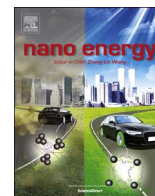




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# Nitrogen-doping induced oxygen divacancies in freestanding molybdenum trioxide single-layers boosting electrocatalytic hydrogen evolution

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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 MoO<sub>3</sub> single-layers are first synthesized by virtue of a lamellar intermediate. Positron annihilation spectrometry discloses that N-doping leads to increased V<sub>o</sub>V<sub>o</sub> divacancies relative to intact MoO<sub>3</sub> single-layers, while the similar electrochemical active area implies that the increased V<sub>o</sub>V<sub>o</sub> divacancies accounts for the former's 6 times higher H<sub>2</sub> evolution activity. In addition, density-functional calculations revealed that the presence of V<sub>o</sub>V<sub>o</sub> 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 MoO<sub>3</sub> atomic-layers increase the concentration of V<sub>o</sub>V<sub>o</sub> divacancies, which are first verified to be highly active sites for H<sub>2</sub> 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

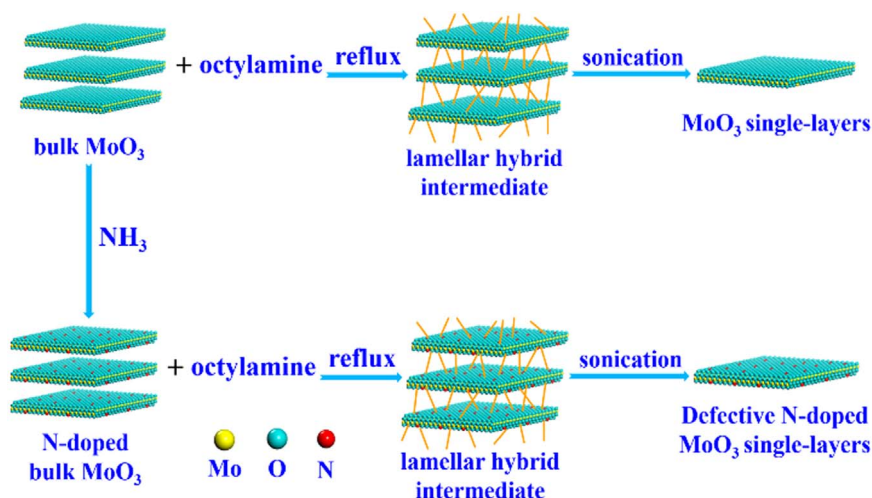
Nowadays, fossil fuels comprise over 80% of global energy sources [1]; however, these limited resources can not last forever, which stimulates us to explore renewable green energy alternatives. In this regard, electrocatalytic water splitting into H<sub>2</sub> is regarded as one of the most promising pathways to produce the clean hydrogen energy [2]. Currently, precious metals, especially platinum, are still regarded as the best electrocatalysts for producing H<sub>2</sub>. 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

transition metal oxides still suffer from low energetic efficiency (i.e., high overpotential requirement), compared to the precious metals-based H<sub>2</sub> 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 well-known, 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.

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**Scheme 1.** Scheme illustration for the formation of freestanding pure MoO<sub>3</sub> single-layers and defective N-doped MoO<sub>3</sub> 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 MoO<sub>3</sub> 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 MoO<sub>3</sub> also exhibits an anisotropic layered structure that involves stacking of MoO<sub>6</sub> octahedral bilayers along the [010] direction, in which the intrinsic structural anisotropy along with the weak van der Waals force makes the synthesis of MoO<sub>3</sub> single-layers to be theoretically feasible [7]. More importantly, as the thickness is down to atomic-scale, the ultrahigh fraction of surface atoms in MoO<sub>3</sub> 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 MoO<sub>3</sub> 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 MoO<sub>3</sub>

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

### 2.2. Synthesis of lamellar hybrid MoO<sub>3</sub> or N-doped MoO<sub>3</sub>-octylamine intermediate

In a typical procedure, 500 mg bulk MoO<sub>3</sub> or N-doped MoO<sub>3</sub> 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 MoO<sub>3</sub> or N-doped MoO<sub>3</sub> single layers

In a typical procedure, 200 mg lamellar hybrid MoO<sub>3</sub>/N-doped MoO<sub>3</sub>-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 μL of the dispersion (containing 50 μg of catalyst) was loaded onto a glassy carbon electrode with 3 mm diameter (loading 0.694 mg cm<sup>-2</sup>). Linear sweep voltammetry with a scan rate of 10 mV s<sup>-1</sup> was conducted in 0.5 M H<sub>2</sub>SO<sub>4</sub> 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<sup>-1</sup> 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<sup>-1</sup>) in -0.19–0.29 V vs. RHE region. The double-layer capacitance (C<sub>dl</sub>) was estimated by plotting the Δj (j<sub>a</sub>–j<sub>c</sub>) at -0.24 V vs. RHE against the scan rates, in which the j<sub>a</sub> and j<sub>c</sub> are the anodic and cathodic current density, respectively. The slope is twice that of the double-layer capacitance C<sub>dl</sub>.

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