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Mechanochemical Coupling of MoS₂ and Perovskites for Hydrogen Generation

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Abstract

In this contribution, we propose to couple MoS₂ with a perovskite oxide via ball milling, which activates the MoS₂ and protects the perovskite oxide. Among the different MoS₂/perovskite combinations studied, MoS₂/LaNiO_{3-δ} (LNO) stands out as the most active material towards hydrogen evolution reaction (HER) with a performance far beyond that of pristine and milled LNO and MoS₂ alone in both alkaline and acidic electrolytes. It is likely that, in alkaline media LNO works as a hydroxyl acceptor, reducing the charge transfer resistance during water disassociation. In contrast, in acidic solutions the electronic interaction occurring in the MoS₂/LNO hybrid contributes to a higher proportion of terminal S₂²⁻ and S²⁻ ions, leading to an increased number of active sites. This contribution serves as the first report of a hybrid material combining the strength of MoS₂ and perovskite oxides, opening up new opportunities to boost the HER activity of transition metal dichalcogenides.

1. Introduction

Hydrogen is among the most environment-friendly and sustainable energy carriers available and it may eventually replace fossil fuels.¹ In that regard, hydrogen production by splitting water is a critically important process for advanced energy conversion and storage systems.²⁻³ Developing highly-efficient and durable hydrogen evolution reaction (HER) catalysts is the cornerstone to enabling water electrolysis and, therefore, has recently stimulated intense research activities.⁴⁻⁵ The state-of-the-art HER catalysts are Pt-based materials, whose high cost and lack of abundance hinder the widespread commercialization of the electrolysis technology. Therefore, catalysts based on non-precious elements with high HER activity are highly needed. Transition metals as well as their sulfides, phosphides, nitrides, and carbides have shown great potential towards HER.⁶⁻¹⁴ Among them, MoS₂ is among the most intensively investigated material due to its promising HER activity, especially in acidic solutions.¹⁵⁻¹⁷ Experimental and computational works have shown that the high activity of MoS₂ towards HER is attributed to its edges, while the bulk of the material is catalytically inert.¹⁸⁻²¹ Researchers have prepared MoS₂ with nanoscale structures and/or internal defects to increase the number of active sites.²²⁻²⁵ In addition, MoS₂ has been also coupled with various conductive supports (*e.g.*, mesoporous carbon, graphene, Au, or Ni) to improve the conductivity and enhance the catalytic activity.²⁶⁻³² However, most of the above methods are designed for HER in acidic electrolytes, and the HER activity of MoS₂ in alkaline electrolytes is still far from satisfactory.³³⁻³⁴ Moreover, many of the proposed strategies involve complex processes,³⁵ which are difficult and expensive especially when scaled-up in industrial applications. Non-precious metal oxides are mostly employed as catalysts for oxygen reactions.³⁶⁻³⁷ In particular, perovskite oxides (ABO₃) have been intensively investigated as oxygen evolution reaction (OER) and oxygen reduction reaction (ORR) catalysts, due to their flexible composition and electronic

structure.³⁸⁻⁴¹ In addition to alkaline electrolytes, perovskite oxides have been also investigated as highly-active OER electrocatalysts in acidic solutions.⁴² Recently, various researchers have reported non-precious metal oxides as highly active HER catalysts,⁴³⁻⁴⁴ and there have been several attempts to use perovskite oxides as alkaline HER electrocatalysts.⁴³⁻⁴⁵ For example, our group has reported that a layered double perovskite oxide ($\text{NdBaMn}_2\text{O}_{5.5}$) has a moderate HER activity in 1 M KOH. However, the HER activity of perovskite oxides is still not comparable to that of traditional catalysts. More importantly, perovskite oxides are subject to corrosion and are not durable during cycling,⁴⁶ especially in acidic media. Therefore, it is challenging to employ perovskite oxides in HER applications.

In contrast to the acidic HER electrolysis where the hydrogen adsorption usually plays a dominant role, in alkaline electrolytes the binding of surface hydroxyl species is also critical.⁴⁷⁻⁴⁸ MoS_2 has a near-optimal hydrogen adsorption energy near 0 eV,¹⁹ however, its capability to adsorb hydroxyl species is not efficient, leading to a poor HER activity in alkaline media.⁴⁹ In order to overcome this issue, coupling MoS_2 with OER-active materials, which can effectively bind and dissociate the hydroxyl species, has recently triggered significant interest from the research community.^{34, 50-51} For example, NiCo layered double hydroxides (LDHs) hybridized with MoS_2 , which are prepared by a two-step hydrothermal synthesis, have been reported to significantly boost the HER activity in alkaline electrolytes.³⁴

In this work, we hybridize MoS_2 with $\text{LaNiO}_{3-\delta}$ (LNO) using a facile ball-milling process. MoS_2 coupled with $\text{Ba}_{0.95}\text{La}_{0.05}\text{FeO}_{3-\delta}$ (BLF), $\text{Pr}_{0.5}(\text{Ba}_{0.5}\text{Sr}_{0.5})_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (PBSCF), and CuO , were also prepared for comparison. The selection of these oxides is motivated by their promising oxygen catalytic activity.⁵²⁻⁵⁴ For example, the OER mass activity of LNO was reported to be ~ 3 -fold that of IrO_2 ;⁵⁵ A dendritic nanostructured CuO has been reported to catalyze 10 mA cm^{-2} at an

overpotential of only 290 mV in 1 M NaOH;⁵³ For PBSCF, its OER activity is found similar to that of RuO₂ in 1 M KOH.⁵⁴ Furthermore, mechanical ball-milling is an economically friendly and scalable method to exfoliate two dimensional materials including MoS₂, graphene, and boron nitride,⁵⁶⁻⁵⁷ and it has been used as a facile approach to prepare mixed composites.⁵⁸⁻⁶⁰ During ball milling, MoS₂ can be activated thanks to the creation of additional defects and the exposure of a greater concentration of edge sites.⁶¹⁻⁶² In addition, both the intimate physical contact and the electronic interaction between the phases constituting the hybrid materials may improve the corrosion tolerance.⁵⁸⁻⁶⁰ From the results, the milled hybrid exhibits a much higher HER activity than the milled MoS₂ and corresponding metal oxides alone. In addition, the milled MoS₂/LNO hybrid achieves the highest HER activity among the materials studied. We should also note that MoS₂/LNO is able to catalyze HER stably in both acidic and alkaline electrolyte for 20 h. This is attributed to the intimate contact and strong electronic interaction between the two components. Upon mechanism analysis, in alkaline media, LNO is likely to work as a hydroxyl acceptor, reducing the charge transfer resistance during water disassociation. In contrast, in acidic solutions the electronic interaction between the two components contributes to an increased proportion of terminal S₂²⁻ and S²⁻ ions, leading to an increased number of electrocatalytically active sites. In short, this work proposes a novel and innovative method, i.e., hybridizing MoS₂ with perovskite oxide to improve the HER activity in both alkaline and acidic electrolytes, and provides an important reference for the rational design of a highly active electrocatalyst for hydrogen production.

2. Results and discussion

Scheme 1. Schematic illustration of the preparation of MoS₂/perovskite hybrid.

Scheme 1 illustrates the preparation of the MoS₂/perovskite hybrid. Individual MoS₂ and perovskite oxide materials are also ball-milled separately for comparison. During the process, the large shearing stress caused by the zirconia balls exfoliate the basal planes of the MoS₂. In addition, the highly-stacked lamellar structures of MoS₂ are crushed and sheared into small pieces with lowered stacking height and shorter slab length, creating more edge sites.⁶¹ The exfoliated MoS₂ sheets will attach to the surface of perovskite particles and become bound together via van der Waals' forces, wrapping perovskite oxides.⁶¹ Experimental details are given in the supporting information section.

Figure 1. (a) Polarization curves of LNO, milled LNO, MoS₂, milled MoS₂, MoS₂/LNO, and commercial Pt/C catalyst in a 0.5 M H₂SO₄ solution (the scan rate was set at 5 mV s⁻¹). (b) Corresponding Tafel plots where the numbers inside parentheses indicate the Tafel slope. (c) Chronopotentiometric curves of milled MoS₂ and MoS₂/LNO obtained at a constant current density of 10 mA cm⁻². For pristine LNO, the overpotential at 5 mA cm⁻² was selected due to the material's sluggish activity. (d-f) Polarization curves, Tafel plots, and chronopotentiometric curves for the same materials in a 0.1 M KOH solution.

The HER activity was tested in both alkaline (0.1 M KOH) and acidic (0.5 M H₂SO₄) solutions, as shown in **Figure 1 (a)** and **(d)**. Pristine LNO and MoS₂ show a relatively low HER activity, while the activity increases dramatically after ball milling. The onset potential, defined as the overpotential where the HER current density reaches 1 mA cm⁻², is compared. Commercial Pt/C shows an onset potential close to 0 V in both acidic and alkaline solutions. After ball milling, the onset potentials of MoS₂ reduce from 0.14 V to 0.08 V in the acidic solution, and from 0.22 V to 0.09 V in the alkaline solution. Similar onset potential drops are also observed for LNO in both

acidic and alkaline solutions. Milled MoS₂/LNO shows remarkably reduced onset potentials, i.e., 0.06 V in acidic solution and 0.07 V in alkaline solution. These results suggest that the treatment of ball milling with perovskite hybridization has efficiently increased the HER activity. **Figure 1 (b) and (e)** show the corresponding Tafel plots in alkaline and acidic solutions. Pt/C has a low Tafel slope of 46 mV dec⁻¹ in the alkaline solution and 30 mV dec⁻¹ in acidic media. These values are consistent with previous reports.^{26, 63} The Tafel slopes of MoS₂ drop after ball milling, and MoS₂/LNO shows a relatively small Tafel slope of 72 mV dec⁻¹ in alkaline media and 42 mV dec⁻¹ in the acidic solution. The Tafel slope drop of MoS₂/LNO in comparison to milled MoS₂ alone also supports improved HER kinetics.

In order to validate the synergistic effect achieved by ball-milling hybridization, we examined the HER activity for the physical mixture of milled MoS₂ and milled LNO (see **Figure S1**). From the results, it is clear that the milled MoS₂/LNO hybrid is superior to the mixture of milled MoS₂ and milled LNO in catalyzing HER in both acidic and alkaline electrolytes. We also tested the HER activity of milled MoS₂ with other perovskite and transition metal oxides, including BLF, PBSCF, and CuO. As reported in **Table S1** and **Figure S2**, they share similar particle sizes and BET surface areas, however, it is clear that milled MoS₂/LNO is the most active material among those studied. In addition, from **Table S2** and **S3**, the HER activity of milled MoS₂/LNO in either alkaline or acidic electrolyte is comparable to, or even better than many state-of-the-art catalysts.

Figure 1 (c) and (f) show the chronopotentiometric response of three representative materials, namely milled MoS₂/LNO, milled MoS₂, and milled LNO. In 0.1 M KOH, we can observe that the overpotential slightly increases for ball-milled MoS₂. In contrast, the MoS₂/LNO hybrid's overpotential is virtually unchanged. In the acidic solution, pure LNO's activity quickly degrades,

likely because of the material's dissolution in an acidic electrolyte. While for the milled MoS₂/LNO hybrid, the overpotential that delivers 10 mA cm⁻² does not change in 20 h.

In order to clarify the mechanism behind the activity enhancement after ball-milling hybridization, we carefully examined the structure, composition, and morphologies of the as-prepared materials. From the SEM images, commercial MoS₂ has a multilayered flake-like structure (**Figure 2(a)**), and the pristine LNO is composed of many relatively small particles (**Figure 2(b)**). The long-term ball milling process crushed and sheared the lamellar structures of MoS₂ into even smaller pieces with reduced stacking height and lowered slab length, thereby creating more exposed edge sites.⁶¹ After ball milling, the resultant small particles then combine to form irregular morphology (**Figure 2(c)** and **Figure S3(a)**). From the TEM image of the milled MoS₂, see **Figure 2(e)**, we could measure the distance between adjacent fringes to be 0.61 nm, a value in good agreement with that of distance between MoS₂ (002) oriented planes. An amorphous surface layer with a thickness of around 3 nm is also observed in the milled MoS₂. Ball milled LNO is composed of irregular particles (**Figure S3(b)**) covered by a thin amorphous surface layer (**Figure S3(c)**). The TEM of MoS₂/LNO is reported in **Figure 2(f)**. With fast Fourier transform (FFT) and corresponding inverse fast Fourier transform (IFFT), the lattice spacing estimated to be 0.38 nm is in good agreement with the (100) oriented plane of LNO. In addition, the LNO nanoparticles are embedded in MoS₂. From the elemental mapping, see **Figure S4**, La, Ni, and O are only found in the particle's center, while Mo and S evenly cover the surface. This result strongly suggests that LNO's surface is covered by MoS₂. The nanostructure of the milled MoS₂/LNO after the chronopotentiometry test in an acidic electrolyte was also examined, see **Figure S5**. It is clear that the morphology of the hybrid fails to change significantly and the embedded LNO does not leach out, supporting the conclusion that the material can be operating stably as shown in **Figure 1(f)**.

Figure 2. SEM image of (a) pristine MoS₂; (b) pristine LNO; (c) ball-milled MoS₂; (d) ball-milled MoS₂/LNO hybrid; TEM image of (e) ball-milled MoS₂ and (f) ball-milled MoS₂/LNO, where the upper right inset is the FFT of the selected area, while the lower right inset depicts the corresponding IFFT.

The structural change after ball milling is further confirmed by the XRD. From **Figure 3(a)**, the pristine MoS₂ (hexagonal, space group: P6₃/mmc) and LNO (cubic, space group: Pm $\bar{3}$ m) show the characteristic peaks of their crystalline structure. The XRD diffraction patterns of milled MoS₂ are broader in comparison to those of pristine MoS₂, suggesting that ball milling reduces the particle size. This is supported by an increased BET surface area, see **Figure S6**, whose primary benefit is a higher exposure of the active sites. In addition, from **Figure S6**, we noticed that compared with milled MoS₂ ($S_{\text{BET}} = 10.1 \text{ m}^2/\text{g}$), milled MoS₂/LNO ($S_{\text{BET}} = 9.8 \text{ m}^2/\text{g}$) is characterized a similar BET surface area. The XRD pattern of milled MoS₂/LNO can be indexed into the mixture of LNO and MoS₂, suggesting that the crystal structure of MoS₂ and LNO is still well preserved after ball milling, in agreement with the TEM measurements.

Figure 3. (a) XRD patterns of LNO and MoS₂ before and after ball-milling, as well as milled MoS₂/LNO. The ■ symbols indicate the peaks pertaining to LNO, while ◇ represents those of MoS₂. (b) S 2p XPS spectrum for MoS₂, milled MoS₂, and milled MoS₂/LNO: experimental data are plotted as black empty circles while the simulated spectra are indicated as a solid line. The magenta and orange areas highlight the contributions from terminal S₂²⁻ and/or S²⁻, while the green and violet areas indicate bridging S₂²⁻ and/or apical S²⁻. (c) Ni 3p XPS for LNO, milled LNO, and milled MoS₂/LNO. (d) Raman spectrum for MoS₂, milled MoS₂, and milled MoS₂/LNO.

The chemical composition and electronic interaction between the two components in the milled MoS₂/LNO hybrid were further investigated by XPS. Using the XPS survey spectrum reported in **Figure S7**, we first verified that the Mo to S molar ratio is virtually unmodified after ball milling,

i.e., 1 : 1.99 before versus 1 : 1.98 after treatment. **Figure 3(b)** and **(c)** present the S 2p and Ni 3p XPS spectrum, respectively. Since the binding energy region of La 3d and Ni 2p overlaps, Ni 3p is used for comparison. After ball milling, the shape and location of S 2p and Ni 3p peaks do not change significantly for the milled MoS₂ and LNO, compared with the untreated materials. However, after mechanically treating the MoS₂ with LNO together, we are able to detect a chemical shift of the S 2p to lower binding energies and of Ni 3p to higher binding energy regions, suggesting a significant electronic interaction between MoS₂ and LNO. First-row transition metal ions can form chemical bonds with S in MoS₂, and a similar electronic interaction-induced chemical shift of XPS has been also reported in MoS₂/CoSe₂⁶⁴ and MoS₂/NiCo-LDH³⁴ hybrid materials. Following previous reports, we fit the S 2p with 4 deconvolved peaks,⁶⁵⁻⁶⁶ see **Figure 3(b)**. In S 2p, the doublet with higher binding energy is attributed to bridging S₂²⁻ and/or apical S²⁻ ligands, while the one with lower binding energy is assigned to terminal S₂²⁻ and/or S²⁻.⁶⁵ The negatively shifted S 2p spectrum of the milled MoS₂/LNO hybrid suggested an increased proportion of terminal S₂²⁻ and/or S²⁻ (32% vs 48% for milled MoS₂ and milled MoS₂/LNO, respectively), which are HER active in acidic electrolytes.^{65, 67-68} The Raman measurement, see the spectrum in **Figure 3(d)**, detected for milled MoS₂/LNO in reference to milled and pristine MoS₂ a hypsochromic shift of the A_{1g} mode from 402 cm⁻¹ to 406 cm⁻¹ and of the E_{2g} mode from 376 cm⁻¹ to 380 cm⁻¹. This further supports that milling changes the MoS₂ and LNO electronic interaction and softens the chemical bond between Mo and S and thereby decreases their vibration frequencies.³⁴

To evaluate the electrochemical active surface area (ECSA) of the investigated samples, we scanned cyclic voltammograms in both alkaline and acidic electrolytes, see **Figure S8** and **S9**. Compared with pristine MoS₂, the ECSA is significantly enhanced by the ball milling, i.e., from

1.99 to 2.81 mF cm⁻² in 0.1 M KOH, and from 4.4 to 6.8 mF cm⁻² in 0.5 M H₂SO₄, see **Figure 4(a)** and **(c)**. This enhancement can be attributed to the reduced particle size and formed amorphous surface (see **Figure 2(e)**). The reduced particle size is beneficial to expose more active sites, while amorphous MoS₂ is reported to be highly-active towards HER.⁶⁹ Interestingly, the ECSA is further increased to 12.2 mF cm⁻² for milled MoS₂/LNO hybrid in the acidic electrolyte. This is attributed to an increased proportion of active species, i.e., terminal S₂²⁻ and S²⁻, caused by the electronic interaction within the composite (revealed in **Figure 3(b)-(d)**). In spite of the increased HER activity, the ECSA of the milled MoS₂/LNO as measured in alkaline media does not change significantly in comparison to that of the milled MoS₂ (see **Figure 4(a)**). This inconsistency suggests that the mechanism contributing to the enhancement is likely different in the two electrolyte solutions. We further tested and fitted the EIS spectrum for HER in alkaline solution. From **Figure 4(b)** and **Table S4**, it is clear that milled MoS₂/LNO is characterized by a smaller charge transfer resistance than milled MoS₂ in alkaline electrolyte. From **Figure 1(b)**, the Tafel slope of both milled MoS₂ (108 mV dec⁻¹) and milled MoS₂/LNO (72 mV dec⁻¹) in alkaline electrolyte are within the 40-120 mV dec⁻¹ range, indicating that HER is governed by the Volmer [H₂O + e⁻ → H_{ad} + OH⁻] and Heyrovsky step [H₂O + e⁻ + H_{ad} → H₂ + OH⁻].⁷⁰⁻⁷¹ OER-active LNO could work as a hydroxyl acceptor, contributing to binding and dissociating hydroxyl species in Volmer and Heyrovsky steps, thus reducing the charge transport resistance of HER.³⁴ The increased adsorption of hydroxyl species on the surface of milled MoS₂/LNO can be assessed by the XPS fitting of O 1s (see **Figure S10**), which detects an increased proportion of hydroxyl species on the surface of the milled MoS₂/LNO in comparison to the milled MoS₂ alone.

Figure 4. Dependence of the capacitive current on the different potential scan rates for MoS₂, milled MoS₂, milled MoS₂/LNO in (a) 0.1 M KOH and (c) 0.5 M H₂SO₄; (b) EIS Nyquist plots which are recorded in the HER potential of -0.2 V vs. RHE in 0.1 M KOH.

Based on the above characterizations, we attribute the HER activity enhancement of ball-milled MoS₂ hybridized with LNO to a number of factors. Firstly, ball milling reduces particle size and amorphizes the surface. Secondly, the incorporation of the well-defined OER catalyst, i.e., LNO, contributes to the adsorption of hydroxyl intermediate in alkaline electrolyte, which is a critical elementary step in alkaline HER electrocatalysis, thus reducing the charge transfer resistance. Additionally, the electronic interaction within milled MoS₂/LNO hybrid contributes to a higher proportion of terminal S₂²⁻ and S²⁻ species, leading to increased HER active species in acidic electrolyte. Lastly, the intimate interaction between MoS₂ and LNO favors charge transfer between the two components, accounting for the higher HER activity of the ball-milled MoS₂/LNO hybrid than that of the physical mixture of MoS₂ and LNO ball-milled separately. In addition, this kind of mechanochemical coupling within milled MoS₂/LNO hybrid is also beneficial for an improved operation durability.

3. Conclusions

In conclusion, using a facile ball-milling method we synthesize a novel MoS₂/LNO hybrid, which shows a significantly enhanced HER activity in both acidic and alkaline solutions, in comparison to pristine and milled LNO and MoS₂ alone. This improvement is attributed to the activation incurred by ball milling and the synergistic coupling between the MoS₂ and LNO. In alkaline media LNO is likely to work as a hydroxyl acceptor, reducing the charge transfer resistance during water disassociation. In contrast, in acidic solutions the electronic interaction occurring in the MoS₂/LNO hybrid contributes to a higher proportion of terminal S₂²⁻ and S²⁻ ions, leading to an increased number of active sites. This work provides a novel and facile method, i.e., mating transition metal dichalcogenides together with perovskite oxides, to boost the HER activity for hydrogen generation.

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