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Electrochemical sulfidation of WS₂ nanoarrays: Strong dependence of hydrogen evolution activity on transition metal sulfide surface composition

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ABSTRACT

The activity of transition metal sulfides for the hydrogen evolution reaction (HER) can be increased by sulfur-enrichment of active metal-sulfide sites. In this report, we investigate the electrochemical sulfidation of atmospherically aged WS₂ nanoarrays with respect to enhancing HER activity. In contrast to MoS₂, it is found that sulfidation diminishes HER activity. Electrochemical and XPS experiments suggest the involvement of insoluble tungsten oxides in the altered HER and electron transfer properties. This demonstrates the strong dependence of the transition metal dichalcogenide (TMD) composition with the successful sulfur incorporation and subsequent HER activity.

1. Introduction

The demand for sustainable sources of electrochemical hydrogen production [1] has triggered the development of the abundant and low-cost TMDs as substitutes to the best performing platinum group metal catalysts for the hydrogen evolution reaction (HER) [2-5].

To improve their HER activity, research has focussed on the preparation of S-rich TMD structures which surpass the 1:2 M:X stoichiometry found in bulk materials [6-8]. Such sulfur enrichment aims to incorporate more bridging S₂²⁻ and terminal S₂⁻ moieties into the TMD structure; both consistently reported as being the active sites involved in proton adsorption and desorption [9,10]. Enhanced HER performance has been reported for S-rich structures such as amorphous MoS₂+x [11-15] and WS₂.64 electrodeposited thin films [9], as well as on wet chemical synthesis-prepared MoS₂+x [16,17] or MX₃/MX₂ physical mixtures [18]. However, some of the proposed structures exhibit diminished HER performances after atmospheric or electrochemically-induced sulfur depletion [14,18] or impurities presence [19].

We report the use of a one step, room temperature electrochemical sulfidation method initially developed for MoS₂ [20], for sulfur-enriching WS₂. In particular, atmospherically-aged WS₂ nanocone arrays which are of interest due to their enhanced electrocatalytic properties [21]. Changes in the electrocatalytic behaviour are understood via monitoring surface composition, morphology, and electron transfer properties over a one month period by XPS, SEM, and voltammetric experiments.

2. Materials and methods

2.1. Fabrication

The plasma-etch fabrication method used is based on a literature method [22-24], recently reported in TMDs for electrocatalytic applications [20,21,25].

In short, WS₂ (defect-free, 99.9995% purity, 2D Semiconductors USA) crystals cut into rectangles of approximately 1.5 × 5 mm were affixed to glassy carbon (GC) type 2 stubs (7 mm diameter, 2 mm thick, Alfa Aesar, UK) with carbon tape. A 20 μL mixture of a 216 ± 4 nm diameter polystyrene-latex nanosphere (NS) suspension (3000 Series Nanosphere, 1 wt% in water, Thermo Scientific, UK) with absolute ethanol in a 1:1 vol. ratio was transferred to a silicon wafer (previously cleaned with piranha solution and oxygen plasma) to form a self-assembled, hexagonal close-packed, NS monolayer. The NS-modified TMDs etching was carried out in an Oxford...
2.2. Electrochemical characterisation

Electrochemical measurements were carried out with a PC-controlled PGSTAT128N potentiostat (Metrohm Autolab BV, Netherlands) in a thermostatted three-electrode electrochemical cell (23 ± 2 °C). The electrodes used were: a bright Pt mesh counter (Alfa Aesar Ltd., UK), a double junction saturated Ag/AgCl reference (electrochemical sulfidation experiments, Sigma-Aldrich), a saturated calomel (SCE) reference electrode (HER experiments, BAS Inc., Japan) and TMD-modified GC stubs connected to a rotating disk working electrode (OrigaLy3 ElectroChem SAS, France).

HER experiments were carried out in a 2 mM HClO4 (ACS ≥ 70%, Sigma-Aldrich), 0.1 M NaClO4 (ACS ≥ 98%, Sigma-Aldrich) solution using a range of voltage scan rates (2–1200 mV s⁻¹). Preconditioning of TMD electrodes prior to HER experiments was via 10 cycles from −0.045 to −1.645 V (vs SCE) at a scan rate of 50 mV s⁻¹. Additional capacitance (voltage range −0.2 to 0.2 V vs NHE, scan rates 10–500 mV s⁻¹) and impedance measurements (voltage range 0 to −1.645 V vs. SCE, frequency range 10⁻¹ to 10⁵ Hz, voltage amplitude 10–100 mV) were performed alongside all HER measurements to apply roughness factor and iR compensation corrections. HER potentials are referenced versus the normal hydrogen electrode (NHE) by means of the Nernstian shift correction (ENHER = 0.242 V + 0.059 pH).

Investigation of heterogeneous electron transfer (HET) rates was performed under the same conditions as of Pumera et al. for ease of reference [5,13], by acquiring five CVs in 10 mM K4Fe(CN)6/K3Fe(CN)6 (BioUltra ≥ 99.5%, Sigma-Aldrich) electrolyte supported by a pH 7.2 phosphate buffer (50 mM potassium phosphate monobasic/potassium phosphate dibasic trihydrate, ≥ 99%, Sigma-Aldrich) at scan rates from 10 to 300 mV s⁻¹. Experimental HET rate constants (k_HET) were calculated by correlating the peak-to-peak separation of the Fe(CN)₆⁴⁻/Fe(CN)₃⁻ redox couple with the dimensionless parameter ψ, using the literature methods of Nicholson and Shain (ψ = 0.1 and ΔΨp < 210 mV) [27], and Klinger and Kochi (ψ < 0.1 and ΔΨp > 210 mV) [28]. A diffusion coefficient of 7.26 × 10⁻⁶ cm² s⁻¹ for the [Fe(CN)₆]⁴⁻/₃⁻ redox pair was used in the calculation [29], assuming α = 0.5. For the nanorods under study, Case 4 diffusion behaviour (1D) was observed [30]. All electrolytes were freshly prepared with ultrapure water (resistivity not < 18.2 MΩ cm, Millipore Milli-Q Direct 8), and thoroughly purged with N₂ (Oxygen-free grade, BOC Gases plc), and experiments run under a N₂ atmosphere. All glassware was cleaned with a dilute solution of KMnO₄ in concentrated H₂SO₄ followed by rinsing with ultrapure water.

2.3. XPS measurements

A Kratos Axis HSI X-ray photoelectron spectrophotometer (Aston University) fitted with a charge neutraliser and operated using a Mg Kα (1253.6 eV) achromatic radiation, was used to record spectra at a pressure of < 1 × 10⁻⁷ Torr using a spot size of 100 μm. Pass energies used were: 160 eV for survey spectra, and 20 eV for high resolution scans of specific energy regions. Data processing was performed using Casa XPS version 2.3.18PR1.0, with spectral energy corrected to the adventitious C 1s peak at 284.6 eV. Shirley backgrounds were applied to high resolution peaks before being fitted with individual components.

For MoS₂, electrochemically-induced surface oxidation (at E > +1 V vs Ag/AgCl) yields the acid-soluble MoO₄²⁻ species [34]. Sulfur incorporation after surface oxidation suggests that MoO₂⁻ species assist in the overall sulfidation mechanism. For WS₂, the cyclic voltammogram obtained during the sulfidation treatment is similar to that of MoS₂ [20].

The application of this method to WS₂ was evaluated by monitoring HER performance, oxidation state, and electron transfer properties over a one month period following this sulfidation treatment on previously tested, atmospherically aged WS₂ samples. This provided the following observations: (i) freshly sulfidated samples did not necessarily present enhanced HER performances compared with pre-sulfidated samples, and (ii) the samples’ HER peak current, after correction for roughness factor, was inferior after a 3-week environmental exposure compared to the pre-sulfidated, atmospherically-exposed state.

Both phenomena can be understood by changes in oxidation state revealed by XPS. For the 31 ± 1 s (R = 2, Z = 6.4) plasma-etched WS₂ sample, the peak current decays to half of its initial value following sulfidation (Fig. 1a). This is correlated to a decrease in the total S/W ratio (from ca. 2:1 to 1.5:1, see Fig. 2c), and the appearance of WO₂ at the crystal surface up to ca. 24% (W 4f7/2/W 4f5/2 doublet lies at 14% increase in the 14% increase in the oxidation state, despite the decay in the total S/W ratio (from ca. 2:1 to 1.5:1, see Fig. 2c), and the appearance of WO₂ at the crystal surface up to ca. 24% (W 4f7/2/W 4f5/2 doublet lies at 218.5 eV) [35]. Previous reports on bulk and chemically-exfoliated WS₂ crystals suggest that incorporation of WO₂ is detrimental for the HER [18,35]. In the case of the 31 ± 1 s sample, this is supported by the changed HER kinetics (Tafel slope increase from 100 to 185 mV dec⁻¹, Fig. 3c) and higher onset potentials (|ηonset| from 173 to 207 mV).

Conversely, the 61 ± 1 s plasma-etched WS₂ sample presented higher peak currents (Fig. 1b) and kinetics (Tafel slope 130 vs. initial 210 mV dec⁻¹, Fig. 3d) following sulfidation, despite the decay in the total S/W ratio (from ca. 2:1 to 1.88:1, see Fig. 2f) and the 14% increase in surface WO₂ content (Fig. 1d and 2c). This initially non-linear trend is found to be linked to the S/W ratio, if calculated solely using the W⁴⁺ XPS components characteristic of WS₂. Sulfur-rich S/W ratios promote enhanced HER performance and vice versa. Maximum peak currents coincide with the highest sulfur-to-metal ratios for both 31 ± 1 s (S/W = 2.08:1, j₀ = 9 mA cm⁻², day 8) and 61 ± 1 s (S/W = 2.18:1, j ≈ 1.6 mA cm⁻², freshly sulfidated) samples. After these peak values, both post-sulfidated 31 ± 1 s and 61 ± 1 s etched samples exhibited
an HER current decrease in subsequent electrochemical testing to values lower or comparable with the freshly sulfidated state, due to lower S:W ratios. This accords with previous investigations which correlated higher sulfur content in TMDs with improved hydrogen turnover frequencies [12,14], and sulfur-depleted W-edge sites of electro-oxidised WS2 with poor catalytic activity [35]. We hypothesize that the electrochemically-induced restructuring gradually depletes the WO2 phase, initially exposing underlying WS2 with high active site densities which are later reconstructed during atmospheric and experimental conditions to a more homogeneous nanostructure (Fig. 2g-h).

The cathodic feature appearing at E ca. − 0.4 V vs NHE in the HER experiments (Fig. 3a and b) is ascribed to the diffusion decay peak profile of proton reduction catalysed by the WS2 active sites, characteristic of the fully-supported, low proton concentration electrolyte used [36,37]. Indeed, the resolution of this peak also seems correlated with the $S^{2-}/W^{6+}$ ratio, and consequently to the active sites present.

With regard to the electron transfer kinetics, both samples exhibit higher $k_{\text{app}}^0$ values ($\approx 4 \times 10^{-5}$ cm$^2$ s$^{-1}$) after undergoing the sulfidation treatment (Fig. 1e-f). This agrees with literature reports which found enhanced electrical conductivities of WOx species vs. WS2 [38], beneficial for mediating in the redox chemistry of surface sensitive species such as Fe(CN)$_6^{3-}$/Fe(CN)$_6^{4-}$ redox probe, for atmospherically aged, sulfidation treated plasma-etched WS2 samples $31 \pm 1$ s ($R = 2$, $Z = 6.4$, first row) and $61 \pm 1$ s (second row), after weekly electrochemical testing over a three-week ambient exposure period.

### 4. Conclusions

In contrast to MoS2, the application of the solution-phase, room-temperature electrochemical sulfidation method to obtain S-rich structures did not lead to S-rich WS2 but to S-deficient WS2 structures with high WO2 surface content. The inferior HER performances but improved electron transfer properties are in agreement with the detrimental effect reported after WO2 incorporation into WS2 for the HER catalysis. The unsuccessful incorporation of electroreduced sulfide in the WS2 structure is suspected to arise from the nature of the sulfidation mechanism: redeposition of acid-soluble MoO4$^{2-}$ species for MoX2 improves S$^{2-}$ incorporation onto the surface, which is not possible in the case of WX2 as the WOx compounds formed are acid insoluble. This demonstrates the key role of the nature of the TMDs in the successful electrochemical incorporation of sulfur in their structure, and reveals that an electrochemistry-based sulfidation method universally applicable for any TMDs remains to be developed.

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Fig. 2. Stacked high-resolution XPS spectra of W 4f and S 2p for a)–b) 31 ± 1 s (R = 2, Z = 6.4) and c)–d) 61 ± 1 s atmospherically aged, sulfidation treated, plasma-etched WS₂ samples over a three-week ambient exposure period. e)–f) Comparison of total S:W XPS atomic photoemission ratios. Representative SEM micrographs g) before and h) after solution phase-sulfidation.

Fig. 3. Left column: Linear sweep voltammograms in the 0 to −1.2 V voltage range of a) 31 ± 1 s (R = 2, Z = 6.4) and b) 61 ± 1 s atmospherically aged, sulfidation treated plasma-etched WS₂ samples over a three-week ambient exposure period. Right column: Tafel plots (η vs. log |j|) of c) 31 ± 1 s (R = 2, Z = 6.4) and d) 61 ± 1 s atmospherically aged, sulfidation treated plasma-etched WS₂ samples over a three-week ambient exposure period. Labels: pre-sulfidated (black), post-sulfidated (red), 8-day atmosphere exposed (green), 15-day atmosphere exposed (blue) and 22-day atmosphere exposed (magenta). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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