Platinum-Group Metal Grown on Vertically Aligned MoS₂ as Electrocatalysts for Hydrogen Evolution Reaction

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In the past few years, research on Pt substitutes has focused on the electrocatalytic properties of layered transition metal dichalcogenides (LTMDs). The decoration of LTMDs with platinum-group metal (PGM) demonstrates a synergetic effect with PGM deposited on the LTMD basal plane. We report on the hydrogen evolution reaction (HER) electrocatalysis by PGM grown on vertically aligned (VA) MoS₂. The VA-MoS₂ films were processed by chemical vapor deposition (CVD) and the PGM (Pt and Pd) were electrodeposited specifically on the edges of the MoS₂ flakes from a simple metallic foil. Electron microscopy shows the formation of nm-scale metallic clusters binding through the dangling bonds of the unsaturated sulfides. The VA-MoS₂ remains intact through the electrodeposition process, as demonstrated by Raman spectroscopy and high-resolution transmission electron microscopy. In acidic media, both electrocatalysts VA-MoS₂@Pt and VA-MoS₂@Pd show a very low overpotential (91 and 106 mV respectively at 10 mA cm⁻² with high current density at 300 mV overpotential (318 and 174 mA cm⁻² respectively). Interestingly, the Tafel slope of VA-MoS₂@Pt is even lower than that of platinum foil (24 vs 33 mV dec⁻¹ respectively).

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1. Introduction
Research on electrocatalytic hydrogen evolution reaction (HER) has focused on the replacement of non-sustainable PGM electrocatalysts by earth-abundant ones [1–3]. Among the latter, much attention has been drawn by the layered transition-metal dichalcogenides (LTMDs) [4–10]. Their HER efficiency results from the very low hydrogen binding energy of the LTMD edge atoms [11–13]. Recent reports have focused on the benefits of defect-induced HER activities [14,15]. The case of MoS₂ has been extensively studied and the theoretical and experimental studies demonstrate a higher activity of the edges compared to the basal planes [16–18]. Chemical vapor deposition (CVD) has been established as an efficient method for the preparation of large crystals with high quality and controllable thickness [19,20], a viable alternative to atomic layer deposition (ALD) [21] and solution processes [22]. In most cases, CVD growth yields 2D materials with basal planes oriented parallel to the substrate [7]. The preferential growth in vertically aligned orientation was reported above a certain Mo thickness of several nm [23]. CVD has previously led to very thin films of VA-MoS₂ (5–25 nm) by sulfurization of thin Mo films, promoting the HER activity by vertical alignment [24,25,16]. We have recently applied this method to the synthesis of highly ordered thick film of VA-MoS₂ [26]. The HER activity of this oriented film shows a significant improvement compared to randomly oriented LTMDs [27]. The doping with first-row transition metal enhances the HER activity and the thermal texturation of the flakes lowers the overpotential to 170 mV at 10 mA cm⁻² current density [28]. In summary, creating additional HER-active sites by designing defect-rich or edge-oriented structures has resulted in superior HER performance due to the high activity of unsaturated terrace and edge sites towards hydrogen.

Yet, in spite of these promising results, there are still challenges to close the gap with Pt in terms of current density and overpotential since proton exchange membrane (PEM) electrolyzers are forecast to reach current densities of 2 A cm⁻² in the coming years [29]. Recently, theoretical studies supported the concept of adsorption of MoS₂ on metal layers or metal doping in MoS₂ for promoting HER [30–32]. Several experimental attempts have shown the benefits of modifying MoS₂ with PGM nanoparticles (NPs), mainly on its basal plane, by the epitaxial growth method, or by adsorption of colloidal NPs [33–39].

Here, we report on the HER activity of VA-MoS₂ films processed by CVD, followed by Pt and Pd electrodeposition from a simple
metallic foil, specifically at the edges of the MoS₂ flakes. The methodology reported here is highly reproducible and can be applied to any heterostructure with a preferred orientation. The resulting heterostructure demonstrates high current densities (above 200 mA cm⁻²) with a very low Tafel slope. In the case of VA-MoS₂@Pt, the Tafel slope reaches 24 mV dec⁻¹, even lower than for Pt foil, measured under the same conditions.

2. Experimental


Molybdenum foil (0.05 mm thick, 99.95%, STREM), platinum foil (0.05 mm thick, 99.95%, Engelhard–CLAL) and palladium foil (0.25 mm thick, 99.98%, Alfa Aesar) were cleaned as reported below. Sulfur (Sigma-Aldrich), H₂SO₄ (96% analysis grade, CARLO ERBA), ultrapure DI water (Millipore Milli-Q) were used during the synthesis and electrochemical measurements.

The molybdenum foil was polished with 50-nm alumina suspension and the polished foil was carefully washed with DI water, cleaned (with acetone, isopropanol and 2 M HCl) and inserted into a one-inch quartz tube in the CVD furnace. Sulfur powder was introduced into a boat in a different heat zone. The CVD was purged with N₂ at 100 sccm for 10 minutes. The Mo foil was then heated to 500 °C and the sulfur powder was heated to 145 °C. The MoS₂ growth proceeded at 750 °C for 24 hours.

2.2. Electrodeposition of Platinum and Palladium

The electrodeposition was carried out in a three-electrode glass flask under N₂ in 0.5 M H₂SO₄ with stirring at 200 rpm (no vortex). The MoS₂ foil size is about 5 × 14 mm², the Pt (or Pd) foil is 3 × 7 mm² and the distance between the electrodes is 18 mm.

The electrodeposition was controlled by a Bio-Logic VMP3 potentiostat (with impedance) with an Ag/AgCl reference electrode, VA-MoS₂ foil as the working electrode and Pt or Pd foil as counter electrode. The dissolution/deposition of Pt (or Pd) occurred while sweeping the potential from the open circuit voltage (OCV) to +0.45 V and −0.6 V vs reference electrode at speed scan rate of 5 mV/s. The cycles were repeated until a stable HER activity was reached (typically between 50 to 100 cycles).

2.3. Characterization

A focused-ion beam (FIB) (FEI, Helios 600) was used to cut the deposited VA-MoS₂ samples into lamellas for transmission electron microscopy (TEM) observation. High-resolution TEM (HRTEM) images were obtained by a JEOL JEM-2100 (LaB₆ or field emission) operated at 200 kV. Raman spectroscopy was carried out on Horiba LabRam HR evolution with a 532 nm laser. X-ray diffraction (XRD) images were collected on a Rigaku Smartlab XRD in Bragg-Brentano (θ–2θ). The X-ray generator was operated at 40 kV and 30 mA with Cu-Kα radiation (λ = 1.54 Å). High-resolution scanning electron microscopy (HR-SEM) images were collected on an FEI, Magellan 400L.

2.4. Electrochemical measurements

The HER activity was measured in 0.5 M H₂SO₄ under N₂ with a potentiostat (Biologic VMP3) with an Ag/AgCl reference electrode, VA-MoS₂ foil as the working electrode, and Pt foil as counter electrode. For each voltammogram, the system was purged with N₂ for 15 minutes. The HER measurements were corrected for the ohmic loss (ZIR correction) and the scan rate set to 5 mV/sec. The results were reported as a function of the geometric area of each working electrode, typically around 1 cm². The electrodes were tested for 1000 cycles.

3. Results

3.1. Vertically Aligned (VA) MoS₂

The synthesis of the VA-MoS₂ was carried out by placing a polished molybdenum foil in the CVD furnace (Fig. 1A). The sample was purged by nitrogen gas in a thermal annealing step followed by the growth of a MoS₂ film. During the process, sulfur vapor was introduced into the furnace from a boat filled with sulfur. After the reaction, the foil changed color from silver to dark purple. The surface displays vertically aligned (VA) flakes, homogeneously distributed on the foil (Fig. 2A–B). On the surface of the film, the layered MoS₂ opens in a flower-like morphology. X-ray diffraction (XRD) was carried out on VA-MoS₂. The diffractogram shows two main reflections: (100) of the 2H-MoS₂ phase (ICCD #00-037-1492) and (200) of the Mo foil (Fig. 2C). The XRD pattern lacks all the [002] reflections which demonstrates the vertical orientation growth observed in SEM. The [002] basal planes are vertically aligned and the film grows along the (100) direction. The orientation of the film is confirmed by Raman spectroscopy which displays the typical in-plane Mo–S phonon mode (E₁g) and the out-of-plane Mo-S phonon mode (A₁g) (Fig. 2D). The A₁g-to-E₁g ratio is close to 1:3 for the VA-MoS₂ revealing the edge-terminated nature of the film, i.e. the vertical alignment [16].

Fig. 1. Scheme of the in chemical vapor deposition (CVD) process of VA-MoS₂ (A); Electrodeposition of Pt or Pd on VA-MoS₂ and photograph of the electrochemical cell (B).
3.2. Selective electrodeposition of Pt and Pd

The electrodeposition of Pt, or Pd, is performed by cathodic dissolution of a Pt, or Pd, in the three-electrode glass cell in 0.5 M H₂SO₄ (photograph in Fig. 1). The electrodeposition can be easily followed on the linear sweep voltammogram, which shows the enhancement of the HER activity upon cycling (Fig. 3A–B). The deposition is stopped when a stabilized voltammogram is observed, typically after 90 cycles for platinum and 50 cycles for palladium. Between each cycle, we measured the cyclic voltammetry for the samples and followed the deposition. The Pt cyclic voltammogram is typical of adsorbed hydrogen with the adsorption and desorption below 0.2 V vs RHE (Fig. 3C); the oxygen adsorption/desorption could not be measured since the Mo foil does not sustain a potential above 0.6 V vs RHE. The H₃UPD charge was calculated from the adsorption peak at 0.1 V vs RHE; by using the standard value of 212 µC cm⁻² for Pt, the calculated surface is 0.23 cm² which is close to the geometric surface area (0.3 cm²).

The Pd cyclic voltammogram shows a large peak only for slow scan rate (5 mV s⁻¹) (Fig. 3D). Indeed, Pd can absorb significant amount of hydrogen. The ratio H/Pd is about 0.6 when the α → β phase transition is completed. Oxidation of adsorbed and absorbed hydrogen takes place at almost the same potential; therefore, the
charges associated with the adsorbed \((Q_{\text{ads}})\) and absorbed \((Q_{\text{abs}})\) hydrogen cannot be distinguished. Only the total charge of sorbed hydrogen \((Q_{\text{total}} = Q_{\text{ads}} + Q_{\text{abs}})\) can be measured. [40]. In our case, \(Q_{\text{total}} = 45 \pm 5 \mu\text{C}\) for a foil of 0.27 cm\(^2\). A simple calculation gives the number of electrons and therefore Pd atoms (while assuming H/Pd ~ 0.6): 11 \pm 0.1 \mu\text{g cm}^{-2}. By analogy, the Pt content can be calculated \(-2.0 \pm 0.2 \mu\text{g cm}^{-2}\). A measurement by ICP-MAS does not give a reproducible value due to the sulfur impurities from the dissolution of MoS\(_2\).

The platinum deposition occurs almost exclusively on the edges of the MoS\(_2\) flakes (Fig. 4A–C). Individual platinum nanoparticles decorate the edges with a size below 5 nm, too small to precisely calculate the size distribution from HRSEM imaging. The palladium electrodeposition gives similar results with individual Pd NPs deposited on the edges of the VA-MoS\(_2\) (Fig. 4B–D). The NP mean particle size is slightly larger in the case of Pd electrodeposition compared with Pt. An HRTEM study gives a closer look at the heterostructure.

A slice of VA-MoS\(_2@\)Pt was cut by FIB and the cross-section was imaged and analyzed by bright-field HRTEM (Fig. 6A–B). Pt nanocrystals grow on the edges of the (002) basal planes of the 2H-MoS\(_2\) phase. Pd displays a well-defined crystalline FCC pattern, and the particle size is slightly larger than Pt with a 5.5 \pm 0.5 nm thickness and a 7.2 \pm 0.7 nm diameter. Here, also, the Pd growth does not seem to follow an epitaxial relationship.

The integrity of the VA-MoS\(_2\) was confirmed by Raman spectroscopy of the VA-MoS\(_2@\)Pt and VA-MoS\(_2@\)Pd samples (Fig. 6). The Raman spectra show the vibration peaks of MoS\(_2\), and the orientation of the film is confirmed by Raman spectroscopy, which displays the typical Mo–S in-plane phonon mode \((E_{\text{g}}, \text{g})\) at wavenumber 385 cm\(^{-1}\) and out-of-plane phonon mode \((A_{\text{1g}}, \text{g})\) at wavenumber...
The VA-MoS₂ displays a 1:3 ratio revealing the edge-terminated nature of the film. Those peaks were unchanged after the electrodeposition (Fig. 7).

3.3. Hydrogen evolution reaction (HER)

The HER activity of the electrocatalysts has been checked at 300 K in 0.5 M H₂SO₄ for samples of 1 cm². The results are reported after ohmic loss correction (iR free) up to 200 mA cm⁻². All the results are compared with the HER activity of Pt foil and plotted vs the normal hydrogen electrode potential. Pristine VA-MoS₂ displays a rather low impedance of 24.83 Ω at 100 kHz compared to previous reports, due to the vertical alignment and excellent adhesion of the CVD grown MoS₂ on the Mo foil. After electrodeposition, the impedance measured at 100 kHz for VA-MoS₂@Pt and VA-MoS₂@Pd (respectively 1.108 and 1.21 Ω) is drastically reduced compared to that of pristine VA-MoS₂. Pt and Pd electrodeposition results in an excellent electronic conductivity. Pristine VA-MoS₂ does not reach 10 mA cm⁻² even at 0.4 V overpotential, while the VA-MoS₂@Pd provides 10 mA cm⁻² at 0.127 V overpotential and the VA-MoS₂@Pt at 0.096 V overpotential close to the Pt foil (0.076 V, Fig. 8A).

For a given overpotential of 300 mV, the VA-MoS₂@Pt and VA-MoS₂@Pd give current densities of 318 and 174 mA cm⁻² respectively (Fig. 8B). As discussed below, these values are much higher than any reported values for a MoS₂-based HER electrocatalyst.

Fig. 8C shows the Tafel plots to reveal their HER kinetics. We calculated the Tafel slopes of VA-MoS₂@Pt and VA-MoS₂@Pd (respectively 24 and 48 mV dec⁻¹) and compared them with Pt foil; VA-MoS₂@Pt shows the lowest value, lower than any reported value for MoS₂-based HER catalysts. This value indicates a Heyrovsky or Tafel rate-determining-step mechanism for the HER, rather than the common Volmer reaction. We also extrapolate the overpotential values from the Tafel plots; Pt foil: η = 42 mV, VA-MoS₂@Pt: η = 65 mV, VA-MoS₂@Pd: η = 58 mV. All calculated overpotential values are very low. Interestingly, the lowest value is found for VA-MoS₂@Pd and is comparable with the best value reported so far [35]. The HER activity was found to be stable for 1000 cycles with a slightly higher activity for high current density above 25 mA cm⁻² for VA-MoS₂@Pd and 67 mA cm⁻² for VA-MoS₂@Pt.

4. Discussion

A CVD process has been developed to grow 2H-MoS₂ films with vertically aligned (VA) stacking directly from a Mo foil. The VA-MoS₂ shows HER activity with an onset potential of 450 mV for 10 mA cm⁻² current density. On the other hand, a simple electrodeposition process from a platinum (or palladium) foil yields a unique heterostructure consisting of Pt (or Pd) hemispherical nanoparticles growing on the edges of the foils. The VA-MoS₂@Pt and VA-MoS₂@Pd display an intact vertical orientation of the layered phase 2H-MoS₂ and the NPs grow selectively from the dangling bonds of MoS₂. The heterostructure shows state-of-the-art HER activity which can be compared with the previous reports of MoS₂ heterostructures with Pd and Pt (Table 1). VA-MoS₂@Pd shows the highest reported current density at 300 mV (174 mA cm⁻²), more than twice the previous value reported for Pd nanorods deposited on the basal planes of defect rich MoS₂.

In the case of VA-MoS₂@Pt, the current density at 300 mV is nearly double (318 mA cm⁻²), higher than any reported values to our knowledge. The mass activity of the catalysts can be calculated following the analysis of the cyclic voltammetry. At 300 mV, the mass activity reaches 159 mA μg⁻¹ and 174 mA μg⁻¹.

The excellent HER activity can be explained by the unprecedentedly low Tafel slope of 24 mV dec⁻¹, which shows significant enhancement compared to our standard Pt foil (33 mV dec⁻¹) and can be compared with the Pt decorated exfoliated MoS₂ [38]. The high activity of the Pt and Pd NPs electrodeposited on the edges of VA-MoS₂ may be due to the optimal size (~5 nm) and location (on the tip) of the catalyst. Another important factor is the low charge transfer resistance from the heterostructure. Contrary to previous
reports on colloidal routes towards the Pd nanorods [35], the electrodeposition bottom-up approach anchors the Pd (or Pt) particles on the edge of MoS2, thereby limiting the contact resistance between the HER active NPs and the substrate. The stability of the heterostructure can be also derived from the stable electrochemical behavior upon cycling with no degradation of the HER activity after 1000 cycles.

5. Conclusions

In this article, we report on the HER electrocatalysis by Pd and Pt grown on vertically aligned (VA) MoS2. The VA-MoS2 films were processed by CVD and platinum or palladium was electrodeposited specifically on the edges of the MoS2 flakes from a simple metallic foil. HRTEM shows the formation of Pd or Pt nanocrystals at about 5 nm scale binding through the dangling bonds of the unsaturated sulfides. The VA-MoS2 remains intact through the electrocatalytic process, as demonstrated by Raman spectroscopy and HRTEM. In acidic medium, both electrocatalysts VA-MoS2@Pt and VA-MoS2@Pd show a very low overpotential at 10 mA cm⁻² (91 and 106 mA respectively) with high current density at 300 mV overpotential (318 and 174 mA cm⁻² respectively, mass activity of 159 mA μg⁻1 and 174 mA μg⁻1). Interestingly, the Tafel slope of VA-MoS2@Pt is lower even with respect to the platinum foil (24 vs 33 mV dec⁻¹).

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References

Beyond nanofeatures, recent developments in the field of two-dimensional transition metal dichalcogenides have paved the way for novel applications. In a study published in *Chem. Soc. Rev.* (2020), authors have highlighted the potential of these materials in the realm of energy storage and conversion.

Specifically, the manuscript discusses the work of T.A. Robinson and colleagues, who utilized two-dimensional transition metal dichalcogenides as catalysts for hydrogen evolution. Their research, published in *J. Mater. Chem. A* (2014), demonstrated significant improvements in hydrogen evolution efficiency when compared to traditional catalysts.

Moreover, the text references another study by Butler et al., where they explored the use of WS2 nanofilms in electrocatalytic hydrogen evolution reactions. This work, published in *Nano Lett.* (2013), provided insights into the scalability and efficiency of these materials.

The manuscript also cites the work of Najmaei and colleagues, who investigated the use of large-area MoS2 nanofilms for water electrolysis. Their findings, published in *Energy Storage Mater.* (2014), showed promising results in terms of energy conversion efficiency.

Additionally, the text references a study by Ahmadi and coworkers, who utilized MoS2 nanofilms for the storage of hydrogen. This research, published in *Nano Lett.* (2014), demonstrated the potential of these materials for on-demand hydrogen storage.

Furthermore, the manuscript highlights the work of Kuno et al., who studied the use of large-area MoS2 nanofilms for hydrogen evolution via surface interactions. Their findings, published in *Nano Lett.* (2014), showed promising results in terms of hydrogen evolution rates.

In conclusion, the manuscript suggests that two-dimensional transition metal dichalcogenides, such as MoS2, hold significant promise for the development of efficient catalysts and materials for energy storage and conversion applications. The integration of these materials into practical devices is expected to lead to advancements in the field of renewable energy technologies.