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# Stability of 2H- and 1T-MoS<sub>2</sub> in the presence of aqueous oxidants and its protection by a carbon shell

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Two-dimensional molybdenum disulfide (MoS<sub>2</sub>) is emerging as a catalyst for energy and environmental applications. Recent studies have suggested the stability of MoS<sub>2</sub> is questionable when exposed to oxidizing conditions found in water and air. In this study, the aqueous stability of 2H- and 1T-MoS<sub>2</sub> and 2H-MoS<sub>2</sub> protected with a carbon shell was evaluated in the presence of model oxidants (O<sub>2</sub>, NO<sub>2</sub><sup>-</sup>, BrO<sub>3</sub><sup>-</sup>). The MoS<sub>2</sub> electrocatalytic performance and stability was characterized using linear sweep voltammetry and chronoamperometry. In the presence of dissolved oxygen (DO) only, 2H- and 1T-MoS<sub>2</sub> were relatively stable, with SO<sub>4</sub><sup>2-</sup> formation of only 2.5% and 3.1%, respectively. The presence of NO<sub>2</sub><sup>-</sup> resulted in drastically different results, with SO<sub>4</sub><sup>2-</sup> formations of 11% and 14% for 2H- and 1T-MoS<sub>2</sub>, respectively. When NO<sub>2</sub><sup>-</sup> was present without DO, the 2H- and 1T-MoS<sub>2</sub> remained relatively stable with SO<sub>4</sub><sup>2-</sup> formations of only 4.2% and 3.3%, respectively. Similar results were observed when BrO<sub>3</sub><sup>-</sup> was used as an oxidant. Collectively, these results indicate that the oxidation of 2H- and 1T-MoS<sub>2</sub> 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 MoS<sub>2</sub> from oxidation, a carbon shell was added to 2H-MoS<sub>2</sub>. In a batch suspension in the presence of DO and NO<sub>2</sub><sup>-</sup>, the 2H-MoS<sub>2</sub> with the carbon shell exhibited good stability with no oxidation observed. The activity of 2H-MoS<sub>2</sub> electrodes was then evaluated for the hydrogen evolution reaction by a Tafel analysis. The carbon shell improved the activity of 2H-MoS<sub>2</sub> with a decrease in the Tafel slope from 451 to 371 mV dec<sup>-1</sup>. The electrode stability, characterized by chronopotentiometry, was also enhanced for the 2H-MoS<sub>2</sub> coated with a carbon shell, with no marked degradation in current density observed over the reaction period. Because of the instability exhibited by unprotected MoS<sub>2</sub>, it will only be a useful catalyst if measures are taken to protect the surface from oxidation. Further, given the propensity of MoS<sub>2</sub> to undergo oxidation in aqueous solutions, caution should be used when describing it as a true catalyst for reduction reactions (e.g., H<sub>2</sub> evolution), unless proven otherwise.

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## 1. Introduction

Two-dimensional molybdenum disulfide (2D MoS<sub>2</sub>) is a nano-material that has been extensively investigated for a wide variety of chemical and physical applications due to its unique chemical and physical properties.<sup>1-5</sup> Of the three crystalline phases (3R, 2H, and 1T), 2H-MoS<sub>2</sub> is the most thermodynamically stable structure and has been the most widely studied for chemical functions. 2H-MoS<sub>2</sub> 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.<sup>6</sup> Applications of MoS<sub>2</sub> include, but are not limited to, photocatalysis due to its solar

active band gap of approximately 1.2–1.7 eV,<sup>7-9</sup> catalytic reduction of contaminants,<sup>10</sup> hydrodesulfurization (HDS) catalysis of sulfur containing compounds in petroleum products,<sup>11-14</sup> and electrocatalysis of water for the production of hydrogen gas.<sup>15-19</sup>

The electrocatalytic ability of MoS<sub>2</sub> to generate H<sub>2</sub> was discovered in the 1970's.<sup>20</sup> More recently, 2H-MoS<sub>2</sub> 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.<sup>21</sup> The Mo (1010) disulfide (S<sub>2</sub><sup>2-</sup>) and sulfide (S<sup>2-</sup>) edge sites of 2H-MoS<sub>2</sub> were demonstrated to be highly active for the HER.<sup>22</sup> These groundbreaking studies set the stage for a meaningful effort on optimization of the 2H-MoS<sub>2</sub> nanoparticles for the HER reaction.<sup>6,23-26</sup> Challenges to deployment of 2H-MoS<sub>2</sub> that have been investigated include increasing the active sites per unit volume,<sup>23,27-30</sup> tuning the activity of the catalyst to promote HER by adjusting Δ*G*<sub>sorp</sub>

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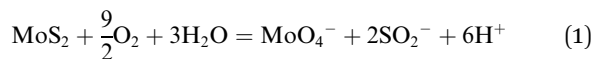
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towards zero,<sup>31–34</sup> and improving the electron transfer kinetics of the catalyst.<sup>7,24,35,36</sup>

1T-MoS<sub>2</sub>, a metastable metallic crystalline phase, has been known since at least the 1970's,<sup>37,38</sup> 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-MoS<sub>2</sub> layers from 2H-MoS<sub>2</sub> stacks using aggressive reagents such as *tert*-butyl lithium, making the technique challenging for wider study.<sup>39</sup> Hydrothermal intercalation of ammonium is a promising alternative synthesis method for 1T-MoS<sub>2</sub>, where high temperature and pressure is used to drive ammonium ions between MoS<sub>2</sub> sheets and exfoliate 1T-MoS<sub>2</sub>.<sup>40,41</sup> 1T-MoS<sub>2</sub> has an octahedral symmetry rather than the trigonal symmetry of 2H-MoS<sub>2</sub>, giving it a metallic band structure that is critical for overcoming electron transfer limitations for electrocatalysis.<sup>28</sup> Further, the octahedral crystal structure shifts the  $\Delta G_{\text{H}}$  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.<sup>42</sup> Due to these properties, 1T-MoS<sub>2</sub> is a more attractive catalyst for the HER than 2H-MoS<sub>2</sub>.<sup>28</sup>

Greater interest in using 2D MoS<sub>2</sub> 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 MoS<sub>2</sub> has been studied as an adsorbent of heavy metals,<sup>43,44</sup> a photocatalyst for various contaminants,<sup>45,46</sup> a membrane separation material,<sup>47,48</sup> an antibacterial agent,<sup>49,50</sup> and a sensor for contaminants.<sup>51</sup> However, thus far, there has been little comprehensive investigation of the stability of MoS<sub>2</sub> under realistic environmental conditions. Other metal sulfides (*e.g.*, ZnS<sup>52</sup> and FeS<sub>2</sub><sup>53</sup>) are known to be unstable under oxidizing conditions, so the evaluation of the MoS<sub>2</sub> stability under relevant conditions is critical. Under more realistic environmental aqueous conditions, the presence of oxygen was shown to cause oxidation of 2D MoS<sub>2</sub>.<sup>54,55</sup> Wang *et al.* demonstrated that 2D MoS<sub>2</sub> oxidizes under aerated aqueous conditions, according to eqn (1):<sup>55</sup>



In the study by Wang *et al.*, dissolution occurred for both 2H- and 1T-MoS<sub>2</sub> with half-lives of approximately 1–30 days, but the dissolution rate was faster for 1T-MoS<sub>2</sub>, due to its larger number of reactive edge sites. This behavior was supported by Lee *et al.*,<sup>54</sup> showing that the oxidation of 2D MoS<sub>2</sub> 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 MoS<sub>2</sub> 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-MoS<sub>2</sub> nanoparticles, and to evaluate the use of a graphitic carbon coating shell as a method for protecting MoS<sub>2</sub> from oxidation. Carbon shells have been shown to increase the stability of MoS<sub>2</sub> for various

applications.<sup>56,57</sup> 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 MoS<sub>2</sub> stability was characterized by measuring the reduction of nitrite or bromate concentrations and the formation of sulfate, a byproduct of MoS<sub>2</sub> oxidation. The electrocatalytic performance and stability of MoS<sub>2</sub> 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-MoS<sub>2</sub> for aqueous applications involving oxidizing conditions.

## 2. Methods and materials

### 2.1 Synthesis of MoS<sub>2</sub> nanoparticles

Commercial MoS<sub>2</sub> nanoparticles (C-MoS<sub>2</sub>) were purchased (Sigma-Aldrich, 804169) to be used as a comparison to the lab-synthesized MoS<sub>2</sub> nanoparticles. 2H-MoS<sub>2</sub> nanoparticles were synthesized by hydrothermal methods adapted from literature.<sup>58</sup> 2H-MoS<sub>2</sub> was synthesized by first dissolving 0.740 g of Na<sub>2</sub>MoO<sub>4</sub> (Alfa Aesar, 12214) in 36 mL of ultrapure water. Then, 254  $\mu\text{L}$  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-MoS<sub>2</sub> was synthesized using adapted method similar to a previous study.<sup>40</sup> First, 1.164 g of (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub> (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-MoS<sub>2</sub>.

### 2.2 Carbon coating of MoS<sub>2</sub> nanoparticles

The MoS<sub>2</sub> was coated with an ultrathin layer of carbon using previously described methods.<sup>59</sup> 0.3 g of the synthesized 2H-MoS<sub>2</sub> nanoparticles were suspended in 80 mL of a 10 mM TRIS buffer (VWR, J831). Then, 0.1, 2.0, or 3.0 g L<sup>-1</sup> of dopamine chloride (Alfa Aesar, A11136) was added to slurry and bath sonicated for 1 hour, during which time dopamine attached to the MoS<sub>2</sub>. 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 N<sub>2</sub> flow, causing the powder to turn black as dopamine was carbonized.

### 2.3 Aqueous stability testing in the presence of nitrite or bromate

The MoS<sub>2</sub> stability in the presence of nitrite (NO<sub>2</sub><sup>-</sup>) or bromate (BrO<sub>3</sub><sup>-</sup>) 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  $1 \text{ g L}^{-1}$  of  $\text{MoS}_2$  and  $\text{NO}_2^-$  or  $\text{BrO}_3^-$  at varying concentrations. The pH of all samples ranged from approximately 6.0 to 6.3, depending on the concentrations of  $\text{NO}_2^-$  and  $\text{BrO}_3^-$  used. Gas bubbling ( $\text{H}_2$  or  $\text{N}_2$ ) was performed by flowing the gas through a glass diffuser into the solution at a flow rate of  $150 \text{ mL min}^{-1}$  to ensure saturation. The total reaction time was 6 h. 1 mL samples were taken at regular intervals and syringe filtered through a  $0.45 \mu\text{m}$  nylon membrane. Samples were subsequently analyzed for concentrations of nitrite, nitrate ( $\text{NO}_3^-$ ),  $\text{BrO}_3^-$ , bromide ( $\text{Br}^-$ ), and sulfate ( $\text{SO}_4^{2-}$ ) 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  $\text{MoS}_2$  materials were collected using a high-resolution transmission electron microscope (TEM; Titan 80–300). Samples were prepped by drop-casting ethanolic suspensions of the  $\text{MoS}_2$  on lacey carbon copper grids. Raman spectra were collected on a Jasco NRS 5100 Micro-Raman spectrometer. The crystal structure was investigated with powder X-ray diffraction (Cu  $K\alpha$ ,  $0.15418 \text{ nm}$ ; Bruker D8 Advance Davinci). The theoretical carbon shell thickness of coated  $\text{MoS}_2$  was estimated assuming spherical  $\text{MoS}_2$  particles and complete attachment and conversion of dopamine to pure carbon.

#### 2.5 Electrochemical characterization of $\text{MoS}_2$ electrodes

$\text{MoS}_2$  electrodes were created by drop casting  $\text{MoS}_2$  suspensions onto carbon paper substrates. Carbon paper (Toray, 5% wet-proof) was cut into  $1.5 \text{ cm} \times 5.0 \text{ cm}$  sheets and placed on an aluminum foil covered hot plate set to  $175 \text{ }^\circ\text{C}$ . 20 mg of  $\text{MoS}_2$  were suspended in 10 mL of ultrapure water and  $62.5 \mu\text{L}$  of 20% Nafion (Ion Power, D-2020-US-25) was added to the suspension and then bath sonicated for 1 h. Then,  $500 \mu\text{L}$  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  $\text{MoS}_2$  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  $\text{H}_2\text{SO}_4$  was used to probe the HER. Prior to analysis, the reactor was bubbled with  $\text{N}_2$  for 20 minutes to flush  $\text{O}_2$ . LSV was conducted at a rate of  $5 \text{ mV s}^{-1}$  from 0.3 to  $-0.4 \text{ V vs. SCE}$ . LSV was repeated three times and potentials adjusted by  $-0.242 \text{ V}$  to correct to the Reversible Hydrogen Electrode (RHE). Tafel plots and slopes were obtained from the

linear portion of the  $\eta \text{ vs. } \log|I|$  taken from the LSV. CA experiments were conducted at  $-0.5 \text{ V vs. SCE}$  for 60 minutes in a solution containing an inert supporting electrolyte, 1 N  $\text{NaClO}_4$ , to reduce solution resistance. Experiments were repeated with the addition of  $7.14 \text{ mM NaNO}_2$  ( $100 \text{ mg-N/L NO}_2^-$ ) to evaluate the stability of the  $\text{MoS}_2$  electrodes in the presence of  $\text{NO}_2^-$ . 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- $\text{MoS}_2$  and C- $\text{MoS}_2$  nanoparticles. The size and shape differences of the two are obvious, with the 2H- $\text{MoS}_2$  consisting of particles/sheets less than  $100 \text{ nm}$  in diameter (Fig. 1A) and the C- $\text{MoS}_2$  (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- $\text{MoS}_2$  particles. The  $\text{MoS}_2$  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- $\text{MoS}_2$  particles, while the 1T- $\text{MoS}_2$  sample had similar but shifted peaks indicative of the 1T crystalline phase. The resolution of the diffraction pattern for the 2H- $\text{MoS}_2$  particles was poor, despite using a long dwell time at each  $2\theta$  ( $>2 \text{ s}$ ). While poor resolution often indicates low crystallinity, peak broadening and low resolution are consistent with nano-sized  $\text{MoS}_2$ ,<sup>40,58</sup> and the behavior may be attributed to the poor interaction of the single or few layer  $\text{MoS}_2$  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  $E_{1g}$  ( $280 \text{ cm}^{-1}$ ),  $^1E_{2g}$  ( $375 \text{ cm}^{-1}$ ), and  $A_{1g}$  ( $404 \text{ cm}^{-1}$ ) vibrations of the 2H crystalline phase,<sup>60</sup> while peaks at  $156$ ,  $225$ ,  $235$ , and  $333 \text{ cm}^{-1}$  are generated by 1T phases marked by the green dashed lines.<sup>40</sup> The spectra of C- $\text{MoS}_2$  and 2H- $\text{MoS}_2$  showed only characteristic peaks of the 2H crystalline phase, while the 1T- $\text{MoS}_2$  spectrum showed characteristic peaks of both 2H and 1T crystalline phases. The nature of the characterized  $\text{MoS}_2$  species can be summarized as follows: 1T- $\text{MoS}_2$  consists of a mixture of single layer 1T and 2H few layer nanoparticles, the 2H- $\text{MoS}_2$  consists of few-layer 2H nanoparticles, and the C- $\text{MoS}_2$  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  $\text{MoS}_2$  materials was evaluated in water containing only dissolved oxygen (DO), which was approximately  $0.26 \text{ mM}$  at conditions tested. The oxidation of  $\text{MoS}_2$  was measured by tracking the byproduct  $\text{SO}_4^{2-}$ , reported as a percent of the total available S in the system (Fig. 2). For each  $\text{MoS}_2$  sample, an immediate increase in  $\text{SO}_4^{2-}$  upon exposure to water was observed, which is presumably due to the rapid oxidation of the surface  $\text{MoS}_2$  into  $\text{Mo}_x\text{O}_y^{n-}$  species



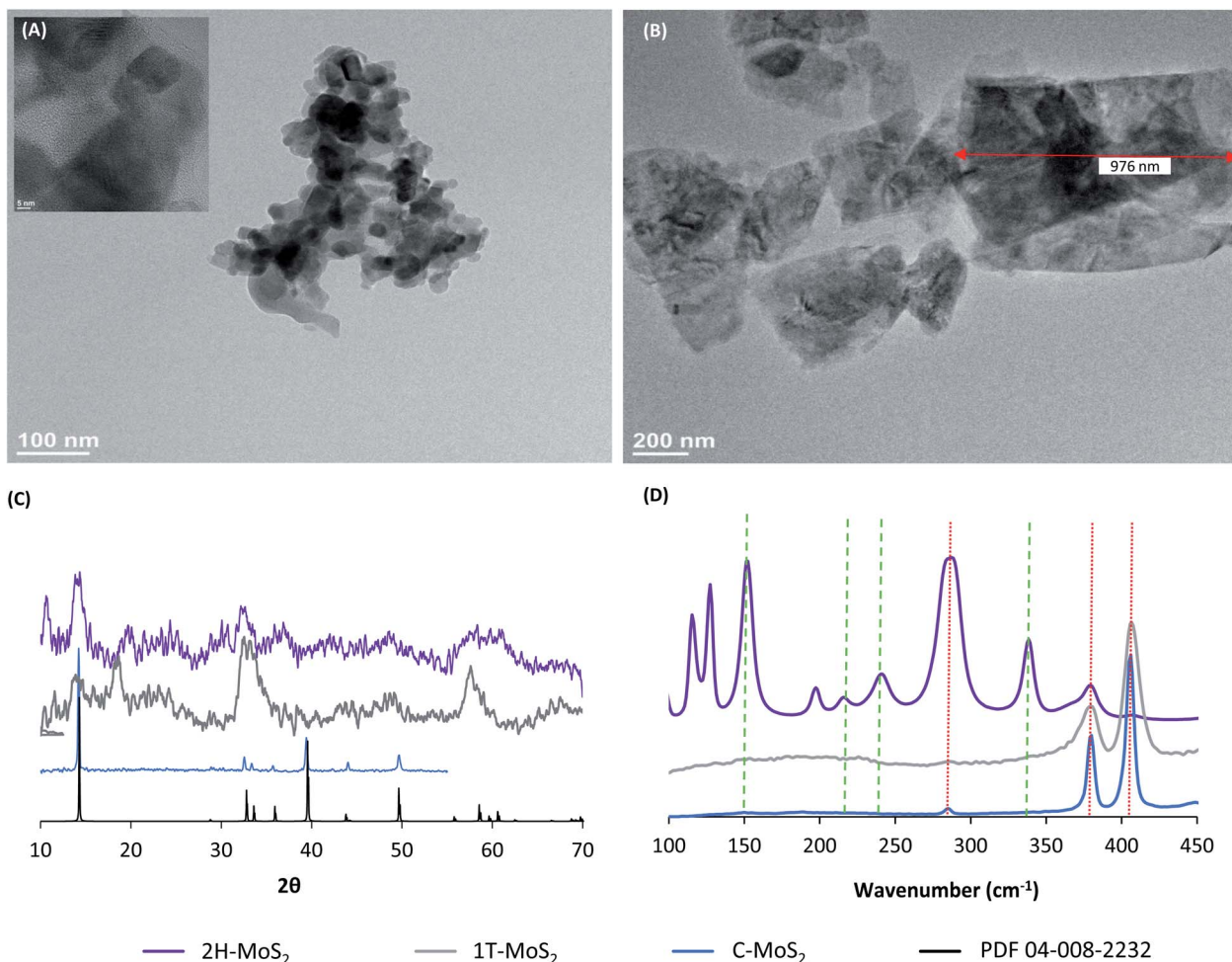


Fig. 1 TEM images of (A) 2H-MoS<sub>2</sub> and (B) C-MoS<sub>2</sub> nanoparticles showing difference in particle sizes and crystallinity, (C) pXRD diffractogram of MoS<sub>2</sub> materials, (D) Raman spectra of MoS<sub>2</sub> species; red dotted lines indicate 2H crystallinity and green dashed lines indicate 1T crystallinity.

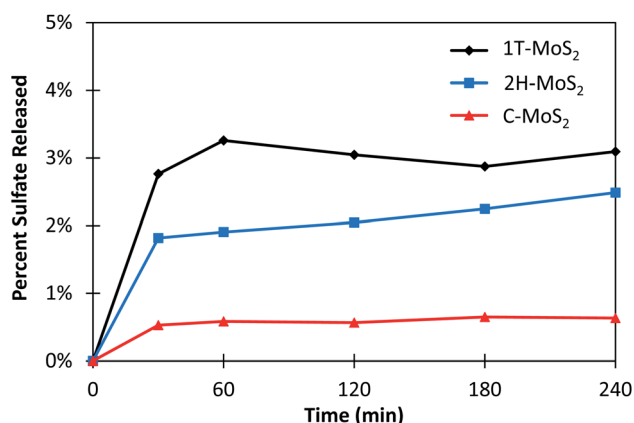


Fig. 2 Dissolution of sulfate measured as a percent of the total available sulfur in solution. 1 g L<sup>-1</sup> of MoS<sub>2</sub> was used in each experiment.

(i.e., eqn (1)). Differences in SO<sub>4</sub><sup>2-</sup> 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 SO<sub>4</sub><sup>2-</sup>

concentration stabilized for 1T- and C-MoS<sub>2</sub> and increased only slightly for 2H-MoS<sub>2</sub> over the time-period tested. The total oxidation of MoS<sub>2</sub>, reported as the percentage of total sulfur in the system converted to SO<sub>4</sub><sup>2-</sup>, was 0.63%, 2.5%, and 3.1% for C-MoS<sub>2</sub>, 2H-MoS<sub>2</sub>, and 1T-MoS<sub>2</sub>, respectively (Table 1). Overall, the MoS<sub>2</sub> materials were relatively stable over the 4 hour measurement period. These results agree with the comparatively long reported half-lives of 2H- and 1T-MoS<sub>2</sub> stability in aqueous solution of up to 30 days.<sup>52</sup>

### 3.3 Effect of nitrite and bromate on MoS<sub>2</sub> stability

The stability of MoS<sub>2</sub> was tested against NO<sub>2</sub><sup>-</sup> and BrO<sub>3</sub><sup>-</sup> as aqueous oxidants because they are known to be easily reduced in the presence of suitable reductants.<sup>61-64</sup> 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 NO<sub>2</sub><sup>-</sup> and the subsequent formation of NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> in the presence of C-, 2H-, and 1T-MoS<sub>2</sub>. The results are summarized in Table 1. Experiments were conducted in the presence of DO and then repeated under H<sub>2</sub> saturated conditions. For C-MoS<sub>2</sub> in the presence of DO (Fig. 3A), NO<sub>2</sub><sup>-</sup> was



Table 1 Summary of results for the batch stability experiments for C-, 2H-, and 1T-MoS<sub>2</sub> under varying conditions

MoS <sub>2</sub> sample	Condition	Initial NO <sub>2</sub> <sup>-</sup> concentration (mM)	NO <sub>2</sub> <sup>-</sup> or BrO <sub>3</sub> <sup>-</sup> removal (%)	NO <sub>2</sub> <sup>-</sup> or Br <sup>-</sup> selectivity (%)	SO <sub>4</sub> <sup>2-</sup> formation (of total available S)
C-MoS <sub>2</sub>	DO	0	—	—	0.63%
C-MoS <sub>2</sub>	DO, NO <sub>2</sub> <sup>-</sup>	3.57	9.4%	0%	0.54%
C-MoS <sub>2</sub>	H <sub>2</sub> , NO <sub>2</sub> <sup>-</sup>	3.57	16%	0%	0.44%
2H-MoS <sub>2</sub>	DO	0	—	—	2.5%
2H-MoS <sub>2</sub>	DO, NO <sub>2</sub> <sup>-</sup>	3.57	100%	7.4%	11%
2H-MoS <sub>2</sub>	H <sub>2</sub> , NO <sub>2</sub> <sup>-</sup>	3.57	88%	2.0%	4.2%
2H-MoS <sub>2</sub>	DO, NO <sub>2</sub> <sup>-</sup> (high)	35.7	46%	16%	29%
2H-MoS <sub>2</sub>	H <sub>2</sub> , NO <sub>2</sub> <sup>-</sup> (high)	35.7	2%	1%	5%
1T-MoS <sub>2</sub>	DO	0	—	—	3.1%
1T-MoS <sub>2</sub>	DO, NO <sub>2</sub> <sup>-</sup>	3.57	100%	8.3%	14%
1T-MoS <sub>2</sub>	H <sub>2</sub> , NO <sub>2</sub> <sup>-</sup>	3.57	84%	3.2%	3.3%
1T-MoS <sub>2</sub>	DO, BrO <sub>3</sub> <sup>-</sup>	0.75	60%	61%	3.5%
1T-MoS <sub>2</sub>	H <sub>2</sub> , BrO <sub>3</sub> <sup>-</sup>	0.75	21%	68%	1.0%

initially removed but reached a steady-state of 9.5% removal after 2 h. SO<sub>4</sub><sup>2-</sup> was formed in conjunction with NO<sub>2</sub><sup>-</sup> removal, reaching a steady-state value of only 0.55% of the total available

S, which was similar to conditions without NO<sub>2</sub><sup>-</sup> (*i.e.*, Fig. 2). Thus, NO<sub>2</sub><sup>-</sup> did not have a major impact on C-MoS<sub>2</sub> oxidation, and the observed NO<sub>2</sub><sup>-</sup> removal can be presumably attributed

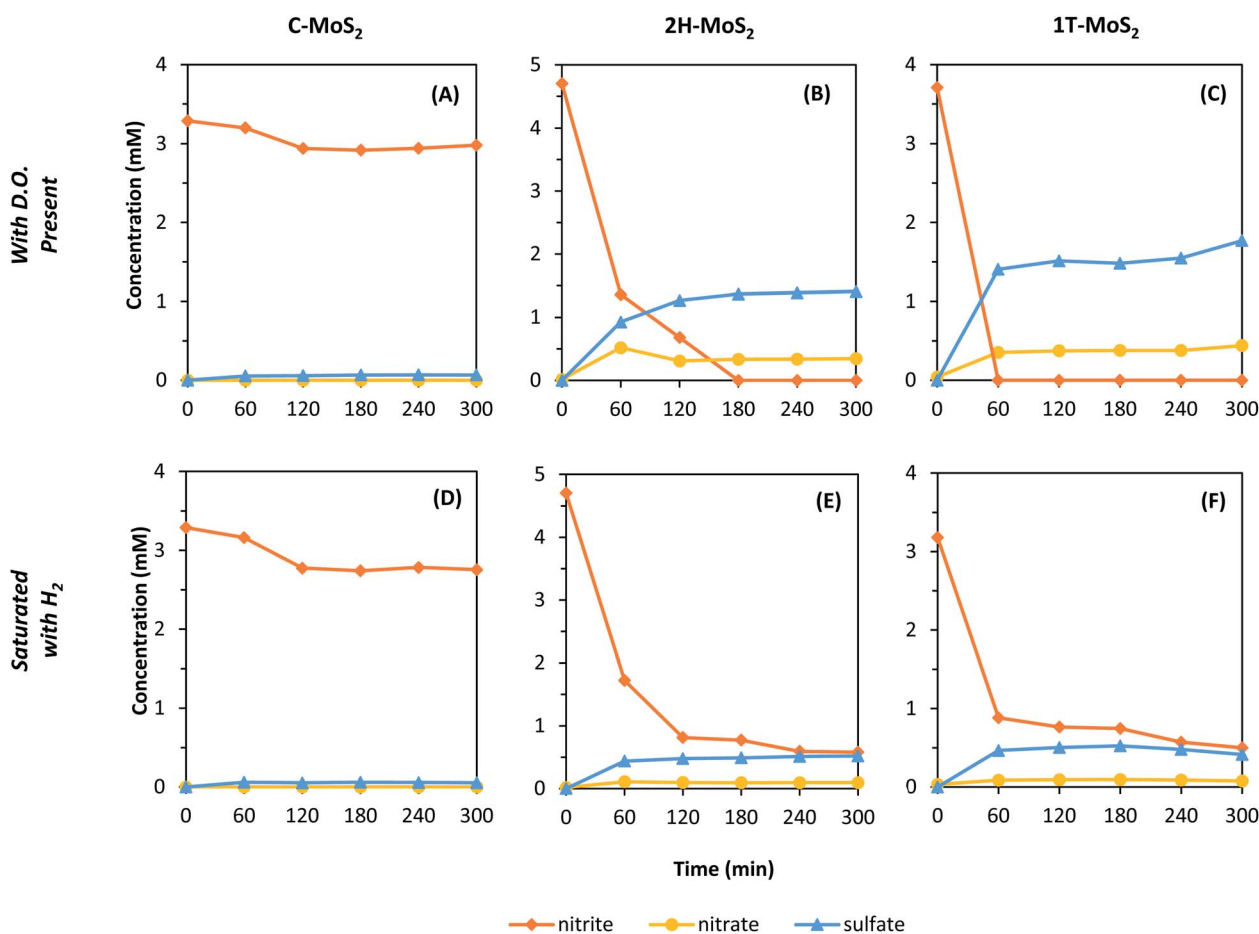


Fig. 3 Loss of NO<sub>2</sub><sup>-</sup> and formation of NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> in the presence of MoS<sub>2</sub> materials. (A–C) are samples with dissolved O<sub>2</sub> and (D–F) are samples that were saturated with H<sub>2</sub>; (A and D) C-MoS<sub>2</sub>, (B and E) 2H-MoS<sub>2</sub>, and (C and F) 1T-MoS<sub>2</sub>. The initial target NO<sub>2</sub><sup>-</sup> concentration was approximately 3.5–4.5 mM in all experiments and the MoS<sub>2</sub> concentration was 1 g L<sup>-1</sup>.



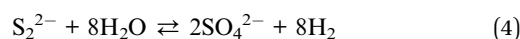
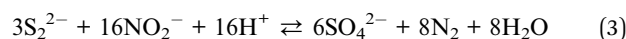
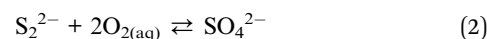
to adsorption of  $\text{NO}_2^-$  to C-MoS<sub>2</sub> or to surface oxidation of C-MoS<sub>2</sub>. For the 2H- and 1T-MoS<sub>2</sub> samples in the presence of DO (Fig. 3B and C),  $\text{NO}_2^-$  was completely removed within 3 h and 1 h, respectively. The formation of  $\text{SO}_4^{2-}$  increased to 11.5% and 13.5% of the total available S for 2H-MoS<sub>2</sub> and 1T-MoS<sub>2</sub>, respectively, indicating the MoS<sub>2</sub> oxidation increased compared to conditions without  $\text{NO}_2^-$  (*i.e.*, Fig. 2).  $\text{NO}_3^-$  formation was also observed for 2H-MoS<sub>2</sub> and 1T-MoS<sub>2</sub> experiments, with a selectivity of 7.7% and 8.3% of the initial N, respectively.  $\text{NO}_3^-$  is a byproduct of  $\text{NO}_2^-$  oxidation, which is somewhat unexpected considering the oxidation of MoS<sub>2</sub> would result in  $\text{NO}_2^-$  reduction. After the reaction was complete, the 2H- and 1T-MoS<sub>2</sub> samples exhibited a bluish color, indicating the formation of Mo(v) species.<sup>65</sup>

MoS<sub>2</sub> could potentially be acting as a hydrogenation catalyst (*i.e.*, H<sub>2</sub> dissociation) and DO may play an intermediate role in the reaction. Thus, to investigate these effects, experiments were repeated with H<sub>2</sub> saturated water with limited DO (Fig. 3D–F). For C-MoS<sub>2</sub>, similar results were observed compared to the experiment with DO, suggesting no specific mechanism related to DO or H<sub>2</sub>. The 2H- and 1T-MoS<sub>2</sub> materials showed more response to the exclusion of DO and presence of H<sub>2</sub>, with smaller changes in  $\text{NO}_2^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{NO}_3^-$  concentrations observed (Table 1). Again, the  $\text{NO}_2^-$  removal was initially rapid for 2H- and 1T-MoS<sub>2</sub>, but then stabilized within 2 h. Though the total  $\text{NO}_2^-$  reduction was still high, with observed removals of 93% (2H-MoS<sub>2</sub>) and 81% (1T-MoS<sub>2</sub>), the  $\text{SO}_4^{2-}$  formation decreased to 4.3% (2H-MoS<sub>2</sub>) and 4.5% (1T-MoS<sub>2</sub>) of the total available S, respectively. These results suggest DO serves an intermediate role in a multi-step process that enhances MoS<sub>2</sub> oxidation and  $\text{NO}_2^-$  reduction. When DO was the only available oxidant, the MoS<sub>2</sub> oxidation was relatively sluggish (*i.e.*, Fig. 2). But, in the presence of  $\text{NO}_2^-$  and DO, the MoS<sub>2</sub> oxidation was rapid with subsequent  $\text{NO}_2^-$  removal and  $\text{SO}_4^{2-}$  formation at levels much higher than with DO only. When DO was removed through H<sub>2</sub> saturation, the  $\text{NO}_2^-$  reduction and  $\text{SO}_4^{2-}$  formation decreased and  $\text{NO}_3^-$  formation was suppressed. Thus, DO was presumably responsible  $\text{NO}_2^-$  oxidation to  $\text{NO}_3^-$ . Further, the reactions were retarded in the presence of H<sub>2</sub>, suggesting that the mechanism of  $\text{NO}_2^-$  reduction is not related to catalytic hydrogenation such as that when using palladium.<sup>64</sup>

In the presence of H<sub>2</sub>,  $\text{NO}_2^-$  removal and  $\text{SO}_4^{2-}$  formation for the 2H- and 1T-MoS<sub>2</sub> samples appeared to stabilize near the end of the reaction period. These experiments were conducted at a relatively low concentration of  $\text{NO}_2^-$  (~0.4 mM) compared to the high MoS<sub>2</sub> loading (1 g L<sup>-1</sup>). Thus, the observed removal could potentially be due to adsorption of  $\text{NO}_2^-$  to MoS<sub>2</sub>. To explore this phenomenon, additional experiments were repeated for 2H-MoS<sub>2</sub> with approximately ten times the initial concentration of  $\text{NO}_2^-$  (*i.e.*, 35.7 mM) (Fig. 4). In the presence of DO (Fig. 4A),  $\text{NO}_2^-$  removal was approximately 47% after 5 h with an  $\text{NO}_3^-$  selectivity of 36%.  $\text{SO}_4^{2-}$  formation was 29% of the total available S, indicating that a substantial portion of the initial MoS<sub>2</sub> was oxidized. Both the  $\text{NO}_3^-$  selectivity and  $\text{SO}_4^{2-}$  formation were higher in this experiment compared to those at lower  $\text{NO}_2^-$  initial concentrations (Table 1). Perhaps more interestingly though were results in solutions saturated with H<sub>2</sub>

(no DO), as the behavior was markedly different (Fig. 4B). After 5 h, the total  $\text{NO}_2^-$  removal and  $\text{SO}_4^{2-}$  formation was only 1.6% and 5.4%, respectively. These results confirm that MoS<sub>2</sub> oxidation in the presence of  $\text{NO}_2^-$  is enhanced by DO. We hypothesize that  $\text{NO}_2^-/\text{MoS}_2$  interactions are specific to a certain MoS<sub>2</sub> sites that are exhausted. When DO is present, a more complex reaction pathway occurs that promotes further degradation of MoS<sub>2</sub> and the removal of  $\text{NO}_2^-$ . It is possible that this stepwise reaction occurs through the oxidative bridging of S<sup>2-</sup> sites to S<sub>2</sub><sup>2-</sup> with DO,<sup>65</sup> which may then react with  $\text{NO}_2^-$  to form  $\text{SO}_4^{2-}$  (*e.g.*, eqn (3)).

For applications that involve the reduction of a target species (*e.g.*,  $\text{NO}_2^-$ ), and thus the potential oxidation of MoS<sub>2</sub>, 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<sub>2</sub><sup>2-</sup> is oxidized to  $\text{SO}_4^{2-}$  while reducing either O<sub>2(aq)</sub>,  $\text{NO}_2^-$ , or H<sub>2</sub>O (*i.e.*, HER).



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

Clearly, though proposed as an advanced material for energy and environmental applications,<sup>66</sup> 2D MoS<sub>2</sub> will not be stable in water containing DO and other oxidants unless its surface is modified.

### 3.4 Stability of carbon-coated MoS<sub>2</sub>

Recently, atomically thin layers of carbon were shown to protect FeP nanoparticles from oxidation under aqueous conditions while maintaining their electrocatalytic activity.<sup>59</sup> Using a similar method, we investigated the use of a carbon-shell coating for protecting MoS<sub>2</sub> exposed to a solution containing a low initial concentration of  $\text{NO}_2^-$  (~4 mM). Because 1T-MoS<sub>2</sub> undergoes phase transition to 2H at approximately 95 °C,<sup>67</sup> 1T-MoS<sub>2</sub> was not appropriate for this coating technique that



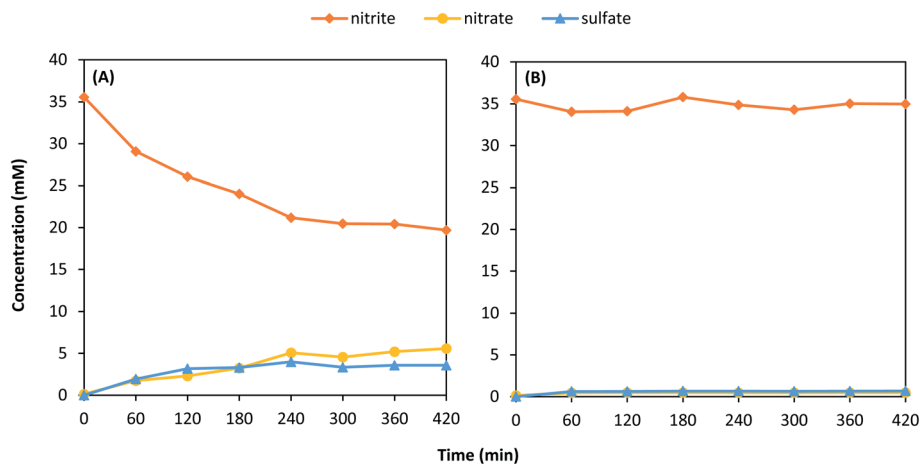


Fig. 4 Removal of  $\text{NO}_2^-$  and formation of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  with initial concentrations of  $35.7 \text{ mM NO}_2^-$  and  $1 \text{ g L}^{-1} 2\text{H-MoS}_2$  for conditions (A) in the presence of DO and (B) under  $\text{H}_2$  saturated conditions.

requires a carbonization step at  $700^\circ\text{C}$ .  $2\text{H-MoS}_2$  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  $3.0 \text{ g L}^{-1}$ ), and the results of  $2\text{H-MoS}_2/\text{C}0.1$  and  $2\text{H-MoS}_2/\text{C}3$  are shown in Fig. 6. For both thicknesses tested, results were markedly different than uncoated  $2\text{H-MoS}_2$  under similar conditions (Fig. 3F).  $\text{NO}_2^-$  initially decreased but then steadied after the first hour reaching only 3.1% and 9.8% for  $2\text{H-MoS}_2/\text{C}0.1$  and  $2\text{H-MoS}_2/\text{C}3$ , respectively. Thus, the carbon shell effectively protected  $\text{MoS}_2$  from oxidation by  $\text{NO}_2^-$  under the tested conditions. Because the  $\text{NO}_2^-$  did not continue to decrease throughout the reaction period, the observed losses are attributed to adsorption of  $\text{NO}_2^-$  to the carbon surface.

### 3.5 Electrochemical characterization of $2\text{H-MoS}_2$ and $2\text{H-MoS}_2/\text{C}$

The carbon coating of  $\text{MoS}_2$  used herein deters physical contact between the  $\text{MoS}_2$  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  $\text{MoS}_2$  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).<sup>59</sup> For example,  $\text{MoS}_2$  may be a suitable electrocatalyst for the HER, requiring a low overpotential to drive the formation of  $\text{H}_2$  as part of the overall water splitting reaction.<sup>68</sup> 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  $\text{MoS}_2$  electrode.

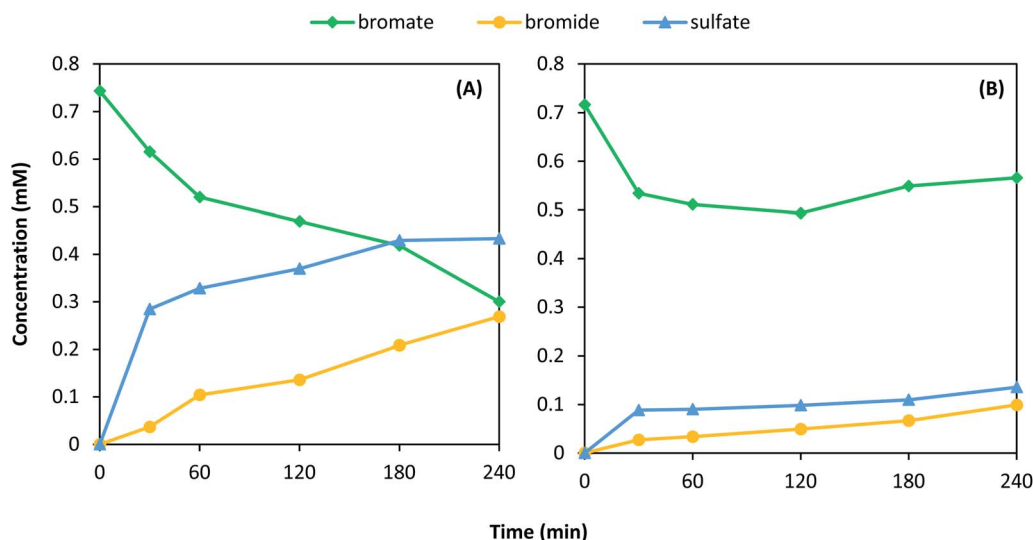


Fig. 5 Removal of  $\text{BrO}_3^-$  and formation of  $\text{Br}^-$  and  $\text{SO}_4^{2-}$  with initial  $\text{BrO}_3^-$  concentration of  $0.75 \text{ mM NaBrO}_3$  and  $1\text{T-MoS}_2$  under (A) atmospheric conditions and (B)  $\text{H}_2$  bubbling.



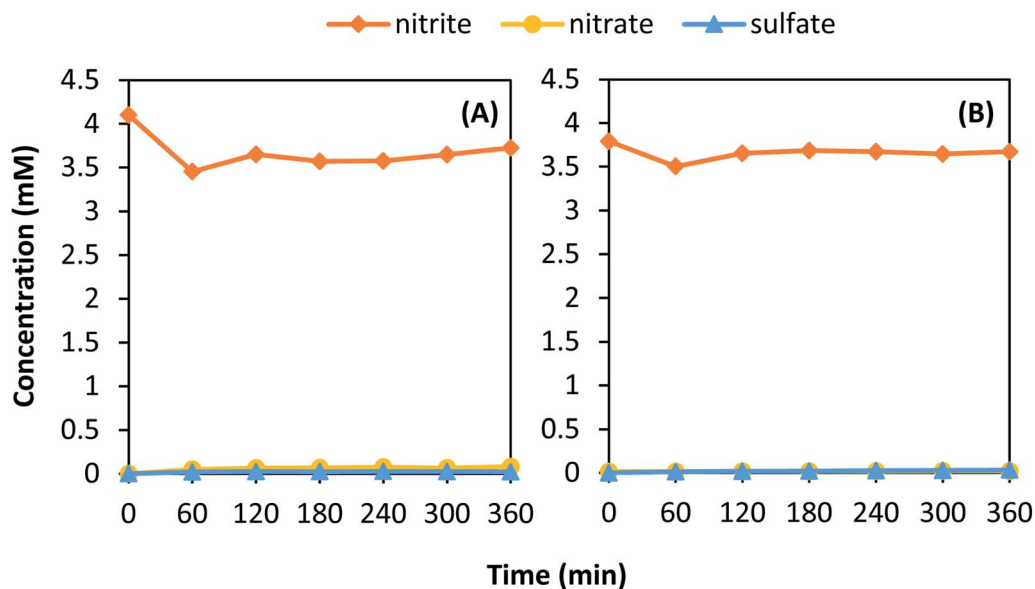


Fig. 6 Removal of  $\text{NO}_2^-$  and formation of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  in the presence of (A) 2H-MoS<sub>2</sub>/C0.1 and (B) 2H-MoS<sub>2</sub>/C3. The initial target  $\text{NO}_2^-$  concentration was approximately 3.75 mM and the MoS<sub>2</sub> concentration was 1 g L<sup>-1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

To examine the effects of the carbon-shell coating on the electroactivity of MoS<sub>2</sub> as an electrocatalyst for the HER, the 2H-MoS<sub>2</sub> was coated with three carbon thicknesses corresponding to 0.1, 2, and 3 g L<sup>-1</sup> 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  $-0.5 \text{ mA cm}^{-2}$ . 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  $-0.3 \text{ mA cm}^{-2}$  and a large Tafel slope of 1487 mV per decade. The C-MoS<sub>2</sub> electrode had an onset potential and Tafel slope of  $-0.325 \text{ V}$  and 898 mV per decade, respectively. It was less active than all 2H-MoS<sub>2</sub> electrodes. The onset potential and Tafel slope of the 2H-MoS<sub>2</sub> electrode was  $-0.115 \text{ V}$  and 451 mV per decade, respectively. Coating the 2H-MoS<sub>2</sub> with a carbon shell increased the activity up to a certain thickness. An improvement was observed for the 2H-MoS<sub>2</sub>/C0.1 and 2H-MoS<sub>2</sub>/C2 electrodes with an onset potential and Tafel slope of  $-0.060 \text{ V}$  and  $-0.085 \text{ V}$  and 371 mV per decade and 378 mV per decade, respectively. A decrease in activity was observed for the thickest coated sample, 2H-MoS<sub>2</sub>/C3, with an onset potential

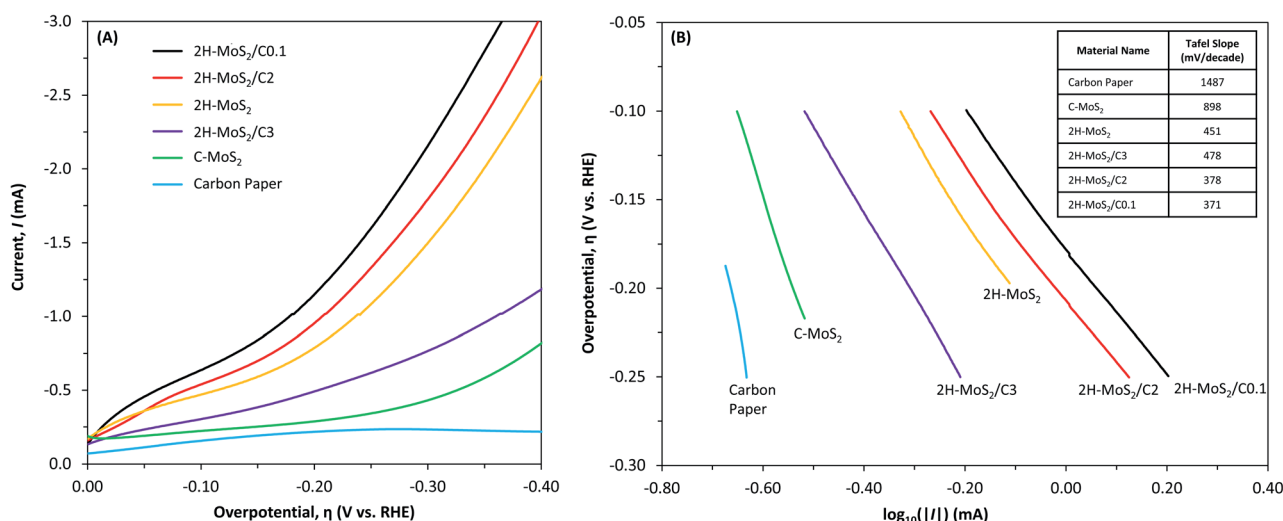


Fig. 7 (A) Linear sweep voltammograms and (B) Tafel plots for carbon paper and MoS<sub>2</sub> electrodes in water (no DO). The supporting electrolyte was 1 N H<sub>2</sub>SO<sub>4</sub>. The table in (B) identifies the Tafel slopes (mV per decade).



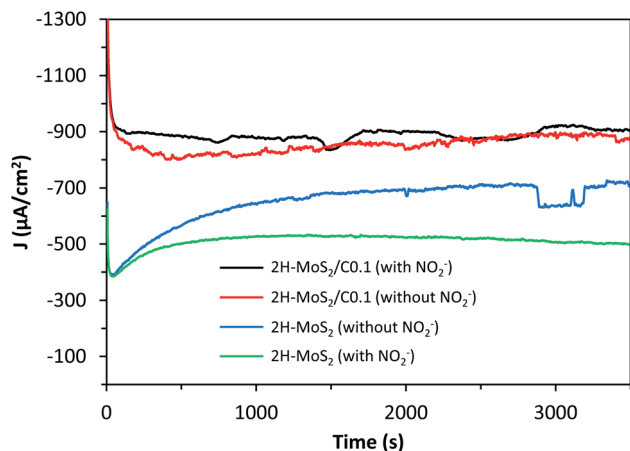


Fig. 8 Chronoamperometry of 2H-MoS<sub>2</sub> and 2H-MoS<sub>2</sub>/C0.1 electrodes in the absence and presence of NO<sub>2</sub><sup>-</sup> (7.14 mM). The applied potential was -0.5 V vs. RHE. Samples were degassed with N<sub>2</sub> prior to measurement. The observed noise in current density is due to effects from stirring.

and Tafel slope of -0.205 V and 478 mV per decade, respectively.

One of the major issues with MoS<sub>2</sub> is its stability when in contact with oxidants, yet the carbon shell may provide some protection while enhancing its activity. The effect of NO<sub>2</sub><sup>-</sup> on the stability of the 2H-MoS<sub>2</sub> and 2H-MoS<sub>2</sub>/C0.1 electrodes was evaluated by characterizing changes in the current density over time at a constant potential (Fig. 8). After 5 h of operation, the current density of the 2H-MoS<sub>2</sub> and 2H-MoS<sub>2</sub>/C0.1 samples was -695 and -820 µA cm<sup>-2</sup>, respectively. In the presence of NO<sub>2</sub><sup>-</sup>, the current densities changed to -500 and -890 µA cm<sup>-2</sup>, respectively. This change corresponds to a major decrease in the absolute current density for the unprotected 2H-MoS<sub>2</sub>, and its current density steadily degraded over time with no apparent steady-state condition reached over the time period tested. Thus, the 2H-MoS<sub>2</sub> electrode was not stable in the presence of NO<sub>2</sub><sup>-</sup>, even under cathodic, reducing conditions. For the protected 2H-MoS<sub>2</sub>/C0.1, relatively no change in the current density was observed in the presence of NO<sub>2</sub><sup>-</sup>, and the increased current density over the unprotected 2H-MoS<sub>2</sub> is attributed to the carbon shell.

## 4. Conclusions

2D MoS<sub>2</sub> has been proposed as a potential sustainable replacement for platinum in energy and environmental applications ranging from electrocatalytic hydrogen production to photocatalytic treatment of contaminants. Due to oxidation of the S<sup>2-</sup> and S<sub>2</sub><sup>2-</sup> edge sites, the 2H and 1T structures of 2D MoS<sub>2</sub> are not suitable catalysts for most applications involving water without altering the water matrix or the MoS<sub>2</sub>. In the presence of DO, NO<sub>2</sub><sup>-</sup> and BrO<sub>3</sub><sup>-</sup> had an obvious negative impact on the stability of 2D MoS<sub>2</sub>, yet the exact reaction mechanism and pathway describing the synergistic effect needs to be elucidated. The observed dissolution of MoS<sub>2</sub> will also presumably cause

structural changes to MoS<sub>2</sub>, as shown previously for water and air matrices.<sup>54,55,65,69</sup> To protect 2D MoS<sub>2</sub> 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 N<sub>2</sub> to remove DO, or (2) add a thin shell of carbon to protect the active edge sites of MoS<sub>2</sub>, but this may also change reaction mechanisms and reduce catalytic activity. For treatment applications, where MoS<sub>2</sub> would be used to reduce or oxidize various contaminants, removing DO may be enough to protect MoS<sub>2</sub>, even in the presence of naturally occurring oxidants.

## Conflicts of interest

The authors declare no conflict of interest.

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