Stability of 2H- and 1T-MoS2 in the presence of aqueous oxidants and its protection by a carbon shell

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Two-dimensional molybdenum disulfide (MoS2) is emerging as a catalyst for energy and environmental applications. Recent studies have suggested the stability of MoS2 is questionable when exposed to oxidizing conditions found in water and air. In this study, the aqueous stability of 2H- and 1T-MoS2 and 2H-MoS2 protected with a carbon shell was evaluated in the presence of model oxidants (O2, NO2−, BrO3−). The MoS2 electrocatalytic performance and stability was characterized using linear sweep voltammetry and chronoamperometry. In the presence of dissolved oxygen (DO) only, 2H- and 1T-MoS2 were relatively stable, with SO42− formation of only 2.5% and 3.1%, respectively. The presence of NO2− resulted in drastically different results, with SO42− formations of 11% and 14% for 2H- and 1T-MoS2, respectively. When NO2− was present without DO, the 2H- and 1T-MoS2 remained relatively stable with SO42− formations of only 4.2% and 3.3%, respectively. Similar results were observed when BrO3− was used as an oxidant. Collectively, these results indicate that the oxidation of 2H- and 1T-MoS2 can be severe in the presence of these aqueous oxidants but that DO is also required. To investigate the ability of a capping agent to protect the MoS2 from oxidation, a carbon shell was added to 2H-MoS2. In a batch suspension in the presence of DO and NO2−, the 2H-MoS2 with the carbon shell exhibited good stability with no oxidation observed. The activity of 2H-MoS2 electrodes was then evaluated for the hydrogen evolution reaction by a Tafel analysis. The carbon shell improved the activity of 2H-MoS2 with a decrease in the Tafel slope from 451 to 371 mV dec−1. The electrode stability, characterized by chronopotentiometry, was also enhanced for the 2H-MoS2 coated with a carbon shell, with no marked degradation in current density observed over the reaction period. Because of the instability exhibited by unprotected MoS2, it will only be a useful catalyst if measures are taken to protect the surface from oxidation. Further, given the propensity of MoS2 to undergo oxidation in aqueous solutions, caution should be used when describing it as a true catalyst for reduction reactions (e.g., H2 evolution), unless proven otherwise.

1. Introduction

Two-dimensional molybdenum disulfide (2D MoS2) is a nanomaterial that has been extensively investigated for a wide variety of chemical and physical applications due to its unique chemical and physical properties.1–3 Of the three crystalline phases (3R, 2H, and 1T), 2H-MoS2 is the most thermodynamically stable structure and has been the most widely studied for chemical functions. 2H-MoS2 is a planar structure consisting of sheets of S–Mo–S that are held together by weak van der Waals forces, maintaining a trigonal geometry. The typical depth of one layer is approximately 0.7 nm.4 Applications of MoS2 include, but are not limited to, photocatalysis due to its solar active band gap of approximately 1.2–1.7 eV,7–9 catalytic reduction of contaminants,10 hydrodesulfurization (HDS) catalysis of sulfur containing compounds in petroleum products,11–14 and electrocatalysis of water for the production of hydrogen gas.15–19

The electrocatalytic ability of MoS2 to generate H2 was discovered in the 1970’s.20 More recently, 2H–MoS2 nanoparticles were proposed as an effective hydrogen evolution reaction (HER) electrocatalyst based on first-principles calculations that suggested hydrogen binding at Mo–S sites was nearly thermoneutral.21 The Mo (1010) disulfide (S22−) and sulfide (S2−) edge sites of 2H–MoS2 were demonstrated to be highly active for the HER.22 These groundbreaking studies set the stage for a meaningful effort on optimization of the 2H–MoS2 nanoparticles for the HER reaction.6,23–26 Challenges to deployment of 2H–MoS2 that have been investigated include increasing the active sites per unit volume,23,27–30 tuning the activity of the catalyst to promote HER by adjusting ΔG

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towards zero,31-34 and improving the electron transfer kinetics of the catalyst.7,28,35,36

1T-MoS2, a metastable metallic crystalline phase, has been known since at least the 1970’s,37,38 but it was not seriously investigated as a catalytic material until recently because of its challenging synthesis procedure. Typical synthesis involves the exfoliation of single layer 1T-MoS2 layers from 2H-MoS2 stacks using aggressive reagents such as tert-butyl lithium, making the technique challenging for wider study.39 Hydrothermal intercalation of ammonium is a promising alternative synthesis method for 1T-MoS2, where high temperature and pressure is used to drive ammonium ions between MoS2 sheets and exfoliate 1T-MoS2.40,41 1T-MoS2 has an octahedral symmetry rather than the trigonal symmetry of 2H-MoS2, giving it a metallic band structure that is critical for overcoming electron transfer limitations for electrocatalysis.28 Further, the octahedral crystal structure shifts the ΔG0 of the basal plane sites to near zero, allowing for their participation in the HER reaction and greatly increasing the active site density on the catalyst.42 Due to these properties, 1T-MoS2 is a more attractive catalyst for the HER than 2H-MoS2.28

Greater interest in using 2D MoS2 for environmental applications has recently emerged. Because of the tunable nature of its physical and chemical properties from changing nanoparticle size, layering, and crystallinity, 2D MoS2 has been studied as an adsorbent of heavy metals,43-44 a photocatalyst for various contaminants,45-46 a membrane separation material,47-48 an antibacterial agent,49,50 and a sensor for contaminants.51 However, thus far, there has been little comprehensive investigation of the stability of MoS2 under realistic environmental conditions. Other metal sulfides (e.g., ZnS52 and FeS253) are known to be unstable under oxidizing conditions, so the evaluation of the MoS2 stability under relevant conditions is critical. Under more realistic environmental aqueous conditions, the presence of oxygen was shown to cause oxidation of 2D MoS2.54,55 Wang et al. demonstrated that 2D MoS2 oxidizes under aerated aqueous conditions, according to eqn (1):55

\[
\text{MoS}_2 + \frac{9}{2}O_2 + 3H_2O = \text{MoO}_4^{2-} + 2SO_4^{2-} + 6H^+ \tag{1}
\]

In the study by Wang et al., dissolution occurred for both 2H- and 1T-MoS2 with half-lives of approximately 1–30 days, but the dissolution rate was faster for 1T-MoS2 due to its larger number of reactive edge sites. This behavior was supported by Lee et al.,34 showing that the oxidation of 2D MoS2 was slowed in the presence of natural organic matter, but that the presence of sunlight and dissolved organic carbon could enhance the oxidation. Despite these results, the dissolution or stability of 2D MoS2 with regards to environmental applications has not been fully addressed.

The primary objectives of this study were to investigate the effect of oxidants present in natural waters on the short-term stability of 1T- and 2H-MoS2 nanoparticles, and to evaluate the use of a graphitic carbon coating shell as a method for protecting MoS2 from oxidation. Carbon shells have been shown to increase the stability of MoS2 for various applications.56-57 Nitrite and bromate were chosen as model oxidants because of their relative ease of reduction as opposed to those with higher activation energies (e.g., nitrate, perchlorate). The MoS2 stability was characterized by measuring the reduction of nitrite or bromate concentrations and the formation of sulfate, a byproduct of MoS2 oxidation. The electrocatalytic performance and stability of MoS2 for the HER were investigated using linear sweep voltammetry and chronoamperometry, respectively. The outcomes are beneficial to identifying the feasibility of using 1T- and 2H-MoS2 for aqueous applications involving oxidizing conditions.

2. Methods and materials

2.1 Synthesis of MoS2 nanoparticles

Commercial MoS2 nanoparticles (C-MoS2) were purchased (Sigma-Aldrich, 804169) to be used as a comparison to the lab-synthesized MoS2 nanoparticles. 2H-MoS2 nanoparticles were synthesized by hydrothermal methods adapted from literature.58 2H-MoS2 was synthesized by first dissolving 0.740 g of Na2MoO4 (Alfa Aesar, 12214) in 36 mL of ultrapure water. Then, 254 µL of thioacetic acid (VWR, AAAL03305) was then added to this solution and stirred for 10 minutes. Finally, the solution was transferred to a 125 mL Teflon lined hydrothermal reactor (Parr 4748) and heated to 200 °C for 24 hours. The sample temperature was cooled naturally to 25 °C, then centrifugally washed with water three times followed by a single ethanol wash. The resulting black pellet was dried to a powder at 50 °C in air. The powder was then ground with a mortar and pestle prior to use. 1T-MoS2 was synthesized using adapted method similar to a previous study.48 First, 1.164 g of (NH4)2MoO4 (Fisher Scientific, S25171) was dissolved in 62.5 mL of ultrapure water. Then 1.148 g of thiourea (VWR, A12828) was added to the solution and stirred for 10 minutes. The solution was then transferred to a 125 mL hydrothermal reactor and heated to 200 °C for 24 hours prior to washing and drying as described previously for 2H-MoS2.

2.2 Carbon coating of MoS2 nanoparticles

The MoS2 was coated with an ultrathin layer of carbon using previously described methods.59 0.3 g of the synthesized 2H-MoS2 nanoparticles were suspended in 80 mL of a 10 mM TRIS buffer (VWR, JR31). Then, 0.1, 2.0, or 3.0 g L⁻¹ of dopamine chloride (Alfa Aesar, A11316) was added to slurry and bath sonicated for 1 hour, during which time dopamine attached to the MoS2. Coated particles were centrifuged, washed with ultrapure water, and then air-dried at 50 °C. The resulting brown powder was pyrolyzed at 700 °C for 2 hours in a tube furnace with N2 flow, causing the powder to turn black as dopamine was carbonized.

2.3 Aqueous stability testing in the presence of nitrite or bromate

The MoS2 stability in the presence of nitrite (NO2⁻) or bromate (BrO3⁻) was tested by tracking the reduction of nitrite or bromate and the formation of sulfate over time. All experiments
were conducted in a 50 mL batch reactor. All experiments contained approximately 1 g L⁻¹ of MoS₂ and NO₂⁻ or BrO₃⁻ at varying concentrations. The pH of all samples ranged from approximately 6.0 to 6.3, depending on the concentrations of NO₂⁻ and BrO₃⁻ used. Gas bubbling (H₂ or N₂) was performed by flowing the gas through a glass diffuser into the solution at a flow rate of 150 mL min⁻¹ to ensure saturation. The total reaction time was 6 h. 1 mL samples were taken at regular intervals and syringe filtered through a 0.45 μm nylon membrane. Samples were subsequently analyzed for concentrations of nitrite, nitrate (NO₃⁻), BrO₃⁻, bromide (Br⁻), and sulfate (SO₄²⁻) by ion chromatography (IC; Dionex ICS 5000+). Unknown peaks attributed to molybdate species were also detected at late elution times in the IC chromatographs, but they were not quantified due to a lack of available standards. All experiments were conducted as single experiments, thus any rates or percent removals or formation cannot be considered absolute. Instead, values are used to report general observations and comparisons.

2.4 Characterization techniques

Images of the MoS₂ materials were collected using a high-resolution transmission electron microscope (TEM; Titan 80–300). Samples were prepared by drop-casting ethanolic suspensions of the MoS₂ on lacy carbon copper grids. Raman spectra were collected on a Jasco NRS 5100 Micro-Raman spectrometer. The crystal structure was investigated with powdered X-ray diffraction (Cu Kα, 0.15418 nm; Bruker D8 Advance Davinci). The theoretical carbon shell thickness of coated MoS₂ was estimated assuming spherical MoS₂ particles and complete attachment and conversion of dopamine to pure carbon.

2.5 Electrochemical characterization of MoS₂ electrodes

MoS₂ electrodes were created by drop casting MoS₂ suspensions onto carbon paper substrates. Carbon paper (Toray, 5% wet-proof) was cut into 1.5 cm × 5.0 cm sheets and placed on an aluminum foil covered hot plate set to 175 °C. 20 mg of MoS₂ were suspended in 10 mL of ultrapure water and 62.5 µL of 20% Nafton (Ion Power, D-2020-US-25) was added to the suspension and then bath sonicated for 1 h. Then, 500 µL of the resulting suspension was drop cast onto the hot carbon paper electrode and then dried.

To perform the electrochemical characterization, a three-electrode system was used in an undivided reactor consisting of a Pt wire as the counter electrode, a standard calomel electrode (SCE) as the reference electrode, and the MoS₂ coated carbon paper electrodes as the working electrode. A Biologic SP200 potentiostat (BioLogic USA) with EC Lab software was used to administer linear sweep voltammetry (LSV) and chronoamperometry (CA) experiments. For LSV, an electrolyte containing only 1 N H₂SO₄ was used to probe the HER. Prior to analysis, the reactor was bubbled with N₂ for 20 minutes to flush O₂. LSV was conducted at a rate of 5 mV s⁻¹ from 0.3 to −0.4 V vs. SCE. LSV was repeated three times and potentials adjusted by −0.242 V to correct to the Reversible Hydrogen Electrode (RHE). Tafel plots and slopes where obtained from the linear portion of the η vs. log|i| taken from the LSV. CA experiments were conducted at −0.5 V vs. SCE for 60 minutes in a solution containing an inert supporting electrolyte, 1 N NaClO₄, to reduce solution resistance. Experiments were repeated with the addition of 7.14 mM NaNO₂ (100 mg-N/L NO₂⁻) to evaluate the stability of the MoS₂ electrodes in the presence of NO₂⁻. All experiments were conducted as single experiments, thus the Tafel slopes and current densities reported cannot be considered to be absolute. Instead, values are used to report general observations and comparisons.

3. Results and discussion

3.1 Materials characterization

Fig. 1 shows TEM images of the 2H-MoS₂ and C-MoS₂ nanoparticles. The size and shape differences of the two are obvious, with the 2H-MoS₂ consisting of particles/sheets less than 100 nm in diameter (Fig. 1A) and the C-MoS₂ (Fig. 1B) consisting of comparatively larger flake-like particles that approach micrometer scale dimensions. HR-TEM (Fig. 1A inset) confirmed the well-organized crystal structure of the 2H-MoS₂ particles. The MoS₂ particles were further characterized by pXRD (Fig. 1C) and Raman spectroscopy (Fig. 1D). The XRD diffraction patterns confirmed the 2H crystalline phase for the 2H- and C-MoS₂ particles, while the 1T-MoS₂ sample had similar but shifted peaks indicative of the 1T crystalline phase. The resolution of the diffraction pattern for the 2H-MoS₂ particles was poor, despite using a long dwell time at each 2θ (>2 s). While poor resolution often indicates low crystallinity, peak broadening and low resolution are consistent with nano-sized MoS₂ and the behavior may be attributed to the poor interaction of the single or few layer MoS₂ with the X-ray beam. Raman spectroscopy was used to confirm the crystal structure. The red dotted vertical lines in the Raman spectra correspond to the E₁g (280 cm⁻¹), E₂g (375 cm⁻¹), and A₁g (404 cm⁻¹) vibrations of the 2H crystalline phase, while peaks at 156, 225, 235, and 333 cm⁻¹ are generated by 1T phases marked by the green dashed lines. The spectra of C-MoS₂ and 2H-MoS₂ showed only characteristic peaks of the 2H crystalline phase, while the 1T-MoS₂ spectrum showed characteristic peaks of both 2H and 1T crystalline phases. The nature of the characterized MoS₂ species can be summarized as follows: 1T-MoS₂ consists of a mixture of single layer 1T and 2H few layer nanoparticles, the 2H-MoS₂ consists of few-layer 2H nanoparticles, and the C-MoS₂ is the 2H phase and consists of many stacked layers forming larger particles.

3.2 Aqueous stability in water containing dissolved oxygen

The short-term aqueous stability of the MoS₂ materials was evaluated in water containing only dissolved oxygen (DO), which was approximately 0.26 mM at conditions tested. The oxidation of MoS₂ was measured by tracking the byproduct SO₄²⁻, reported as a percent of the total available S in the system (Fig. 2). For each MoS₂ sample, an immediate increase in SO₄²⁻ upon exposure to water was observed, which is presumably due to the rapid oxidation of the surface MoS₂ into Mo₇O₂⁹⁻ species.
Differences in $\text{SO}_4^{2-}$ release may be attributed to the reactivity of the surface sites, and to some degree, the surface area of available sites. After the initial period, the $\text{SO}_4^{2-}$ concentration stabilized for $1T$- and $C$-$\text{MoS}_2$ and increased only slightly for $2H$-$\text{MoS}_2$ over the time-period tested. The total oxidation of $\text{MoS}_2$, reported as the percentage of total sulfur in the system converted to $\text{SO}_4^{2-}$, was 0.63%, 2.5%, and 3.1% for $C$-$\text{MoS}_2$, $2H$-$\text{MoS}_2$, and $1T$-$\text{MoS}_2$, respectively (Table 1). Overall, the $\text{MoS}_2$ materials were relatively stable over the 4 hour measurement period. These results agree with the comparatively long reported half-lives of $2H$- and $1T$-$\text{MoS}_2$ stability in aqueous solution of up to 30 days.52

3.3 Effect of nitrite and bromate on $\text{MoS}_2$ stability

The stability of $\text{MoS}_2$ was tested against $\text{NO}_2^-$ and $\text{BrO}_3^-$ as aqueous oxidants because they are known to be easily reduced in the presence of suitable reductants.63–64 These experiments also served to probe the importance of the presence of DO compared to other oxidants. Fig. 3 shows the kinetic results for the reduction of $\text{NO}_2^-$ and the subsequent formation of $\text{NO}_3^-$ and $\text{SO}_4^{2-}$ in the presence of $C$, $2H$, and $1T$-$\text{MoS}_2$. The results are summarized in Table 1. Experiments were conducted in the presence of DO and then repeated under $\text{H}_2$ saturated conditions. For $C$-$\text{MoS}_2$ in the presence of DO (Fig. 3A), $\text{NO}_2^-$ was
initially removed but reached a steady-state of 9.5% removal after 2 h. \( \text{SO}_4^{2-} \) was formed in conjunction with \( \text{NO}_2^- \) removal, reaching a steady-state value of only 0.55% of the total available \( S \), which was similar to conditions without \( \text{NO}_2^- \) (i.e., Fig. 2). Thus, \( \text{NO}_2^- \) did not have a major impact on C-MoS\(_2\) oxidation, and the observed \( \text{NO}_2^- \) removal can be presumably attributed...
to adsorption of NO$_2^-$ to C-MoS$_2$ or to surface oxidation of C-MoS$_2$. For the 2H- and 1T-MoS$_2$ samples in the presence of DO (Fig. 3B and C), NO$_2^-$ was completely removed within 3 h and 1 h, respectively. The formation of SO$_4^{2-}$ increased to 11.5% and 13.5% of the total available S for 2H-MoS$_2$ and 1T-MoS$_2$, respectively, indicating the MoS$_2$ oxidation increased compared to conditions without NO$_2^-$ (i.e., Fig. 2). NO$_3^-$ formation was also observed for 2H-MoS$_2$ and 1T-MoS$_2$ experiments, with a selectivity of 7.7% and 8.3% of the initial N, respectively. NO$_2^-$ is a byproduct of NO$^+_2$ oxidation, which is somewhat unexpected considering the oxidation of MoS$_2$ would result in NO$_2^-$ reduction. After the reaction was complete, the 2H- and 1T-MoS$_2$ samples exhibited a bluish color, indicating the formation of Mo(v) species.$^{65}$

MoS$_2$ could potentially be acting as a hydrogenation catalyst (i.e., H$_2$ dissociation) and DO may play an intermediate role in the reaction. Thus, to investigate these effects, experiments were repeated with H$_2$ saturated water with limited DO (Fig. 3D–F). For C-MoS$_2$, similar results were observed compared to the experiment with DO, suggesting no specific mechanism related to DO or H$_2$. The 2H- and 1T-MoS$_2$ materials showed more response to the exclusion of DO and presence of H$_2$, with smaller changes in NO$_2^-$, SO$_4^{2-}$, and NO$_3^-$ concentrations observed (Table 1). Again, the NO$_2^-$ removal was initially rapid for 2H- and 1T-MoS$_2$, but then stabilized within 2 h. Though the total NO$_2^-$ reduction was still high, with observed removals of 93% (2H-MoS$_2$) and 81% (1T-MoS$_2$), the SO$_4^{2-}$ formation decreased to 4.3% (2H-MoS$_2$) and 4.5% (1T-MoS$_2$) of the total available S, respectively. These results suggest DO serves an intermediate role in a multi-step process that enhances MoS$_2$ oxidation and NO$_2^-$ reduction. When DO was the only available oxidant, the MoS$_2$ oxidation was relatively sluggish (i.e., Fig. 2). But, in the presence of NO$_2^-$ and DO, the MoS$_2$ oxidation was rapid with subsequent NO$_2^-$ removal and SO$_4^{2-}$ formation at levels much higher than with DO only. When DO was removed through H$_2$ saturation, the NO$_2^-$ reduction and SO$_4^{2-}$ formation decreased and NO$_3^-$ formation was suppressed. Thus, DO was presumably responsible for NO$_2^-$ oxidation to NO$_3^-$.

In the presence of H$_2$, NO$_2^-$ removal and SO$_4^{2-}$ formation for the 2H- and 1T-MoS$_2$ samples appeared to stabilize near the end of the reaction period. These experiments were conducted at a relatively low concentration of NO$_2^-$ (~0.4 mM) compared to the high MoS$_2$ loading (1 g L$^{-1}$). Thus, the observed removal could potentially be due to adsorption of NO$_2^-$ to MoS$_2$. To explore this phenomenon, additional experiments were repeated for 2H-MoS$_2$ with approximately ten times the initial concentration of NO$_2^-$ (i.e., 35.7 mM) (Fig. 4). In the presence of DO (Fig. 4A), NO$_2^-$ removal was approximately 47% after 5 h with an NO$_2^-$ selectivity of 36%. SO$_4^{2-}$ formation was 29% of the total available S, indicating that a substantial portion of the initial MoS$_2$ was oxidized. Both the NO$_2^-$ selectivity and SO$_4^{2-}$ formation were higher in this experiment compared to those at lower NO$_2^-$ initial concentrations (Table 1). Perhaps more interestingly though were results in solutions saturated with H$_2$ (no DO), as the behavior was markedly different (Fig. 4B). After 5 h, the total NO$_2^-$ removal and SO$_4^{2-}$ formation was only 1.6% and 5.4%, respectively. These results confirm that MoS$_2$ oxidation in the presence of NO$_2^-$ is enhanced by DO. We hypothesize that NO$_2^-$/MoS$_2$ interactions are specific to a certain MoS$_2$ sites that are exhausted. When DO is present, a more complex reaction pathway occurs that promotes further degradation of MoS$_2$ and the removal of NO$_2^-$.

For applications that involve the reduction of a target species (e.g., NO$_2^-$), and thus the potential oxidation of MoS$_2$, we caution the use of the word “catalyst” unless the reaction can be verified to be occurring through a truly catalytic pathway and not a sacrificial reduction pathway. Eqn (2)–(4) are examples of the latter, where the edge site S$_2^-$ is oxidized to SO$_4^{2-}$ while reducing either O$_2$(aq), N$_2$O$_2^-$, or H$_2$O (i.e., HER).

\[
\begin{align*}
S_2^{2-} + 2O_2(aq) & \rightarrow SO_4^{2-} \quad (2) \\
3S_2^{2-} + 16NO_2^- + 16H^+ & \rightarrow 6SO_4^{2-} + 8N_2 + 8H_2O \quad (3) \\
S_2^{2-} + 2H_2O & \rightarrow 2SO_4^{2-} + 8H_2 \quad (4)
\end{align*}
\]

To determine whether the MoS$_2$ instability was unique to NO$_2^-$, or was a response to aqueous oxidants in general, the experiment was repeated for 1T-MoS$_2$ using BrO$_3^-$ as an oxidant in the presence and absence of DO (Fig. 5). The instability of 1T-MoS$_2$ with BrO$_3^-$ was similar to NO$_2^-$ (Table 1). In the presence of DO, BrO$_3^-$ removal reached 60% after 7 h, with a bromide (Br$^-$) selectivity of 61% (Fig. 5A). The remainder of BrO$_3^-$ was possibly adsorbed to MoS$_2$. SO$_4^{2-}$ formation was also observed, reaching a maximum of 3.5% of initial total available S. When DO was excluded (Fig. 5B), BrO$_3^-$ removal and SO$_4^{2-}$ formation decreased, reaching values of only 21% and 1.0%, respectively. The Br$^-$ selectivity (68%) was similar to conditions with DO (61%), and it formed steadily throughout the reaction period. Overall, these observed BrO$_3^-$ results presented similar patterns as experiments with NO$_2^-$, suggesting a similar reaction pathway that is not exclusive to NO$_2^-$. The obvious difference is that even in the presence of DO, no oxidation of BrO$_3^-$ was observed due to the instability of perbromate.

Clearly, though proposed as an advanced material for energy and environmental applications,$^{46}$ 2D MoS$_2$ will not be stable in water containing DO and other oxidants unless its surface is modified.

### 3.4 Stability of carbon-coated MoS$_2$

Recently, atomically thin layers of carbon were shown to protect FeP nanoparticles from oxidation under aqueous conditions while maintaining their electrocatalytic activity.$^{59}$ Using a similar method, we investigated the use of a carbon-shell coating for protecting MoS$_2$ exposed to a solution containing a low initial concentration of NO$_2^-$ (~4 mM). Because 1T-MoS$_2$ undergoes phase transition to 2H at approximately 95 °C,$^{67}$ 1T-MoS$_2$ was not appropriate for this coating technique that
requires a carbonization step at 700 °C. 2H–MoS2 was coated with carbon coatings of theoretical thicknesses of approximately 3 nm and 70 nm, and then tested for aqueous stability using similar techniques as previously described. The samples were named according to the dopamine concentration used during the synthesis (0.1 or 3.0 g L⁻¹), and the results of 2H–MoS2/C0.1 and 2H–MoS2/C3 are shown in Fig. 6. For both thicknesses tested, results were markedly different than uncoated 2H–MoS2 under similar conditions (Fig. 3F). NO₂⁻ initially decreased but then steadied after the first hour reaching only 3.1% and 9.8% for 2H–MoS2/C0.1 and 2H–MoS2/C3, respectively. Thus, the carbon shell effectively protected MoS2 from oxidation by NO₂⁻ under the tested conditions. Because the NO₂⁻ did not continue to decrease throughout the reaction period, the observed losses are attributed to adsorption of NO₂⁻ to the carbon surface.

3.5 Electrochemical characterization of 2H–MoS2 and 2H–MoS2/C

The carbon coating of MoS2 used herein deters physical contact between the MoS2 and aqueous species, limiting its use in treatment applications such as adsorption, membrane separation, and heterogeneous catalysis. One of the main proposed applications of nanostructured MoS2 is as an electrocatalyst. In electrochemical systems, electron transfer reactions can still occur through the carbon shell, and in some cases this reaction can still be catalytic (or active). For example, MoS2 may be a suitable electrocatalyst for the HER, requiring a low overpotential to drive the formation of H2 as part of the overall water splitting reaction. In addition, the graphitic nature of the carbon coating may also provide both a conductive pathway for electron transfer and a high surface area for target species adsorption, both of which may enhance the performance of the MoS2 electrode.
To examine the effects of the carbon-shell coating on the electroactivity of MoS$_2$ as an electrocatalyst for the HER, the 2H–MoS$_2$ was coated with three carbon thicknesses corresponding to 0.1, 2, and 3 g L$^{-1}$ additions of dopamine, and then analyzed using LSV. The LSV results (Fig. 7A) were used to obtain the onset potential and the Tafel curve (Fig. 7B). The onset potential is defined herein as the potential required to reach $-0.5$ mA cm$^{-2}$. The Tafel curve was used to obtain the Tafel slope, which indicates the potential required to increase the current ten-fold and is an indicator of the catalytic efficiency. A lower onset potential and Tafel slope implies greater efficiency.

The carbon paper substrate showed little activity at the potential range tested, achieving a maximum current density less than $-0.3$ mA cm$^{-2}$ and a large Tafel slope of 1487 mV per decade. The C–MoS$_2$ electrode had an onset potential and Tafel slope of $-0.325$ V and 891 mV per decade, respectively. It was less active than all 2H–MoS$_2$ electrodes. The onset potential and Tafel slope of the 2H–MoS$_2$ electrode was $-0.115$ V and 451 mV per decade, respectively. Coating the 2H–MoS$_2$ with a carbon shell increased the activity up to a certain thickness. An improvement was observed for the 2H–MoS$_2$/C0.1 and 2H–MoS$_2$/C2 electrodes with an onset potential and Tafel slope of $-0.060$ V and $-0.085$ V and 371 mV per decade and 378 mV per decade, respectively. A decrease in activity was observed for the thickest coated sample, 2H–MoS$_2$/C3, with an onset potential.

**Fig. 6** Removal of NO$_2^-$ and formation of NO$_3^-$ and SO$_4^{2-}$ in the presence of (A) 2H–MoS$_2$/C0.1 and (B) 2H–MoS$_2$/C3. The initial target NO$_2^-$ concentration was approximately 3.75 mM and the MoS$_2$ concentration was 1 g L$^{-1}$. DO was not removed. C0.1 and C3 indicates the g L$^{-1}$ concentration of dopamine used in the synthesis, respectively.

**Fig. 7** (A) Linear sweep voltammograms and (B) Tafel plots for carbon paper and MoS$_2$ electrodes in water (no DO). The supporting electrolyte was 1 N H$_2$SO$_4$. The table in (B) identifies the Tafel slopes (mV per decade).
the stability of the 2H MoS2, as shown previously for water and air matrices.\textsuperscript{54,75,87,89} To protect 2D MoS2 from oxidation, we propose two potential strategies with respect to the electrocatalytic HER that evolved from this research: (1) use pretreated water (e.g., tap water) containing relatively low concentrations of oxidants that is saturated with N2 to remove DO, or (2) add a thin shell of carbon to protect the active edge sites of MoS2, but this may also change reaction mechanisms and reduce catalytic activity. For treatment applications, where MoS2 would be used to reduce or oxidize various contaminants, removing DO may be enough to protect MoS2, even in the presence of naturally occurring oxidants.

Conflicts of interest

The authors declare no conflict of interest.

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