# Operando Synthesis of a Dendritic and Well-Crystallized Molybdenum Oxide/Silver Catalyst for Enhanced Activity in the Hydrogen Evolution Reaction

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Dendritic  $MoO_3/Ag$  with good crystallinity has been prepared through an operando method. In the hydrogen evolution reaction (HER), this catalyst, which was designed to utilize the best properties of each component material, showed a high catalytic activity. After the precursor was drop-cast onto a glassy carbon electrode, a reductive potential was applied to the coated electrode, and H<sub>2</sub> evolution occurred within the range of potentials. The overpotential required to evolve H<sub>2</sub> at the benchmark rate decreased progressively with subsequent vol-

## Introduction

The development of renewable and clean energy sources to replace fossil fuels that cause global environmental problems is highly anticipated. As a result, interest in H<sub>2</sub> has increased significantly in recent years. H<sub>2</sub> is considered to be an efficient fuel of the future because it burns cleanly. At present, almost 90% of H<sub>2</sub> is produced from fossil fuels such as coal and natural gas; however, it also could be produced from abundant renewable energy sources using electrochemical methods.<sup>[1]</sup> Electrocatalytic H<sub>2</sub> production by water splitting is one example; this process could potentially address the need for the sustainable production of fuels and for solar energy storage in a manner that is renewable and carbon free.<sup>[2]</sup> In contrast to steam reformed H<sub>2</sub> utilized widely, H<sub>2</sub> produced electrocatalytically has a much lower CO content, which can mitigate the poisoning effect that often decreases the operational activity of catalysts used currently in hydrogen fuel cells.<sup>[3]</sup> Several device configurations can potentially enable solar- and electricity-driven water electrolysis, which include photovoltaic (PV) electrolyzers,<sup>[4]</sup> integrated PV electrolyzers,<sup>[5]</sup> and photo-electrochemical and electrochemical water-splitting cells.[1,6-8] Research in electrochemical water splitting, in particular, has experienced rapid growth in recent years. However, the development of materials that can meet the requirements of high catalytic activity and durability represents a significant challenge.

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tammetric cycles, until a steady state was reached at which only 145 mV of overpotential was required to pass  $-10 \text{ mA cm}^{-2}$  of current density. During the electrocatalysis, the precursor was converted to catalyst through an operando method. This operando-synthesized MoO<sub>3</sub>/Ag catalyst has a low Tafel slope (43 mV dec<sup>-1</sup>), low overpotential (145 mV), and excellent durability for HER. It has the potential to be a promising material for HER.

One strategy is to meet the various requirements by utilizing multiple materials. Enhancements in the activity of silicon photocathodes by depositing H<sub>2</sub> evolution catalysts on the Si surface, for example, have already been demonstrated.<sup>[9]</sup> The H<sub>2</sub> evolution catalyst is a key component that needs to be able to drive current densities at low overpotentials and remain stable in the chosen electrolyte. Currently, state-of-the-art H<sub>2</sub> evolution catalysts consist of Pt or Pt-based materials<sup>[10]</sup> because of their negligible overpotential and excellent kinetics for driving the hydrogen evolution reaction (HER). However, the widespread use of Pt may be limited by its scarcity and high cost,<sup>[11]</sup> and thus the development of non-noble metal alternatives remains attractive. Typically, such alternatives include Ni or Nibased materials,<sup>[12,13]</sup> which operate in alkaline electrolytes. Their long-term durability in strong acids, however, remains a significant challenge. As a result, these catalysts are difficult to integrate into systems that operate in acid, such as photoelectrochemical cells that contain tungsten oxide,<sup>[14]</sup> p-type silicon,<sup>[15]</sup> or gallium indium-phosphide.<sup>[16]</sup>

Among layered inorganic materials, MoO<sub>3</sub>, which has interesting catalytic, photochromic, and electrochromic properties, has been used widely in catalytic materials, sensors, smart windows, lubricants, and electrochemical storage.<sup>[17–19]</sup> MoO<sub>3</sub> has two basic structures: the thermodynamically stable orthorhombic MoO<sub>3</sub> ( $\alpha$ -type) and the metastable monoclinic MoO<sub>3</sub> ( $\beta$ -type) with ReO<sub>3</sub>-type structure. The most important characteristic of  $\alpha$ -MoO<sub>3</sub> is its structural anisotropy, considered as a layered structure.<sup>[20]</sup> Each layer is composed of two sublayers formed by corner sharing of octahedra along the [100] direction with edge sharing of octahedra along the [001] direction. Alternating stacks of these layered sheets, bound by van der Waals interactions along the [010] direction, lead to the formation of  $\alpha$ -MoO<sub>3</sub>.<sup>[21]</sup> The intrinsic structural anisotropy of  $\alpha$ -MoO<sub>3</sub>



can be used to tune its properties by interlayer structural modification and annealing.<sup>[19]</sup> MoO<sub>3</sub> nanorods are promising cathodes in reversible lithium ion batteries, and MoO<sub>3</sub> is a valuable candidate for use in gas sensors.<sup>[22]</sup> MoO<sub>3</sub> nanobelt films are excellent field emitters, and MoO<sub>3</sub> nanofibers have been used as a catalyst for the HER.<sup>[23]</sup> There are several reports on the hydrothermal synthesis of MoO<sub>3</sub> nanostructures, which is known to produce materials with high purity, homogeneity, crystallinity, and unique properties.<sup>[24-26]</sup> Wei et al. reported MoO<sub>3</sub> nanobelts synthesized on a Si substrate by a microwaveassisted hydrothermal method.<sup>[27]</sup> Ag<sub>2</sub>O has attracted much attention because of its high catalytic activity as well as its selectivity as a catalyst.<sup>[28-37]</sup> XRD results show that the heterojunction of Ag<sub>2</sub>O and MoO<sub>3</sub> can result in a better crystallinity of MoO<sub>3</sub>, which can effectively enhance the HER catalytic performance of MoO<sub>3</sub>.

Herein, we synthesized  $MoO_3/Ag_2O$ , which was collected and deposited onto electrodes. The covered electrodes are then introduced into aqueous acid and used to drive the HER. The asprepared  $MoO_3/Ag_2O$  exhibited a low catalytic activity, but the activity improved under the conditions of the HER, which convert  $MoO_3/Ag_2O$  into  $MoO_3/Ag$ . The synthesis can be categorized as operando because the  $MoO_3/Ag$  catalyst is produced under the conditions of the reaction that it catalyzes.

#### **Results and Discussion**

#### SEM

SEM images of MoO<sub>3</sub>, Ag<sub>2</sub>O, and the materials obtained before and after sweeping MoO<sub>3</sub>/Ag<sub>2</sub>O in H<sub>2</sub>SO<sub>4</sub> for seven cycles are shown in Figure 1. After the reductive conversion of the MoO<sub>3</sub>/ Ag<sub>2</sub>O during the electrochemical experiments, significant changes in the morphology of the material can be observed. The SEM image of MoO<sub>3</sub> is shown in Figure 1A, and it can be seen that the MoO<sub>3</sub> has a shuttle-shaped nanorod structure



**Figure 1.** Typical SEM images of the surface morphology of A)  $MoO_3$  and B)  $Ag_2O$  and the materials obtained C) before and D) after sweeping  $MoO_3/Ag_2O$  in  $H_2SO_4$  for seven cycles.

with a wide middle and two tapered ends. SEM images of MoO<sub>3</sub>, obtained under different resolutions, are shown in Figure S1. This material presents a coral-reef-like porous structure under low resolution (Figure S1 A). Under a higher resolution, it can be seen that this coral-reef-like structure is composed of shuttle-shaped nanorods (Figure S1B-D). The width of the middle of these shuttle-shaped nanorods is  $\approx$  100–200 nm and the length is  $\approx$  500–1000 nm (Figure 1 A). The surface of these nanorods is not smooth, and there are some folds and grooves. The SEM image of  $Ag_2O$  is shown in Figure 1B in which Ag<sub>2</sub>O shows a nanoflake morphology with a thickness of less than 100 nm. It can be seen from this SEM image that some of these nanoflakes are flat and some of them are vertical, and the size of these nanoflakes is  $\approx$  100–400 nm. The SEM image of MoO<sub>3</sub>/Ag<sub>2</sub>O is shown in Figure 1C; the nanoflakes are well dispersed in different directions on the surface of the nanorods, and the agglomeration of nanoflakes can also be observed. The SEM image of the material obtained after the reductive conversion of MoO<sub>3</sub>/Ag<sub>2</sub>O is presented in Figure 1D. It can be seen that this material has a dendritic structure that is totally different from that of the  $MoO_3/Ag_2O$  precursor. With the reduction of Ag<sub>2</sub>O, MoO<sub>3</sub>/Ag<sub>2</sub>O does not maintain its original structure, which indicates that the reduction of Ag<sub>2</sub>O has an effect on the morphology of the composite.

#### TEM and XRD

The microstructure and phase structure of the  $MoO_3/Ag_2O$  precursor were further studied by TEM and XRD.  $MoO_3/Ag_2O$  presents a structure in which some nanoflakes are modified on the surface of nanorods that vary in length (Figure 2 A). The highresolution transmission electron microscopy (HRTEM) images of different locations shown in Figure 2 A are presented in Figure 2 B and C. The HRTEM image of the nanorods demonstrates their single-crystalline structure clearly (Figure 2 B). The



Figure 2. A) TEM image of  $MoO_3/Ag_2O$  obtained under a low magnification. B,C) HRTEM images and corresponding FFT analysis (inset) of the different locations in A. D) XRD patterns of a)  $MoO_3$  and b)  $MoO_3/Ag_2O$ .

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result shows two sets of crystal lattice fringes with spacings of 0.39 and 0.35 nm, which correspond to the interplanar distances of the (002) and (200) planes of MoO<sub>3</sub>, respectively. The results suggest that these nanorods grow strongly along both the [100] and [001] directions.<sup>[21]</sup> The fast Fourier transform (FFT) pattern of the HRTEM image is shown inset. The FFT pattern recorded perpendicular to the growth axis is composed of a highly ordered diffraction lattice and a homogeneous array of diffraction dots. This result indicates that the MoO<sub>3</sub> nanorods contained in MoO<sub>3</sub>/Ag<sub>2</sub>O have a single-crystal structure. This can be indexed to an orthorhombic  $\alpha$ -MoO<sub>3</sub> phase with a zone axis along the [010] direction, which implies that preferential growth occurred along the c axis.<sup>[38]</sup> TEM and HRTEM images of single MoO<sub>3</sub> are shown in Figure S2. Compared with the MoO<sub>3</sub> contained in MoO<sub>3</sub>/Ag<sub>2</sub>O there are no clear lattice stripes observed in the HRTEM image of single MoO<sub>3</sub>, which indicates that the combination of Ag<sub>2</sub>O and MoO<sub>3</sub> results in an improved crystallinity of MoO<sub>3</sub>. For crystalline MoO<sub>3</sub>, the facile vectorial electron transport along the axis is considered to be responsible for its excellent electrocatalytic activity for the HER. The HRTEM image of the nanoflakes shown in Figure 2A is presented in Figure 2C. The clear lattice stripes observed in this HRTEM image show that the nanoflakes have a well-defined, single-crystal structure, and the lengths of the lattice stripes are  $\approx$  0.26 nm, which shows that the nanoflake is a single crystal of Ag\_2O; the lattice distance is  $\approx 0.26 \text{ nm},$ which is the interplanar distance of the (100) facets.<sup>[39]</sup> The FFT pattern that corresponds to the HRTEM image is shown inset. Single MoO<sub>3</sub> exhibits a weak XRD diffraction peak (Figure 2D, Curve a). The XRD pattern of MoO<sub>3</sub>/Ag<sub>2</sub>O is shown in Figure 2D, Curve b, in which it can be seen that the (200) diffraction peak is much stronger than the normally strong (111) diffraction peak in the pattern of Ag<sub>2</sub>O. The highly intense (200) diffraction peak could be ascribed to the high orientation of the (100) crystal plane of Aq<sub>2</sub>O as they always lie parallel to the substrate.<sup>[30]</sup> All diffraction peaks correspond to those reported for Ag<sub>2</sub>O (JCPDS 12-0793), which indicates the existence of Ag<sub>2</sub>O. In addition, the sharp diffraction peaks imply the good crystallization of Ag<sub>2</sub>O; this conclusion is consistent with the result obtained from HRTEM. The other diffraction peaks of the XRD pattern shown in Curve (b) can be indexed readily to orthorhombic  $\alpha$ -MoO<sub>3</sub> with lattice constants of a = 3.962 Å, b =13.85 Å, and c = 3.697 Å (ICDD 05-0508). For the MoO<sub>3</sub> contained in  $MoO_3/Ag_2O$ , the intensities of the (020) and (040) diffraction peaks are stronger than that of single MoO<sub>3</sub>, which indicates that Ag<sub>2</sub>O promoted anisotropic growth as well as the preferred orientation of MoO<sub>3</sub>.<sup>[19]</sup> The diffraction peaks that appear at  $2\theta = 12.8$  and  $25.7^{\circ}$  in Curve b correspond to the (020) and (040) planes of orthorhombic  $\alpha$ -MoO<sub>3</sub>, respectively, and are attributed to planes normal to the [010] direction.<sup>[21]</sup>

A TEM image of the material obtained after sweeping  $MoO_3/Ag_2O$  in  $H_2SO_4$  for seven cycles is shown in Figure 3A. After the reductive conversion of the  $MoO_3/Ag_2O$  during the electrochemical experiments, substantial changes to the microstructure were evident relative to the structure of the material before electrochemical measurements were performed (Figure 2A). The material obtained after the reductive conversion

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**Figure 3.** A) TEM image of the material obtained after sweeping  $MoO_3/Ag_2O$  in  $H_2SO_4$  for seven cycles. B) HRTEM image and C) corresponding FFT analysis of the data shown in A. D) XRD pattern of the material obtained after sweeping  $MoO_3/Ag_2O$  in  $H_2SO_4$  for seven cycles.

of MoO<sub>3</sub>/Aq<sub>2</sub>O presents a dendritic structure, and the trunk and branches can be distinguished clearly. To obtain more precise information about their structures and further prove the reductive conversion of Aq<sub>2</sub>O, the HRTEM image of the material obtained after the reductive conversion of MoO<sub>3</sub>/Ag<sub>2</sub>O was recorded (Figure 3B). The HRTEM image of the converted material displays well-defined lattice fringes, which contain two types of materials. The lattice spacing with values of 0.35 and 0.39 nm are consistent with the lattice spacing of orthorhombic  $\alpha$ -MoO<sub>3</sub>, whereas the spacing with a value of 0.23 nm is consistent with the reduction product of Ag<sub>2</sub>O. The lattice spacing of orthorhombic  $\alpha$ -MoO<sub>3</sub> (0.35 and 0.39 nm) remained unchanged from that in MoO<sub>3</sub>/Ag<sub>2</sub>O (Figure 2B), which corresponds to the interplanar distances of the (002) and (200) planes, respectively. However, the lattice spacing of Aq<sub>2</sub>O (Figure 2C) was clearly different after the electrochemical measurements, and the measured interplanar spacing for the lattice fringes is 0.23 nm, which corresponds to the (111) lattice plane of Ag.<sup>[33]</sup> The HRTEM result indicates that the reduction product of  $Ag_2O$  is Ag, and the material obtained after the reductive conversion of the MoO<sub>3</sub>/Ag<sub>2</sub>O is well-crystallized MoO<sub>3</sub>/Ag. The XRD pattern of the material obtained after the reductive conversion of MoO<sub>3</sub>/Ag<sub>2</sub>O was studied to further verify its reduction product. Compared with the XRD pattern shown in Figure 2D, Curve b, the position of the diffraction peaks of MoO<sub>3</sub> remained unchanged (Figure 3D), and the peaks correspond to the (020), (110), (040), and (021) planes of orthorhombic  $\alpha$ -MoO<sub>3</sub>. However, the position of the other diffraction peaks in the pattern shown in Figure 2D, Curve b was clearly different after the electrochemical measurements and showed clear peaks that correspond to the (111), (200), (220), and (311) diffraction peaks of Ag, which also indicates that the reduction product of Aq<sub>2</sub>O is Aq in the crystalline state. Our HRTEM and XRD results indicate that the material obtained



after the reductive conversion of  $MoO_3/Ag_2O$  is well-crystallized  $MoO_3/Ag$ .

#### X-ray photoelectron spectroscopy

The chemical composition and electronic structure of the materials were analyzed by X-ray photoelectron spectroscopy (XPS). The high-resolution XPS spectra of the Mo 3d, Ag 3d, and O 1s regions for the materials before and after the reductive conversion of  $MoO_3/Ag_2O$  during the electrochemical experiments are displayed in Figure 4. According to a previous study,



**Figure 4.** The high-resolution XPS spectra of the A) Mo 3d and B) Ag 3d regions for the materials before (Pre cycling) and after (Post cycling) the reductive conversion of the  $MoO_3/Ag_2O$  during the electrochemical experiments. High-resolution XPS spectra of the O1s region of the materials C) before and D) after the reductive conversion of  $MoO_3/Ag_2O$ .

the Mo3d region was fitted by doublets with fixed spectroscopic parameters, such as spin–orbit separation (3.1 eV), Mo3d<sub>3/2</sub> to Mo3d<sub>5/2</sub>, intensity ratio (R=0.66), and full width at half maximum (FWHM; 1.6 eV), but with independent and variable positions and intensities as optimized by the program.<sup>[38]</sup> The Mo3d XPS spectrum (Pre cycling) of the material obtained before the reductive conversion of MoO<sub>3</sub>/Ag<sub>2</sub>O shows a perfect fit to the two peaks that corresponded to the predominant oxidation state as signified by the peaks with binding energy (BE) values of Mo3d<sub>5/2</sub> and Mo3d<sub>3/2</sub> at 232.6 eV, characteristic of Mo in a formal Mo<sup>6+</sup> oxidation state, and 235.7 eV, respectively, which is similar to the BE of single MoO<sub>3</sub> (Figure S3). The spin– orbit separation between the Mo3d<sub>5/2</sub> and Mo3d<sub>3/2</sub> peaks is 3.1 eV, and their FWHM values are 1.6 and 1.5 eV, respectively. Moreover, the Mo3d<sub>5/2</sub> peak is symmetric and no shoulders are observed, which indicates that these peaks can be attributed to MoO<sub>3</sub> in the precursor MoO<sub>3</sub>/Ag<sub>2</sub>O. The high-resolution XPS spectrum of the Mo3d region for the material obtained after the reductive conversion of MoO<sub>3</sub>/Ag<sub>2</sub>O is displayed in Figure 4A (Post cycling). The Mo3d<sub>5/2</sub> and Mo3d<sub>3/2</sub> signals of MoO<sub>3</sub> at BE = 232.8 and 235.9 eV remained unchanged after cycling, and the spin–orbit separation between the Mo3d<sub>5/2</sub> and Mo3d<sub>3/2</sub> peaks is also 3.1 eV. The Ag3d XPS spectrum of the

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material obtained before the reductive conversion of MoO<sub>3</sub>/ Ag<sub>2</sub>O shows the peak of Ag 3d<sub>5/2</sub> at BE = 367.8 eV (Figure 4B, Pre cycling), and the Ag  $3d_{3/2}$  peak is located at BE = 373.8 eV. These values are lower than those reported for bulk metallic silver  $(BE_{Ag\,3d_{5/2}}\!=\!368.3~eV~and~BE_{Ag\,3d_{3/2}}$ = 374.3 eV).<sup>[40]</sup> However, the BE of the oxide  $(BE_{Ag_2O3d_{5/2}} =$ 367.7 eV)<sup>[41]</sup> fits better than that of metallic silver, so we can confirm the existence of Ag<sub>2</sub>O. In addition, the energy separation between the Ag  $3d_{5/2}$  and Ag  $3d_{3/2}$ 2 peaks is 6.0 eV, which agrees with the conclusion obtained above. However, the Ag3d peaks of the material obtained after the reductive conversion of MoO<sub>3</sub>/Ag<sub>2</sub>O (Figure 4B, Post cycling) were clearly different from that of the material before cycling (Figure 4B, Pre cycling). The Ag3d peaks were shifted positively after electrolysis. It can be observed in the Ag3d XPS spectrum (Post cycling), that the Ag  $3d_{5/2}$  peak is centered at BE = 368.3 eV and the peak Ag 3d<sub>3/2</sub> is located at BE = 374.3 eV. These values are higher than that of  $Ag_2O$  ( $BE_{Ag_3d_{5/2}} = 367.8 \text{ eV}$  and

 $BE_{Ag 3d_{3/2}} = 373.8 \text{ eV}$ ; however, the BE of bulk metallic silver ( $BE_{Ag 3d_{5/2}} = 368.3 \text{ eV}$  and  $BE_{Ag 3d_{3/2}} = 374.3 \text{ eV}$ ) fits better than that of oxides, so we can confirm the conversion from Ag<sub>2</sub>O to Ag.

The O1s XPS spectrum of the material obtained before the reductive conversion of  $MoO_3/Ag_2O$  was decomposed with the Gaussian distribution as shown in Figure 4C, and the BE components are 528.9 and 531.4 eV. The component located at BE = 528.9 eV is attributed to the O<sup>2-</sup> ions in Ag<sub>2</sub>O.<sup>[42]</sup> The other component located at BE = 531.3 eV originates from the lattice oxygen in MoO<sub>3</sub>, however, it is shifted compared with that reported in the literature (BE = 530.6 eV).<sup>[38]</sup> The reason for this shift is the oxygen vacancies in the matrix of metal



oxide.<sup>[38]</sup> Importantly, before electrolysis, the O1s peaks appeared at BE = 528.9 and 531.4 eV (Figure 4C) and are attributed to the O<sup>2-</sup> ions in Ag<sub>2</sub>O and the lattice oxygen in MoO<sub>3</sub>, respectively. After electrolysis, the O1s peak at 528.9 eV disappears, and the only peak in the spectrum shown in Figure 4D originates from the lattice oxygen in MoO<sub>3</sub>, which implies the reduction of Ag<sub>2</sub>O. Thus, the XPS results demonstrate that after the reductive conversion of MoO<sub>3</sub>/Ag<sub>2</sub>O, the converted material is MoO<sub>3</sub>/Ag, which possesses oxygen vacancies.

#### **Electrochemical determination**

The H<sub>2</sub> evolution activities of these materials were evaluated in H<sub>2</sub>SO<sub>4</sub>. The linear sweep voltammograms of various electrodes, bare glassy carbon electrode (GCE), MoO<sub>3</sub>/GCE, Ag<sub>2</sub>O/GCE, and MoO<sub>3</sub>/Ag<sub>2</sub>O/GCE, are shown in Figure 5 A. Compared with bare GCE, MoO<sub>3</sub> shows better catalytic activity for the HER. The cathodic current density increased with overpotential, but the degree of increase is tiny. Supposedly, this tiny increase is caused by the morphology and structure of MoO<sub>3</sub>, which has a number of active sites, proven through the following electrochemical capacitance surface area measurements. Compared with that of MoO<sub>3</sub>, the cathodic current density of Ag<sub>2</sub>O in-

creased with overpotential by a larger degree. If the surface of the GCE was modified with MoO<sub>3</sub>/Ag<sub>2</sub>O, the obtained MoO<sub>3</sub>/ Ag<sub>2</sub>O/GCE shows a more satisfactory catalytic performance for HER then single MoO<sub>3</sub> or Ag<sub>2</sub>O. The lower overpotential and higher cathodic current density originated from its special structure that has more active sites. The XRD study shows that the MoO<sub>3</sub> contained in MoO<sub>3</sub>/Ag<sub>2</sub>O has an improved crystal structure compared with single MoO<sub>3</sub>, and facile vectorial electron transport along the axis is considered to be responsible for the excellent electrocatalytic activity for the HER. The 1st, 3<sup>rd</sup>, 7<sup>th</sup>, and 10<sup>th</sup> linear sweep voltammograms obtained by sweeping the MoO<sub>3</sub>/Ag<sub>2</sub>O-coated GCE in H<sub>2</sub>SO<sub>4</sub> are shown in Figure 5B, for which a reductive potential was applied to the coated electrode. H<sub>2</sub> evolution occurred within the range of potentials applied to the electrode. The onset potential of H<sub>2</sub> evolution shifted clearly to less negative potentials between the first and seventh cycles, and a steady state was reached by the seventh cycle. During the initial voltammetric cycle, an overpotential of 275 mV was required to drive the HER at a benchmark current density of  $-10 \text{ mA cm}^{-2}$ . The overpotential required to evolve  $H_2$  at the benchmark rate decreased progressively with subsequent voltammetric cycles until a steady state was reached at which only 145 mV of overpo-



tential was required to pass  $-10 \text{ mA cm}^{-2}$  of current density.

During the electrocatalysis,  $MoO_3/Ag_2O$  was converted to the more active  $MoO_3/Ag$  through an operando method of synthesis. Compared with the overpotential of the first cycle (275 mV), the overpotential at the steady state (145 mV) decreased by 130 mV (Figure 5 C). The steady-state negative potential sweep data are illustrated in Figure 5 D.

Durability is an important parameter for an electrocatalyst. To probe the durability of the MoO<sub>3</sub>/Ag catalyst, continuous HER at a static overpotential (145 mV) was conducted using the MoO<sub>3</sub>/Ag-modified GCE (Figure 6). At a given potential, the MoO<sub>3</sub>/Ag catalyst showed a catalytic current density of  $-10 \text{ mA cm}^{-2}$ . Significantly, even after a long period of 7200 s, the current density is almost constant. Plots of current density versus time show a serrated periodicity rule because of the formation of H<sub>2</sub> bubbles on the electrode surface. The durability test proved that this operandosynthesized HER catalyst pos-

**Figure 5.** A) Comparison of the HER catalytic activities for various electrodes in  $H_2SO_4$  solution. B) Linear sweep voltammetry data for  $MoO_3/Ag_2O$  in  $H_2SO_4$  solution. The current density increases in subsequent cycles until the seventh cycle in which the current density reached a steady state. C) Partially enlarged details of B to obtain the needed overpotential. D) Current–potential plot for the glassy carbon substrate and immediately after the seventh cycle.

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Figure 6. Time dependence of the current density of the  $MoO_3/Ag$  catalyst under a static overpotential of 145 mV. The modified electrode was immersed in  $H_2SO_4$  solution and poised at the indicated potential for 7200 s.

region. This double layer charging current  $i_c$  is proportional to both the scan rate  $\nu$  and the electrochemically active surface area of the electrode  $A_{echem}$  [Eq. (1)]:<sup>[43]</sup>

$$i_{\rm c} \propto \nu \times A_{\rm echem}$$
 (1)

We measured the non-Faradic capacitive current associated with electrochemical double layer charging upon repeated potential cycling, and the results are shown in Figure 8A and B. The capacitive currents of the materials obtained before (Pre cycling) and after (Post cycling) the reductive conversion were measured as a function of scan rate (Figure 8C). The slope of the linear regression equation reflects the relative size of the electrochemically active surface area of the electrode to a certain extent. Therefore, a comparison of the slopes can roughly determine the size of the active areas of the electrodes. This method and theory were used to compare the active areas of GCE, MoO<sub>3</sub>, and Ag<sub>2</sub>O (Figure S4). The dependence of the cur-



Figure 7. The durability tests of A)  $MoO_3/Ag$  and B) Pt/C performed by conducting the cycling test repeatedly from the 1<sup>st</sup> to the 1000<sup>th</sup> cycle.

sesses excellent durability, which is significant for real applications. The durability of the MoO<sub>3</sub>/Ag catalyst was further investigated by conducting repeated cycling tests (Figure 7 A).

The intrinsic active site of a catalyst is an important metric to compare catalysts and to guide catalyst development. To estimate this key factor, electrochemical capacitance surface area measurement was used to determine the active surface area of the materials.<sup>[43]</sup> This technique enables independent estimation of the current density of electrochemically active sites. Although the analysis shown here utilizes known properties of the materials, which may not reflect the changed materials created during electrochemical testing perfectly, it provides useful insights for future improvements to the catalyst design. To find the electrochemically active surface area of these materials, we measured the non-Faradic capacitive current associated with electrochemical double layer charging upon repeated potential cycling. A potential range of 0.15-0.35 V versus the reversible hydrogen electrode (RHE) was selected for the capacitance measurements because no clear electrochemical features that correspond to the Faradic current were observed in this rent on the scan rate in this region is linear for all materials (Figure 8C), which is consistent with the capacitive charging behavior. MoO<sub>3</sub>/Ag obtained after the reductive conversion has a larger slope  $(1.7 \times 10^{-3})$  than the precursor MoO<sub>3</sub>/Ag<sub>2</sub>O (9.6× 10<sup>-4</sup>). A conclusion can be obtained from above results that the active area of MoO<sub>3</sub>/Ag catalyst is larger than that of MoO<sub>3</sub>/Ag<sub>2</sub>O.

Tafel analysis was performed on the Tafel polarization curves of operando-synthesized MoO<sub>3</sub>/ Ag (Figure 8D). The Tafel equation, which relates the current and overpotential for an electro-

catalytic reaction such as  $\mathsf{H}_2$  evolution, is shown in Equation (2):

$$\eta = a + b \times \log(i) \tag{2}$$

in which  $\eta$  is the overpotential, *i* is the catalytic current, *a* is the intercept, and *b* is the Tafel slope. A more complete version of this equation can be derived by simplification of the Butler–Volmer equation [Eq. (3)]:

$$\eta = -\frac{RT}{anF}\ln(i_0) + \frac{RT}{anF}\ln(i)$$
(3)

in which  $i_0$  is the exchange current, *i* is the current, *n* is the number of electrons involved in the electrode reaction,  $\alpha$  is the so-called cathodic charge transfer coefficient, *F* is the Faraday constant, *R* is the universal gas constant, and *T* is the absolute temperature. Tafel analysis has been used to distinguish different mechanistic pathways. In acidic solutions, H<sub>2</sub> evolution on a electrode surface mainly involves three reactions





**Figure 8.** Electrochemically active surface area measurements of the materials obtained A) before (pre cycling) and B) after (post cycling) the reductive conversion of the  $MoO_3/Ag_2O$  during the electrochemical experiments. C) Capacitive current measured at 0.25 V vs. RHE plotted as a function of scan rate. The ratios of the capacitive currents were used to determine the relative roughness factor. D) The Tafel plot of the  $MoO_3/Ag$  catalyst.

[Eqs. (4)–(6)].<sup>[44]</sup> The common first step is the Volmer step, which is the primary discharge step, followed by either combination or an ion+atom reaction to give H<sub>2</sub>. If Equation (4) is fast and followed by the Heyrovsky reaction, which is a slow ion+atom reaction, the Tafel slope is 40 mV dec<sup>-1</sup>. If we assume a low surface coverage of hydrogen, a fast discharge reaction followed by a rate-determining combination reaction results in a theoretical Tafel slope of 30 mV dec<sup>-1</sup>. If Equation (4) is rate-determining or the surface coverage is close to 1, the Tafel slope will be 120 mV dec<sup>-1</sup>.

Discharge reaction (Volmer step) [Eq. (4)]:

$$H_3O^+ + e^- \to H_{ad} + H_2O \ b = 120 \text{ mV}$$
 (4)

Ion+atom reaction (Heyrovsky step) [Eq. (5)]:

$$H_{ad} + H_3O^+ + e^- \rightarrow H_2 + H_2O \ b = 40 \text{ mV}$$
 (5)

Combination reaction (Tafel step) [Eq. (6)]:

$$H_{ad} + H_{ad} \to H_2 \ b = 30 \text{ mV}$$
(6)

Indeed, for many electrodes, Tafel slopes of  $\approx$  30, 40, or 120 mVdec<sup>-1</sup> have been observed. However, deviations from these values are also common. Many factors may be the ori-

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gins of such deviation, for example, the surface coverage of hydrogen might be intermediate and potential dependent, or the discharge reaction may have a significant activation barrier.[44,45] According to the Tafel slopes calculated from the plots shown in Figure 8D, we can estimate the rate-determining steps of our material. As the Tafel slope of the MoO<sub>3</sub>/Ag catalyst is 43 mV dec<sup>-1</sup>, the main HER mechanism on it is the Heyrovsky step. The Tafel slope of MoO<sub>3</sub>/Aq<sub>2</sub>O calculated from the plots shown in Figure S5 is 86 mV dec<sup>-1</sup>, which is between the Heyrovsky and Volmer step. The low HER overpotential and Tafel slope mean that there are adequate active sites for reaction. These parameters indicate that the MoO<sub>3</sub>/Ag catalyst is well designed for the HER reaction.

It is well known that Pt exhibits excellent electrocatalytic activity and nearly no overpotential for HER. Pt/C with different Pt contents also has an efficient electrochemical  $H_2$  evolution activity. In this work, Pt/C (Pt con-

tent 10%) was compared with MoO<sub>3</sub>/Ag to evaluate their durability for the HER, and their activity and durability were investigated. The linear sweep voltammograms of MoO<sub>3</sub>/Ag and Pt/C are shown in Figure 7 A and B, respectively. In the first cycle, compared with MoO<sub>3</sub>/Ag, Pt/C has a lower overpotential required to drive the HER at a benchmark current density of  $-10 \text{ mA cm}^{-2}$ ; however, the overpotential required to evolve H<sub>2</sub> at the benchmark rate increased progressively with subsequent voltammetric cycles. After 1000 cycles it increased to 370 mV, which is an increase of 240 mV compared with that required in the first cycle (130 mV). However, for the  $MoO_3/Ag$ catalyst, the overpotential required to drive the HER at a benchmark current density of -10 mA cm<sup>-2</sup> is almost constant (Figure 7 A). From the 1<sup>st</sup> to 1000<sup>th</sup> cycle, the overpotential changes slightly and provides a stable level of  $\approx$  145 mV. Compared with Pt/C, MoO<sub>3</sub>/Ag has a better durability under acid conditions. The operando-synthesized HER catalyst MoO<sub>3</sub>/Ag retained its activity throughout extended reductive potential cycling. Therefore, for practical applications under acid conditions, MoO<sub>3</sub>/Ag is more meaningful and useful than Pt/C as a material for H<sub>2</sub> evolution. To make a comparison with previous studies, the characteristics of different catalyst for the HER are summarized in Table 1. It can be seen that the proposed catalyst offered reasonable catalytic activity for H<sub>2</sub> evolution, which is higher than that of most of other catalysts. In particu-



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Table 1. Catalytic properties of catalysts for H <sub>2</sub> evolution.							
Catalyst	Synthetic method	Onset potential [mV vs. RHE] <sup>[a]</sup>	Overpotential [mV] <sup>[b]</sup>	Tafel slope [mV dec <sup>-1</sup> ] <sup>[c]</sup>	Ref.		
MoS <sub>2</sub>	hydrothermal method	54	200	100	[46]		
MoSe <sub>2</sub>	operando method	150	250	105	[47]		
MoSe <sub>2</sub> /graphene	hydrothermal method	50	175	69	[48]		
MoP	hydrothermal method	50	155	54	[49]		
Mo <sub>2</sub> C	solid-state reaction	120	210	63	[50]		
MoS <sub>2</sub>	chemical vapor deposition	100	220	73	[51]		
MoO <sub>3</sub> /Ag	operando method	48	145	43	This work		
[a] The onset potential for the HER. [b] The overpotential which is required to pass $-10 \text{ mA cm}^{-2}$ of current density. [c] The unit of the Tafel slope is mV dec <sup>-1</sup>							

lar, the Tafel slope has a low value. This comparison confirms that  $MoO_3/Ag$  is an appropriate catalyst for the HER.

### Conclusions

A highly active, stable, dendritic MoO<sub>3</sub>/Ag catalyst has been prepared through an operando synthesis method and it was tested with respect to its application in the hydrogen evolution reaction (HER). For crystalline MoO<sub>3</sub>, the facile vectorial electron transport along the axis contributes to the high current density, and the presence of Ag<sub>2</sub>O enhanced the crystallinity of MoO<sub>3</sub> to obtain the precursor MoO<sub>3</sub>/Ag<sub>2</sub>O, which shows a low catalytic activity for the HER. Further voltammetric cycling of the MoO<sub>3</sub>/Ag<sub>2</sub>O-modified electrode in the potential region at which the HER occurs led to a substantial increase in the catalytic activity. By the seventh cycle, the overpotential needed to drive a catalytic current of  $-10 \text{ mA/cm}^2$  had decreased from 275 to 145 mV. We performed extensive spectroscopic and electrochemical characterization to investigate the catalytic activity of this material and understand its properties for the HER. The operando-synthesized MoO<sub>3</sub>/Ag catalyst has a low Tafel slope (43 mV dec<sup>-1</sup>) and overpotential (145 mV) needed to drive a catalytic current of  $-10\;mA\,cm^{-2}$  and this material was found to retain its activity throughout extended reductive potential cycling. Compared with Pt/C, the durability of this material is better under acidic conditions. This highly active, perdurable material is a promising candidate that could help to enable the widespread deployment of cost-effective systems for electrochemical H<sub>2</sub> production.

### **Experimental Section**

The synthesis of MoO<sub>3</sub> was based on a simple and convenient hydrothermal technique. Ammonium heptamolybdate tetrahydrate (0.5 g) and cetyl trimethyl ammonium bromide (0.4 g) were dissolved in distilled water (20.0 mL). HNO<sub>3</sub> solution (7.5 mL, 3.0 m) was added,<sup>[29]</sup> and the mixture was transferred into a 100 mL Teflon-lined stainless-steel autoclave, which was heated at 180 °C for 20 h. The obtained precipitates were collected by filtration, washed with redistilled water and ethanol, and dried at 100 °C. To obtain MoO<sub>3</sub> with a good crystallinity to enhance the electrocatalytic activity for HER, MoO<sub>3</sub>/Ag<sub>2</sub>O was synthesized by linear sweep voltammetry (LSV). The linear sweep potential began at 0.2 V and

ended at 0.6 V vs. Pt with a scan rate of 10 mV s<sup>-1</sup> (Figure S6), and the electrolyte was 0.2 м AgNO<sub>3</sub> (0.2 м)/NH<sub>3</sub> (0.7 м) solution with a pH of 12 adjusted with NaOH.<sup>[52]</sup> The optimum number of scans in AgNO<sub>3</sub>/NH<sub>3</sub> solution is 4. To perform a control experiment, we also synthesized Aq<sub>2</sub>O. The synthesis process of Aq<sub>2</sub>O is similar to that of MoO<sub>3</sub>/Ag<sub>2</sub>O except the working electrode is bare GCE. The morphology of the material was investigated by SEM (J4800 Japan) and TEM (Tecnai G2 F30, FEI, USA). The phase structures of the samples were measured by XRD (Rigaku D/max-2400, Cu K radiation). The chemical composition and valence state were determined by XPS (ESCALAB250xi, X-ray monochromatization 200 W Spot/power: Mono 650 µm). The electrochemical experiments were performed by using an electrochemical cell with a three-electrode configuration and an electrochemical workstation (CHI660C, CHI, USA). Catalyst-modified GCE was used as the working electrode, and a Pt wire and saturated calomel electrode (SCE) served as the counter electrode and reference electrode, respectively. All tests were performed in 80 mL of 0.5 м H<sub>2</sub>SO<sub>4</sub> electrolyte.

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