to a reversible hydrogen electrode (RHE). Cyclic voltammetry (CV) was conducted between -1 and 0.0 V vs. RHE at 50 mV s⁻¹ to investigate the cycling stability. The Nyquist plots were measured with frequencies ranging from 100 kHz to 0.1 Hz at an applied potential of -1 V vs. RHE. The impedance data were fitted to a simplified Randles circuit to extract the series and charge transfer resistances. ECSA was evaluated by measuring the capacitive current associated with double-layer charging from the scan-rate dependence of cyclic voltammetry. Cyclic voltammetry was performed at various scan rates (20, 40, 60, 80, 100, 120, 140, 160, 180 and 200 mV s⁻¹) in -0.19-0.29 V vs. RHE region. The double-layer capacitance (C_{dl}) was estimated by plotting the Δj (j_a-j_c) at $-0.24\,V$ vs. RHE against the scan rates, in which the j_a and j_c are the anodic and cathodic current density, respectively. The slope is twice that of the double-layer capacitance C_{dl}.



Fig. 1. Characterizations for the N-doped MoO₃ single-layers: (A) XRD pattern for the N-doped MoO₃ single-layers-based thin film, (B) IR spectrum, (C) TEM image, (D) HRTEM image, (E) AFM image and (F) the corresponding height profile.

3. Characterization

The field emission scanning electron microscopy (FE-SEM)

images were performed by using a FEI Sirion-200 SEM. Transmission electron microscopy (TEM) images and high-resolution TEM image were performed by using a JEOL-2010 TEM with an

 Table 1

 Position lifetime parameters for N-doped MoO₃ single-layers, and MoO₃ single-layers.

Sample	τ ₁ (ps)	τ ₂ (ps)	I ₁ (%)	I ₂ (%)
MoO3 single-layers	211.7(\pm 3.2)	390.3(± 4.6)	56.3	43.7
N-doped MoO3 single-layers	208.6(\pm 2.2)	381.4(± 4.4)	61.4	38.6

acceleration voltage of 200 kV. XRD patterns were recorded by using a Philips X'Pert Pro Super diffractometer with Cu K α radiation (λ =1.54178 Å). X-ray photoelectron spectra (XPS) were acquired on an ESCALAB MKII with Mg K α (h υ =1253.6 eV) as the excitation source. The binding energies obtained in the XPS spectral analysis were corrected for specimen charging by referencing C 1s to 284.8 eV. Atomic force microscopy (AFM) study in the present work was performed by means of Veeco DI Nanoscope MultiMode V system. The Fourier transform infrared (FT-IR) spectra were acquired on a NICOLET FT-IR spectrometer in a KBr tablets, scanning from 4000 to 400 cm⁻¹ at room temperature.

4. Results and discussion

Of note, freestanding MoO₃ single-layers with/without N-doping were first successfully synthesized, taking advantage of lamellar intermediate precursors which were obtained by refluxing the corresponding bulk MoO₃/N-doped MoO₃ in the solvent of octylamine (Scheme 1 and Fig. S1-2). It should be noted that the octylamine played a vital role in the formation of the lamellar intermediates, which could be verified by the corresponding small-angle XRD patterns in Fig. S3. After the following fast heat treatment at a relatively low temperature of 200 °C associated with a sonication process, N-doped MoO₃ single-layers and MoO₃ single-layers were successfully fabricated, respectively. Taking the N-doped MoO₃ single-layers as an example, their characterizations were shown as follows. XRD pattern in Fig. 1A could be readily indexed to the orthorhombic MoO₃ (JCPDS 75-0912), with the exclusive presence of the (020), (040) and (060) diffraction peaks, revealing the highly preferred [010] orientation of the N-doped MoO₃ single-layers-based film. Meanwhile, XPS spectra in Fig. S4 demonstrated the formation of pure N-doped MoO₃, while the corresponding element mapping revealed that the element N uniformly distributed in the synthetic MoO₃ single-layers (Fig. S5). Also, the corresponding IR spectrum in Fig. 1B implied the absence of octylamine on the as-synthesized products, suggesting the formation of clean N-doped MoO₃. TEM image in Fig. 1C revealed their sheet-like morphology, while the HRTEM image in Fig. 1D demonstrated their orientation along the [010] projection, fairly consisting with the XRD pattern analysis. Atomic force microscopic (AFM) image and the corresponding height profiles in Fig. 1E and F showed their average thickness of 0.7 nm, which agreed with the 0.69 nm thickness of a unit cell along the [010] direction. Thus, the above results demonstrated the formation of clean N-doped MoO₃ single-layers. Moreover, Fig. S6-7 also illustrated the successful synthesis of clean MoO₃ single-layers. Therefore, the above results demonstrated the fabrication of freestanding MoO₃ single-layers with/without N-doping, in which the introduction of N-doping may bring about vacancy defects in the MoO₃ single-layers.

To verify the above expectations, positron annihilation spectrometry (PAS) measurements were performed on the N-doped MoO₃ single-layers and MoO₃ single-layers, owing to the fact that PAS is a non-destructive technique for determining the type and relative concentration of defects even at the ppm level [9]. By using the two-component analysis method of positron lifetime spectrum, the experimental results for the two samples were shown in Table 1, while the calculated theoretical lifetimes of positron in the bulk state and the localized state for reasonably existent vacancies were shown on Table 2. As revealed by the positron lifetime spectra in Fig. 2A and the corresponding derived lifetime parameters in Table 1, both the samples exhibited two distinct lifetime components, in which the longer component (τ_2) could be ascribed to the positron annihilation as trapped in the large defect clusters of these samples [10]. According to the theoretically calculated positron lifetime values in Table 2, the shorter component (τ_1) for the N-doped MoO₃ single-layers and MoO₃ single-layers could be attributed to the same $V_0^{-}V_0^{-}$ divacancies (Fig. 2E and F). Interestingly, as shown by the Mo 3d spectra in Fig. 2B and C, the appearance of Mo^{5+} and Mo^{4+} peaks further verified the presence of oxygen vacancies in these two samples. In addition to the lifetime of the positron, the relative intensity (I) for the samples could provide more information on the concentration of these defects. The relative intensity of positron lifetime in Table 1 quantified that the N-doped MoO₃ single-layers possessed higher concentration of $V_{0}^{..}V_{0}^{..}$ divacancies compared with the MoO₃ single-layers, further confirmed by their relatively larger content of Mo⁵⁺ and Mo⁴⁺ ions in Fig. 2C and D. Theoretically, two doped N atoms could lead to three oxygen vacancies. In this regard, the formation energy of oxygen divacancies was calculated to be 2.95 eV (Fig. 2B), which was smaller than that of two separated oxygen vacancies (3.52 eV), thus demonstrating the feasibility of forming oxygen divacancies. Therefore, the above results strongly demonstrated that the MoO₃ single-layers confined N-doping

To gain in-depth understanding on the correlation between $V_0^{-}V_0^{-}$ divacancies and electrocatalytic H₂ evolution, the electrochemical performances for the N-doped MoO₃ single-layers and MoO₃ single-layers were performed and the results were shown in Fig. 3. Actually, Fig. 3A displayed the linear sweeps in a cathodic direction for the N-doped MoO₃ single-layers and MoO₃ singlelayers, respectively. As expected, the MoO₃ single-layers exhibited negligible current densities over all the applied potentials. Contrastingly, the N-doped MoO₃ single-layers showed obviously increased current densities compared with the MoO₃ single-layers, suggesting the former's superior activity. For instance, the N-doped MoO₃ single-layers exhibited an initial H₂ evolution at a small overpotential (n) of 0.21 V, much smaller than that of MoO_3 single-layers (0.57 V). At the applied potential of -1.0 V vs. RHE, the current density of N-doped MoO3 single-layers was 562 mA cm⁻², which was 6 times higher than that of MoO₃ singlelayers, strongly demonstrating the former's high electrocatalytic activity. In addition, the evolved H₂ contents were also measured by gas chromatography. As shown in Fig. S9, the experimental evolved rates of H₂ gases are close to the corresponding theoretical values of H₂ gases, indicating that there are no obvious electriccorrosion occurred on both the N-doped MoO₃ single-layers and MoO₃ single-layers. To further verify this viewpoint, N-doped

could help to tune the concentration of $V_0^{"}V_0^{"}$ divacancies, hence

allowing for promoted catalytic performances.

Table 2

Calculated position lifetime values for MoO₃.

Defect	Bulk	Vö	V'''''	<i>V</i> ₀ <i>V</i> ₀	$V_{Mo}^{\prime\prime\prime\prime\prime\prime}V_{O}^{\cdot\cdot}$	$V_{Mo}^{\prime\prime\prime\prime\prime\prime}V_{O}^{\cdot\prime}V_{O}^{\prime\prime}$
Lifetime (ps)	185	198	195	212	232	252



Fig. 2. (A) Positron lifetime spectrum for N-doped MoO₃ single-layers, and MoO₃ single-layers; schematic representation of trapped positrons for MoO₃ single-layers (E) with $V_o^*V_o^*$ divacancies, and (F) without vacancies; (B) calculated formation energies for different types of oxygen vacancies; Mo 3d XPS spectra for (C) N-doped MoO₃ single-layers and (D) MoO₃ single-layers.

MoO₃ single-layers with higher oxygen divacancy amount were also fabricated and the corresponding polarization curve demonstrated their further improved electrocatalytic activity relative to the N-doped MoO₃ single-layers with lower oxygen divacancy amount, further confirming the crucial role of oxygen divacancies (Fig. S10). Moreover, the N-doped MoO₃ single-layers possessed a Tafel slope of 101 mV dec⁻¹, much smaller than that of MoO₃ single-layers (Fig. S8), illustrating their faster kinetics of H₂ evolution. The lowered Tafel slope of the N-doped MoO₃ single-layers was advantageous for practical applications, since it would lead to a faster increment of water reduction rate with increasing overpotential [11]. Furthermore, it is noticeable that a catalyst's



Fig. 3. (A) Polarization curves, (C) charging current density differences plotted against scan rates and (D) Nyquist plots for N-doped MoO₃ single-layers and MoO₃ single-layers; (B) durability test for N-doped MoO₃ single-layers, showing negligible current loss even after 1000 CV cycles.

stability is a major issue to be addressed. Thus, the stability of the above catalyst was investigated by performing continuous cyclic voltammetry. Fig. 3B revealed that negligible difference was observed between the curves measured at the initial cycle and after 1000 CV cycles, suggesting the excellent durability of the N-doped MoO₃ single-layers during long-term cycling.

Of note, the greatly promoted electrocatalytic H₂ evolution could be attributed to the higher concentration of $V_0^{\alpha}V_0^{\alpha}$ divacancies, induced by the N-doping in MoO₃ single-layers. To further verify the crucial role of $V_0^{-}V_0^{-}$ divacancies in HER performances, electrochemical active surface area (ECSA) was performed for the MoO₃ single-layers and N-doped MoO₃ single-layers (Fig. 3C). Interestingly, the N-doped MoO₃ single-layers possessed nearly the same ECSA as that of the MoO₃ single-layers, which cannot account for the former's 6 times higher catalytic activity. This implied that the superior catalytic performance of the N-doping in MoO₃ single-layers was not due to the higher ECSA, but instead the increased concentration of $V_0^{-}V_0^{-}$ divacancies [12], which endured much higher intrinsic catalytic activity toward H₂ evolution. Moreover, the presence of $V_o^{"}V_o^{"}$ divacancies also helped to improve the overall electronic conductivity, which was verified by the lowered interfacial charge-transfer resistance of the N-doped MoO₃ single-layers (Fig. 3D). To further confirm the crucial role of $V_0^{-}V_0^{-}$ divacancies in tailoring electronic conductivity, we performed density functional theory (DFT) calculations to investigate the variation in density of states (DOS) [13]. Fig. 4A and C revealed that the MoO₃ single-layers with $V_0^{-}V_0^{-}$ divacancies exhibited increased states density near the edge of the valence band relative to the perfect MoO₃ single-layers, in which the enhanced charge density

came from the strong hybrid between the surface Mo and O atoms (Fig. 4A and B). In other words, the presence of $V_o^* V_o^*$ divacancies resulted in the exposure of Mo atoms, which hence effectively interacted with the neighboring in-plane O atoms to generate more active electrons on the surface, finally ensuring fast electron transfer kinetics during H₂ evolution process. Therefore, the $V_o^* V_o^*$ divacancies with higher intrinsic activity could serve as the highly active sites to trigger the H₂ evolution reaction, hence achieving remarkably promoted HER performances.

5. Conclusions

In conclusion, atomically-thin layers with element doping were first put forward as an excellent platform to investigate the dopant-induced modification of catalytically active sites. As an example, freestanding MoO₃ single-layers with/without N-doping were first successfully synthesized, taking advantage of a lamellar intermediate. Positron annihilation spectrometry disclosed the distinct concentrations of $V_0^{-}V_0^{-}$ divacancies in the synthetic N-doped MoO₃ single-layers and MoO₃ single-layers, while the nearly same ECSA cannot account for the former's 6 times higher HER activity. This implied that the increased $V_0^{-}V_0^{-}$ divacancies with higher intrinsic activity could serve as the highly active sites, further confirmed by the DFT calculations which revealed that the presence of $V_0^* V_0^*$ divacancies leads to the strong in-plane hybrid of surface Mo and O atoms and hence results in increased DOS near the edge of the valence band, which finally accounts for their improved electronic conductivity. This result fairly agreed with their lowered interfacial electron transfer resistance and hence



Fig. 4. Calculated DOS of (A) defective MoO₃ single-layers with $V_0^-V_0^-$ divacancies and (C) perfect MoO₃ single-layers; charge density contour plots for the valence band maximum of (B) defective MoO₃ single-layers with $V_0^-V_0^-$ divacancies and (D) perfect MoO₃ single-layers.

favored fast electron transfer kinetics during H₂ evolution process, further demonstrated by their lowered initial overpotential from 0.57 to 0.21 V as well as lowered Tafel slope from 156 to 101 mV/dec. This work not only first demonstrated that the $V_o^- V_o^-$ divacancies confined in MoO₃ single-layers could act as the highly active sites to trigger H₂ evolution reaction, but also disclosed that the N-doping was beneficial for increasing the divacancy concentration. Therefore, the doping engineering has dual abilities to tailor the two prerequisites (catalytically active sites and electrical conductivity) of an efficient electrocatalyst, hence holding great promise for achieving highly efficient electrocatalysts for hydrogen evolution.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.nanoen.2016.09.015.

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