



Ultrathin WS₂ Nanoflakes as a High-Performance Electrocatalyst for the Hydrogen Evolution Reaction**

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Abstract: Much has been done to search for highly efficient and inexpensive electrocatalysts for the hydrogen evolution reaction (HER), which is critical to a range of electrochemical and photoelectrochemical processes. A new, high-temperature solution-phase method for the synthesis of ultrathin WS₂ nanoflakes is now reported. The resulting product possesses monolayer thickness with dimensions in the nanometer range and abundant edges. These favorable structural features render the WS₂ nanoflakes highly active and durable catalysts for the HER in acids. The catalyst exhibits a small HER overpotential of approximately 100 mV and a Tafel slope of 48 mV/decade. These ultrathin WS₂ nanoflakes represent an attractive alternative to the precious platinum benchmark catalyst and rival MoS₂ materials that have recently been heavily scrutinized for the electrocatalytic HER.

Hydrogen is frequently advocated as the alternative energy carrier of the future by virtue of its high energy density and zero environmental impact of the combustion product.^[1,2] Its sustainable production from the splitting of water molecules driven by renewable solar energy has attracted tremendous attention because of its potential impact on the way of energy generation.^[2–4] To achieve the best efficiency, this key process usually demands the assistance of high-performance hydrogen evolution reaction (HER) electrocatalysts.^[4] Although precious platinum group metals, such as platinum and

palladium, have traditionally been the most efficient catalysts for the HER, the search for active alternatives that are abundant on earth has been actively pursued, and some encouraging progress has been made.^[4]

A large amount of current research is devoted to layered MoS₂ structures because of their appealing electrocatalytic properties for the HER.^[5–12] It has been proposed and experimentally corroborated that the active sites are situated in sulfided Mo edges.^[5,6] Through proper compositional and structural engineering, this compound is able to catalyze hydrogen generation at small overpotentials of approximately 100 mV with remarkable durability in acidic medium.^[8] WS₂ has an analogous structure to MoS₂, and these compounds share a set of physical and chemical properties. WS₂ was also found to be HER active more than 20 years ago.^[13,14] However, there have only been a few scattered studies focusing on WS₂ based HER electrocatalysts to date.^[7,15–19] Their electrocatalytic performance is also far from satisfactory with typical overpotentials of over 150 mV. Very recently, lithium intercalation followed by forced hydration was found to exfoliate bulk WS₂ into metastable tetragonal monolayered sheets (1T-WS₂).^[16] Individually, these sheets exhibited excellent HER activity,^[16] whereas collectively they displayed a strong propensity towards restacking and an irreversible phase transition to hexagonal 2H-WS₂,^[2,21] which led to a significant deterioration of the electrochemical performance.^[18] It was suggested that decorating WS₂ monolayers with nanoparticles could help alleviate the restacking problem, but the improvement was very limited.^[18] It stays elusive whether or not WS₂ can be on par with or even surpass the HER activity of MoS₂ for practical applications. Herein, we describe an effective high-temperature solution-phase method for the synthesis of WS₂ nanoflakes with monolayer thickness, dimensions in the nanometer range, and abundant edges. The product was shown to be a highly active and durable HER catalyst in acids, matching the activity of MoS₂.

The synthesis started with dissolving and heating a WCl₆ precursor in a mixed solvent of oleylamine (OM) and 1-octadecene under N₂ atmosphere (Figure 1). Elemental sulfur dissolved in OM was injected into the resulting solution at 300 °C (see the Experimental Section). OM has a high boiling point of over 360 °C, and elemental sulfur displays a considerable solubility in this medium.^[22] Together, these properties make OM an ideal solvent for the high-temperature solution-phase synthesis of sulfide nanocrystals.^[23,24] During the course of the reaction, the tungsten precursor solution first gradually turned blue (Supporting Information Figure S1), probably because of the reaction between WCl₆ and OM, which gives rise to a tungsten–oleylamine (W–OM) complex.^[23] Upon

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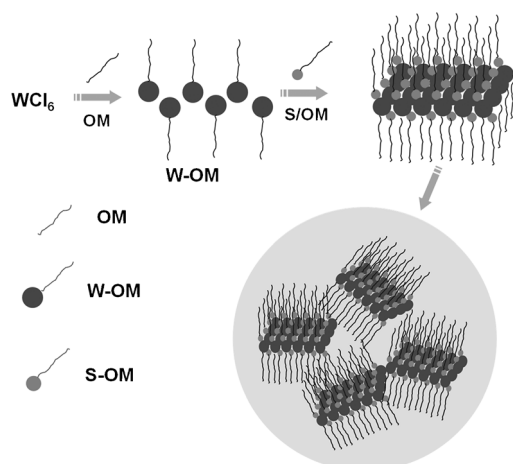


Figure 1. Synthesis of ultrathin WS₂ nanoflakes.

injection of the sulfur solution, the solution immediately turned black, suggesting rapid WS₂ formation (Figure S1). The as-made product was washed and finally annealed in argon atmosphere at 500 °C to remove any organic residues. We have explored a variety of synthetic parameters, such as solvents, precursor concentrations, reaction temperature, and time, and identified the current conditions as the most suitable for optimal product formation.

Scanning and transmission electron microscopies (SEM and TEM) were used to examine the microstructures of the final product. It appears to be particulate with a primary size in the range of 50–200 nm, as determined by SEM (Figure 2a). By high-resolution TEM, these primary particles were unraveled to be a collection of many loosely assembled WS₂ nanoflakes with mostly atomic thickness (Figure 2b,c). Even though we were unable to resolve individual nanoflakes because of their ultrathin thickness and poor contrast, the dark contrast lines in these images are believed to be the standing edges of WS₂ nanoflakes. The lack of clear orientational order over a large scale indicates that these ultrathin nanoflakes remain crystallographically independent within the primary particles. The lateral dimension of each WS₂ nanoflake was estimated to be about 5–20 nm. To probe the composition and spatial distribution of the constituent

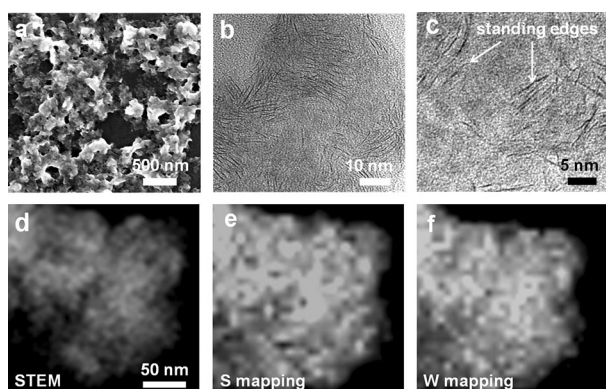


Figure 2. Microscopic characterization of WS₂ nanoflakes. a) SEM and b, c) high-resolution TEM images of WS₂ nanoflakes. Arrows in (c) mark the standing edges of monolayers. d) STEM image and e, f) EDS elemental maps of WS₂ nanoflakes.

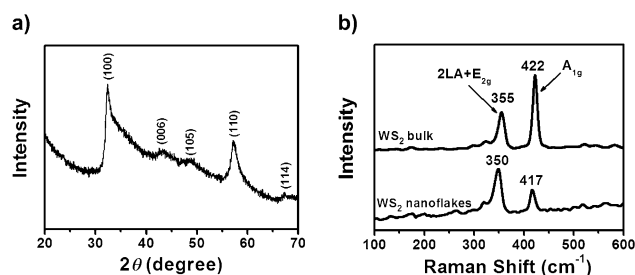


Figure 3. a) XRD pattern and b) Raman spectra of WS₂ nanoflakes.

elements, we carried out energy-dispersive X-ray spectroscopy (EDS) under scanning transmission electron microscopy (STEM). Tungsten and sulfur species were detected with a ratio close to 1:2 over a large area. Figure 2d–f shows the elemental mapping for tungsten and sulfur. Their distributions have a perfect spatial correspondence and are uniform throughout the primary particles. High-resolution tungsten and sulfur X-ray photoelectron spectra (XPS) of the WS₂ nanoflakes display peaks at binding energies characteristic of WS₂ (Figure S2).

The X-ray powder diffraction (XRD) pattern of the final product confirmed the identity of the hexagonal 2H-WS₂ phase with no discernible impurity (Figure 3a). The broadening of diffraction peaks reflects the nanoscale dimension of the final product. Most interestingly, both the (100) and (110) peaks exhibit an apparent asymmetry, reminiscent of the turbostratic stacking of layered compounds, which is commonly found in synthetic carbons and clays.^[25,26] Turbostratically disordered layered compounds may be viewed as piles of randomly stacked sheets with no order between successive layers. The observed feature suggests that the WS₂ product does not crystallize well in all three dimensions, which is in accordance with the ultrathin thickness that was revealed through the above-mentioned high-resolution TEM analysis. We believe that the WS₂ nanoflakes are surface-passivated with solvent molecules. As a result, it is difficult for them to communicate and become in crystallographic order with one another. High-temperature annealing in the final step of the synthesis removes organic residues, but does not lead to restacking of the nanoflakes within the primary particles.

Further insight into the structure of the WS₂ nanoflakes was garnered from their Raman spectrum. Among many weaker peaks, it shows two pronounced peaks centered at 350 and 417 cm⁻¹, which are assignable to the longitudinal acoustic (2LA) and E_{2g} modes and the A_{1g} modes in 2H-WS₂, respectively (Figure 3b).^[27] Importantly, the intensity of the 2LA + E_{2g} peak is approximately twice the intensity of the A_{1g} peak. It has been reported that under 514 nm laser excitation, the relative intensity of the former peak to the latter peak increases dramatically with decreasing WS₂ layer number, with a ratio greater than unity recorded only at the monolayer thickness.^[27] Moreover, the frequency of the A_{1g} optical mode is also found to be sensitive to the number of WS₂ layers. It blue-shifts with an increase in layer number because of the increase in restoring force that is caused by van der Waals interactions among the layers.^[27] Our ultrathin WS₂ nanoflakes exhibit an A_{1g} peak positioned at 417 cm⁻¹, which is in perfect agreement with the value reported for WS₂

monolayers.^[27] All of these facts combined unambiguously corroborate the atomic thickness of individual WS₂ nanoflakes even though they further assemble to larger primary particles.

To assess their electrocatalytic performance in the HER, WS₂ nanoflake powders were thoroughly mixed with Ketjen superconducting carbon black and Nafion in a mixture of ethanol and H₂O and then drop-cast onto glassy carbon electrodes as the working electrode. Electrochemical measurements were carried out using the standard three-electrode setup with a saturated calomel electrode (SCE) and a graphite rod as the reference and counter electrodes, respectively (see the Experimental Section). For reference purposes, a commercial Pt benchmark (20 wt % Pt/C, Johnson Matthey), which is known to have negligible HER overpotentials, was included for comparisons side by side. Cyclic voltammetry (CV) curves show the normalized current density versus the potential for the WS₂ nanoflake catalyst along with the Pt benchmark and commercial WS₂ micropowders (Figure 4a). Electrocatalytic hydrogen evolution on the nanoflake catalyst begins at low cathodic potentials that correspond to an overpotential of approximately 100 mV, above which the HER current density increases rapidly. The HER overpotential observed with our nanoflake catalyst is superior to most values that have been reported for WS₂ based catalysts thus far, which have typical overpotentials of over 150 mV (Table S1).^[7,15–19] It also compares favorably to some of the best MoS₂ based HER catalysts (MoS₂/rGO) that have been developed by us and other groups.^[8] Tafel analysis of the HER polarization curves give rise to a slope of approximately 48 mV/decade for the WS₂ nanoflake catalyst (Figure 4b), which is far smaller than previously reported values.^[7,15–19] It is close to the value of approximately 40 mV/decade observed with MoS₂, indicating a possible Volmer–Heyrovsky reaction pathway with electrochemical desorption of hydrogen as the rate-limiting step.^[8] This is not surprising in light of the structural similarity between these two sulfide compounds. We also investigated the effect of the heat-treatment temperature on the electrocatalytic performance of the WS₂ nanoflakes (Figure S3). It seems that the as-made WS₂ product exhibits a much inferior performance, which is probably due to surface passivation with bulky organic molecules. Annealing at high temperatures ($\geq 500^\circ\text{C}$) decomposes the organic residues and exposes the active sites; however, too high an annealing temperature (such as 700°C) may lead to aggregation of the product, thus giving rise to diminishing surface areas and hence lower HER activity.

Aside from a stringent requirement for high activity, another important criterion for electrocatalyst selection is good durability. To investigate the durability under electrocatalytic operation, the WS₂ nanoflake catalyst was continuously cycled for a total of more than 10 000 cycles in H₂SO₄ (0.5 M). The electrocatalytic activity was periodically monitored by measuring the CV curves after every 1000 potential cycles and then plotting the change in cathodic current density

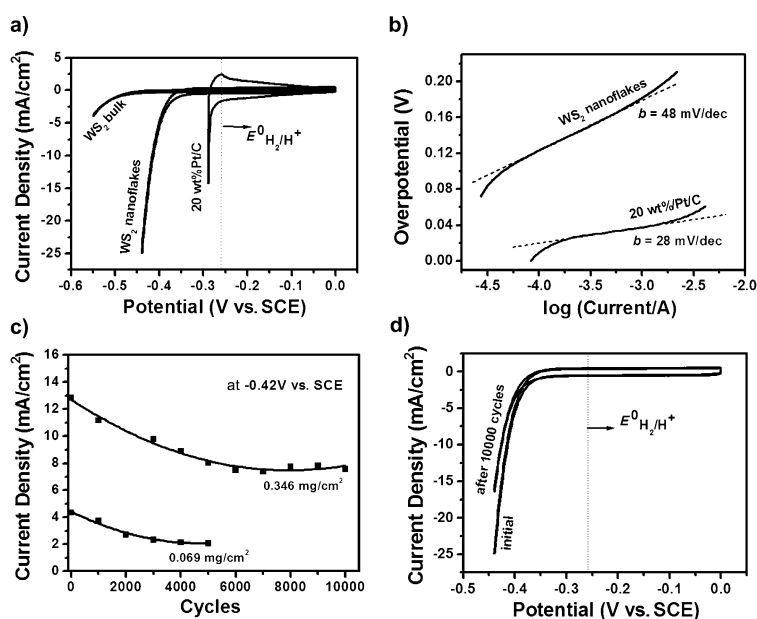


Figure 4. Electrochemical measurements for the WS₂ nanoflake catalyst in H₂SO₄ (0.5 M). a) CV curve of the WS₂ nanoflake catalyst along with those of the Pt benchmark catalyst and commercially available WS₂ micropowders. b) Corresponding Tafel plots. c) Change in the HER cathodic current density (at -0.42 V vs. SCE) with the number of potential cycles. d) CV curves of the WS₂ nanoflake catalyst before and after 10 000 potential cycles. The theoretic value for the HER is indicated by dotted lines in (a) and (d).

at -0.42 V versus the SCE (Figure 4c). Experiments were performed both with a normal catalyst loading (0.35 mg cm^{-2}) and with an ultralow loading (0.07 mg cm^{-2}) to exclude an interference of the catalyst loading or film thickness with the results. Under both conditions, the cathodic current densities show a similar trend: They decrease initially but become stabilized after a couple of thousands of potential cycles. The CV curves of WS₂ nanoflakes before and after 10 000 cycles are compared in Figure 4d. The activity loss appears to be small, corresponding to an increase in overpotential of $< 10\text{ mV}$. The remarkable durability indicates that the primary particulate structure of assembled WS₂ nanoflakes is highly stable and does not collapse or restack over the course of the cycling investigation.

We ascribe the excellent HER performance of our catalyst to its advantageous ultrathin nanoflake morphology with abundant accessible edges. HER active sites for MoS₂ are situated at sulfided Mo edges.^[5,6] The structural analogy between MoS₂ and WS₂ prompted us to conjecture that the edge structure may also play a decisive role in HER electrocatalysis on WS₂. Unfortunately, layered WS₂ and MoS₂ crystals typically have a natural tendency to form closed fullerenes, nanotubes, or stacked multilayered geometries,^[28–30] all of which have rather limited edge densities. Previously, the preparation of MoS₂ or WS₂ monolayers was only feasible through lithium intercalation and forced exfoliation of bulk materials.^[11,16] These monolayers easily restack and risk losing their nanoscale features.^[20,21] Here, we successfully prepared WS₂ nanoflakes with monolayer thickness and a size of 5–20 nm, as revealed by detailed structural characterization. Even though these nanoflakes further

assemble to form larger primary particles, they do not restack and still preserve their individual two-dimensional geometry with abundant accessible edges (Figure 1b,c), which are believed to contribute to the observed high HER activity.

In summary, we have developed a simple yet effective high-temperature solution-phase method for the synthesis of ultrathin WS₂ nanoflakes. This strategy leads to favorable monolayered nanosized products with abundant edges, which further assemble to form larger particulate structures. In acids, the WS₂ nanoflake catalyst exhibited efficient and durable activity for the hydrogen evolution reaction, with an impressively small overpotential of approximately 100 mV and a Tafel slope of 48 mV/decade. Given its excellent HER performance and low cost, this WS₂ nanoflake catalyst can compete with the extensively studied MoS₂ materials in every aspect of the performance and may find applications in a myriad of electrochemical or photoelectrochemical processes.

Experimental Section

Typical procedure for the synthesis of ultrathin WS₂ nanoflakes: WCl₆ (1 mmol) was added to a mixture of oleylamine (OM; 20 mL) and 1-octadecene (ODE; 10 mL) in a three-necked flask (50 mL) at room temperature. The solution was heated to 140°C to remove water and oxygen under vigorous magnetic stirring in the presence of argon for protection for ca. 30 min. Afterwards, the temperature of the solution was rapidly raised to 300°C and kept there for another 30 min in nitrogen atmosphere. A sulfur solution that was prepared by dissolving sulfur powder (2 mmol) in OM (5 mL) was then injected into the flask at 300°C within 10 min. The reaction was kept at 300°C for 1 h. After the reaction mixture had been cooled down to room temperature, WS₂ nanoflakes were precipitated by adding excess absolute ethanol (ca. 30 mL), collected by centrifugation, and washed repetitively with ethanol. To remove the organic residue, the as-made product was annealed in Ar at 500°C for 2 h.

Characterizations: X-ray diffraction (XRD) was performed on a Shimadzu XRD-6000 X-ray diffractometer at a scanning rate of 0.05° s⁻¹. Scanning electron microscopy (SEM) images were taken with a Zeiss scanning electron microscope. Transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) were conducted on an FEI Tecnai F20 transmission electron microscope at an acceleration voltage of 200 kV. X-ray photoelectron spectra (XPS) were collected with an SSI S-Probe XPS Spectrometer. Raman spectra of powder samples were recorded on a LabRAM HR Raman microscope with a laser excitation wavelength of 514 nm.

Electrochemical measurements: WS₂ nanoflakes (1 mg), Ketjen black (0.5 mg), and a Nafion solution (5 wt %, 5 µL) were dispersed in a water/ethanol mixture (1:1, v/v; 0.2 mL) with the assistance of sonication (at least 30 min) to form a homogeneous ink. Then, 5 µL of the catalyst ink (containing 25 µg of catalyst) were loaded onto a glassy carbon electrode with a diameter of 3 mm (catalyst loading ca. 0.35 mg cm⁻²). Cyclic voltammetry (CV) was carried out in a standard three-electrode configuration at a scan rate of 10 mV s⁻¹ with the glassy carbon electrode, a saturated calomel electrode, and a graphite rod as the working, reference, and counter electrodes, respectively. Tafel plots were collected at a scan rate of 5 mV s⁻¹.

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