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Highly Active Hydrogen Evolution Catalysis from Metallic WS$_2$ Nanosheets

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We report metallic WS$_2$ nanosheets that display excellent catalytic activity for the HER that is the best reported for MX$_2$ materials. They are chemically exfoliated from WS$_2$ nanostructures synthesized by chemical vapour deposition, including by using a simple and fast microwave-assisted intercalation method. Structural and electrochemical studies confirm that the simultaneous conversion and exfoliation of semiconducting 2H-WS$_2$ into nanosheets of its metallic 1T polymorph result in facile electrode kinetics, excellent electrical transport, and proliferation of catalytic active sites.

Broader context

The scalable and sustainable production of hydrogen fuel through water splitting demands efficient and robust earth-abundant electrocatalysts for the hydrogen evolution reaction (HER). Layered chalcogenide materials, such as MoS$_2$ and WSe$_2$, are promising earth-abundant alternative electrocatalysts to noble metals for hydrogen evolution reaction (HER), but their catalytic performance still needs to be improved. Here we develop metallic WS$_2$ nanosheets that show extraordinary catalytic activity for the HER via facile chemical exfoliation from WS$_2$ nanostructures synthesized by chemical vapour deposition, including by using a simple and fast microwave-assisted intercalation reaction method. The structural and chemical changes that take place during the exfoliation of the WS$_2$ nanosheets explain their excellent attributes and result in high electrocatalytic current density at low catalytic overpotential, which is the best HER performance reported for MX$_2$ catalysts.

Our strategy begins with the chemical vapour deposition (CVD) synthesis of flower-like WS$_2$ nanostructures with a high density of exposed edges. Similar to our previously reported CVD method for producing MoS$_2$ nanostructures, the mild synthesis conditions around 550 °C (see SI for experimental details) make the deposition of WS$_2$ nanosheets still lags behinds that of the MoS$_2$ analog. Here we develop metallic WS$_2$ nanosheets that display extraordinary catalytic activity for the HER via facile preparation methods, including by using a simple and short microwave-assisted intercalation reaction. These solution processable exfoliated catalysts that can be dropcasted onto any inert conducting substrates are capable of achieving an electrocatalytic current density of 10 mA/cm$^2$ at the low potential of $-142$ mV vs. RHE, which is the best HER performance reported for MX$_2$ catalysts.
of WS₂ possible on many different substrates, including graphite, tungsten foil, and fluorine-doped tin oxide/glass. Moreover, these WS₂ nanostructures with a thickness of about 10 layers are dominated by well-defined crystalline edges, thus increasing the density of active sites (Fig. 1b). Lattice resolved high-resolution transmission electron microscopy (HRTEM) show highly crystalline multilayered platelets (Fig. 1c) that, importantly, do not form closed fullere-like structures (Fig. 1d). The corresponding selected-area electron diffraction (SAED) pattern is unequivocally indexed to 2H-fullerene-like structures (Fig. 1d). The corresponding selected-area multilayered platelets (Fig. 1c) that, importantly, do not form closed transmission electron microscopy (HRTEM) show highly crystalline density of active sites (Fig. 1b). Lattice resolved high-resolution dominated by well-defined crystalline edges, thus increasing the exfoliated upon reaction with excess water, which generates H₂ and prismatic 2H structure, causing a transition to the octahedral 1T structural polymorphs in WS₂ materials. Lithium intercalation of WS₂ is known to be more difficult for WS₂ than MoS₂. We further added to bisect the W₄f₅/₂, W₄f₇/₂, and WS₅p₃/₂ peaks in the 2H-WS₂ spectrum in Fig. 2a and the three peaks present in the 2H-WS₂ S₂p spectrum in Fig. 2b. The 1T-WS₂ sample displays the presence of new chemical species clearly shifted toward lower binding energies after chemical exfoliation in both the W₄f and S₂p regions. These results are consistent with the known metallic nature of 1T-WS₂ and similar to past XPS studies on 1T-MX₂ materials. The small shoulder at ~35 eV corresponding to a W₄f₇/₂ species (Fig. 4a) confirms that the exfoliated 1T-WS₂ nanosheets are more susceptible to oxidation. In general, WS₂ samples appear to be more susceptible to oxidation than MoS₂ and there were minor variations in the degree of oxidation from sample to sample, depending on how well the reaction vessels were sealed during the exfoliation. The underlying Au substrate was used to manually align all XP spectra and the Cls data from the adventitious carbon for each sample were compared to rule out charging effects (see more details in SI and Fig.

We focus the structural characterization discussions on such drop-casted WS₂ nanosheets. SEM shows a uniform drop-casted film composed of many smaller sheets and particles covering a graphite disk (Fig. 1f). HRTEM (Fig. 1g) shows the more disordered structure of exfoliated nanosheets and confirms they are still open structures (Fig. 1b). The superlattice structure observed in the SAED pattern (red circles in Fig. 1i) is consistent with past reports of chemically exfoliated WS₂ and suggests the product may be a mixture of 1T- and 2H-WS₂.

We further characterized the 1T-WS₂ nanosheets to highlight their differences from the as grown 2H-WS₂ nanostructures using X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), current-sensing atomic force microscopy (CSAFM), Raman spectroscopy, and PXRD. Fig. 2a and 2b show high-resolution XP spectra of the W₄f (Fig. 2a) and S₂p (Fig. 2b) regions, respectively. As a visual aid, black dotted lines have been added to bisect the W₄f₅/₂, W₄f₇/₂, and WS₅p₃/₂ peaks in the 2H-WS₂ spectrum in Fig. 2a and the three peaks present in the 2H-WS₂ S₄p spectrum in Fig. 2b. The 1T-WS₂ sample displays the presence of new chemical species clearly shifted toward lower binding energies after chemical exfoliation in both the W₄f and S₂p regions. These results are consistent with the known metallic nature of 1T-WS₂ and similar to past XPS studies on 1T-MX₂ materials. The small shoulder at ~35 eV corresponding to a W₄f₇/₂ species (Fig. 4a) confirms that the exfoliated 1T-WS₂ nanosheets are more susceptible to oxidation. In general, WS₂ samples appear to be more susceptible to oxidation than MoS₂ and there were minor variations in the degree of oxidation from sample to sample, depending on how well the reaction vessels were sealed during the exfoliation. The underlying Au substrate was used to manually align all XP spectra and the Cls data from the adventitious carbon for each sample were compared to rule out charging effects (see more details in SI and Fig.

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difficult intercalation reaction and the propensity of exfoliated WS2 nanosheets to restack into their thermodynamically favoured 2H phase,12b, 12c it is likely that both the 1T and 2H polymorphs coexist in these exfoliated samples. PXRD supports this hypothesis, showing weakened reflections corresponding to the 2H polymorph (Fig. S1).

We demonstrate that the metallic WS2 nanosheets produced by our chemical exfoliation treatment exhibit extraordinary catalytic activity for the HER. We dropcasted the exfoliated 1T-WS2 nanosheets (a total volume of 6 µL suspension) onto graphite disks and evaluated their catalytic activity in 0.5 M H2SO4 using a standard rotating disk electrode (RDE) apparatus in a three-electrode electrochemical measurement (see experimental details in the SI). The total mass of the deposited 1T-WS2 nanosheets is quite small and using quartz crystal microbalance measurements we estimated that the amount of the WS2 nanosheets loading to be 1.0±0.2 mg/cm2 (see ESI for more details). Polarization curves (Fig. 3a) of the electrocatalytic current density (j) plotted against potential vs. the reversible hydrogen electrode (RHE) show the HER activity of 1T-WS2 nanosheets obtained from both oven and microwave-assisted intercalation methods compared to the as-grown WS2 nanostructures. As-grown WS2 on graphite exhibits an onset of HER activity at approximately ‒200 mV vs. RHE and significant hydrogen evolution (j = 10 mA/cm²) is not reached until ‒330 mV vs. RHE. Dropcasted 1T-WS2 nanosheets that have been exfoliated after lithium intercalation at 80 °C for 48 h in an oven show dramatically improved HER activity, where the onset of catalytic activity has been shifted to significantly lower voltages of about ‒75 mV vs. RHE. After correcting for iR losses, these 1T-WS2 nanosheets achieve an electrocatalytic current density of 10 mA/cm² at an unprecedented low overpotential of ‒142 mV vs. RHE (purple trace). This exceptional catalytic activity is further highlighted in Fig. 3a by comparing the 1T-WS2 nanosheets against other recently reported high performing HER Mox catalysts of various morphologies and chemistry.2, 6, 15 Interestingly, unlike MoS2, WS2 in its original semiconducting form is not well known as a good HER catalyst, but the best catalytic performance is achieved for the metallic WS2 nanosheets here. The 1T-WS2 nanosheets here are also significantly improved from both the previously reported 1T-WS2 nanosheets exfoliated from commercial powders (green trace)6c and the 1T-MoS2 nanosheets previously reported by us (cyan trace)6b and others (light green trace).6b amorphous MoS2 catalysts,15a and even shows better performance than a nanocomposite of MoS2 nanoparticles with reduced graphene oxide (RGO).15b Furthermore, this overpotential required to achieve j = 10 mA/cm² is very competitive among the recently reported non-noble metal catalysts, perhaps only less than that achieved by Ni3P nanoparticles.1e

![Fig. 2](image-url)  
**Fig. 2** Comparison of the as-grown 2H- and exfoliated 1T-WS2 nanosheets. High resolution XP spectra of the (a) W4f and (b) S2p regions, showing a new chemical species exhibiting a clear shift to lower binding energies after chemical exfoliation. (c) Overall UP spectra and (d) zoom-in of the low binding energy edge of the UP spectra showing the valence band maxima with respect to the Fermi Level. (e-h) CSAFM micrographs and corresponding conductivity maps for the as-grown (e, g) and exfoliated (f, h) WS2 nanosheets. All images are 2 µm by 2 µm and the conductivity maps were taken at a +20 mV bias. (i) Current–voltage curves on individual nanostructures, further contrasting the differences in conductivity.
The enhanced HER activity is further illustrated by comparing the Tafel slopes (Fig. 3b) of the 1T-WS₂ nanosheets (70 mV/decade after iR correction) with both oven and microwave intercalation) with the as-grown 2H-WS₂ nanostructures (85 mV after iR correction). The earlier onset of catalytic activity and lower Tafel slope suggest the free energy of hydrogen binding to 1T-WS₂ is closer to equilibrium. Additionally, we used electrochemical impedance spectroscopy (EIS) to investigate the electrode kinetics under the catalytic HER operating conditions. Nyquist plots (Fig. 3c) and data fittings to a simplified Randles circuit reveal dramatically reduced charge-transfer resistances ($R_\text{ct}$) for the exfoliated metallic WS₂ nanosheets (6 Ω for the oven intercalation; 5 Ω for the microwave intercalation) in contrast to the as-grown 2H-WS₂ nanostructures (200 Ω). Moreover, the small series resistances observed for all samples illustrate that the simple drop-casting method allows high-quality electrical integration of the metallic catalyst with the conductive support. The EIS data confirm that 1T-WS₂ nanosheets are highly active catalysts that exhibit facile kinetics toward hydrogen evolution.

We also estimated the relative differences in electrochemically active surface area before and after chemical exfoliation using a simple cyclic voltammetry (CV) method. Current response in the potential window used for the CV (0.1–0.2 V vs. RHE) at different scan rates (20 – 180 mV/s) should be due only to the charging of the double-layer (Fig. 3d, 3e). The double-layer capacitances ($C_\text{dl}$) for both samples, which should be directly proportional to the surface area, are extracted by plotting the $\Delta V = j_a - j_c$ at a given potential (0.15 V vs. RHE) against the CV scan rates (Fig. 3f). The proliferation of active sites due to chemical exfoliation is illustrated by the more than an order-of-magnitude increase (a factor of 18) in $C_\text{dl}$ for the 1T-WS₂ nanosheets (48 mF/cm²) as compared to the as-grown 2H-WS₂ nanostructures (2.7 mF/cm²). While this increase in electrochemically active surface area demonstrates the proliferation of the active sites, which certainly contributes to the improved catalytic performance, the more than two-order-of-magnitude increase in catalytic activity as seen in Fig. 3a and 3b far exceeds the increase of surface area. The dramatic shift in onset potential and the reduction in Tafel slope suggest that the phase transition to the metallic 1T-polymorph is more important to enhancing the catalytic activity. This is consistent with recent results showing exfoliated semiconducting 2H-MoS₂ nanosheets exhibited only marginally improved activity, suggesting that the number of edge sites is not the only important factor behind improving the catalytic performance of MX₂ materials but the chemical nature of the MX₂ nanostructures plays a more important role in enhancing the HER catalysis, in other words, the metallic 1T nanosheets are intrinsically more catalytically active than the original semiconductor 2H-MX₂ nanostructures.

Note that superior HER catalytic performance has been achieved here compared with the metallic WS₂ nanosheets chemically exfoliated from commercial WS₂ powders. To better understand this, we carried out side-by-side exfoliation reactions starting from both CVD synthesized WS₂ nanostructures and the commercial bulk WS₂ powder. Even though both were exposed to identical microwave-assisted intercalation conditions, the nanosheets exfoliated from CVD grown WS₂ nanostructures show superior catalytic performance than the nanosheets obtained from the bulk powder (Fig. S6). This is likely first due to incomplete lithium intercalation, conversion, and exfoliation of the bulk WS₂ powder, which has larger particle sizes (< 2 μm) and irregular morphologies. Indeed, Raman, PXRD, and SEM data (Fig. S6d-g) show only small
differences in the n-butyl lithium treated commercial WS 2 powder. Furthermore, even if much longer and harsher intercalation reactions (100 °C for 2 days) were performed on the bulk WS 2 powder to result in more complete intercalation as confirmed by SEM and Raman, the catalytic performance of the exfoliated 1T-WS 2 nanosheets originated from bulk power is still inferior to that of the CVD synthesized nanosheets (Fig. S7). This suggests that the few-layer nanostructures with well defined crystalline edges enabled by our CVD synthesis promote better catalytic performance.

Finally, we monitored the catalytic performance of the metastable 1T-WS 2 nanosheets under continuous operation. Even after 500 continuous cycles or nearly 4 h of sustained hydrogen evolution at j = 10 mA/cm 2, the catalytic performance of the chemically exfoliated nanosheets remains superior to the as-grown WS 2 nanostuctures (Fig. S8). The slow decline in catalytic activity is likely due to the potential loss of the dropcasted material from the surface of the graphite electrode and due to the slow reconversion to thermodynamically favored 2H-WS 2. To address the latter, the metastable 1T-WS 2 may be further stabilized using various methods, such as tuning the electronic structure via doping. 19

Conclusions
We have developed methods to significantly enhance the electrocatalytic activity of WS 2 for the HER by controlling its nanostructures and structural polymorphs. Moreover, we demonstrated that microwave-assisted reaction can be used to significantly speed up the intercalation and exfoliation treatment and the exfoliated metallic WS 2 nanosheets can be harvested and drop-cast while still achieving high performance. These facile procedures to chemically exfoliated 1T-WS 2 nanosheets result in favourable kinetics, metallic conductivity, and active site proliferation, which enable the best HER catalytic activity among any MX 2 materials. These results confirm that exfoliation and polymorph control is generally applicable for enhancing the catalytic and other applications of the family of MX 2 materials.

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Notes and references
Metallic WS$_2$ nanosheets chemically exfoliated from chemical vapour deposited WS$_2$ nanostructures display excellent catalytic activity for the hydrogen evolution reaction.