Interface strain in vertically stacked two-dimensional heterostructured carbon-MoS$_2$ nanosheets controls electrochemical reactivity

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Two-dimensional (2D) materials offer numerous advantages for electrochemical energy storage and conversion due to fast charge transfer kinetics, highly accessible surface area, and tunable electronic and optical properties. Stacking of 2D materials generates heterogeneous interfaces that can modify native chemical and physical material properties. Here, we demonstrate that local strain at a carbon-MoS$_2$ interface in a vertically stacked 2D material directs the pathway for chemical storage in MoS$_2$ on lithium metal insertion. With average measured MoS$_2$ strain of $\sim 0.1\%$ due to lattice mismatch between the carbon and MoS$_2$ layers, lithium insertion is facilitated by an energy-efficient cation-exchange transformation. This is compared with low-voltage lithium intercalation for unstrained MoS$_2$. This observation implies that mechanical properties of interfaces in heterogeneous 2D materials can be leveraged to direct energetics of chemical processes relevant to a wide range of applications such as electrochemical energy storage and conversion, catalysis and sensing.
Interlayer spacing of Pt relevant to fuel cells. In this manner, 2D materials provide Pt catalysts can improve the oxygen reduction reaction capability and electrochemical processes remains virtually unstudied. Only required for electrochemical measurements. As a result, the impact by uniform material fabrication routes that can be used on scales beyond silicon.

Fabrication of interface-strained materials. MoS$_2$ nanosheets were produced through liquid exfoliation of bulk MoS$_2$ powders in $n$-methyl-2-pyrrolidone (NMP) solvents and subsequent centrifugation. Transmission electron microscopy (TEM) of a representative exfoliated MoS$_2$ nanosheet is shown in Fig. 1a,b. Interlayer spacing of ~0.61 nm is observed for MoS$_2$ nanosheets, with thicknesses ranging from 2–15 atomic layers (Supplementary Fig. 1, Supplementary Note 1). Ultrathin carbon layers are grown directly on the MoS$_2$ surface through MoS$_2$ catalysed decomposition of C$_2$H$_2$ precursors using a temperature ramp chemical vapour deposition process (Supplementary Fig. 2) that is capable of gram-scale batch processing. This generates vertically stacked architectures where ultrathin carbon layers are formed on both sides of the MoS$_2$ nanosheets, with a representative TEM image of this architecture shown in Fig. 1c, and corresponding elemental analysis map in Fig. 1d. To produce an appreciable mass of material for electrochemical tests, electrophotoredox was used to assemble the vertically stacked carbon-interfaced MoS$_2$ (C-MoS$_2$) nanosheets into conformal films on metal substrates from NMP dispersions following chemical vapour deposition (Fig. 1e; Supplementary Fig. 3, Supplementary Note 2). All aspects of synthesis and processing of C-MoS$_2$ materials are chosen to be compatible with scalable processing, and ongoing research efforts to improve the simplicity and scalability of liquid exfoliation can further improve this.

Results

Fabrication of interface-strained materials. MoS$_2$ nanosheets were produced through liquid exfoliation of bulk MoS$_2$ powders in $n$-methyl-2-pyrrolidone (NMP) solvents and subsequent centrifugation. Transmission electron microscopy (TEM) of a representative exfoliated MoS$_2$ nanosheet is shown in Fig. 1a,b. Interlayer spacing of ~0.61 nm is observed for MoS$_2$ nanosheets, with thicknesses ranging from 2–15 atomic layers (Supplementary Fig. 1, Supplementary Note 1). Ultrathin carbon layers are grown directly on the MoS$_2$ surface through MoS$_2$ catalysed decomposition of C$_2$H$_2$ precursors using a temperature ramp chemical vapour deposition process (Supplementary Fig. 2) that is capable of gram-scale batch processing. This generates vertically stacked architectures where ultrathin carbon layers are formed on both sides of the MoS$_2$ nanosheets, with a representative TEM image of this architecture shown in Fig. 1c, and corresponding elemental analysis map in Fig. 1d. To produce an appreciable mass of material for electrochemical tests, electrophotoredox was used to assemble the vertically stacked carbon-interfaced MoS$_2$ (C-MoS$_2$) nanosheets into conformal films on metal substrates from NMP dispersions following chemical vapour deposition (Fig. 1e; Supplementary Fig. 3, Supplementary Note 2). All aspects of synthesis and processing of C-MoS$_2$ materials are chosen to be compatible with scalable processing, and ongoing research efforts to improve the simplicity and scalability of liquid exfoliation can further improve this.

 controlling electrochemical processes using strain. To assess how the vertically stacked architecture and interface strain influences electrochemical processes, we combined electrophoretically assembled vertically stacked 2D C-MoS$_2$ nanosheets with Li metal electrodes, and a 1.0 M lithium hexafluorophosphate solution in ethylene carbonate and diethyl carbonate electrolyte, and compared the electrochemical
properties against similar electrode materials produced with pristine MoS$_2$ nanosheets (Supplementary Figs 5, 6, Supplementary Notes 4, 5). Cyclic voltammetry scans of these electrodes and corresponding differential capacity plots based on galvanostatic measurements are shown in Fig. 3. As these two electrode materials differ only by the presence of a vertically stacked C-MoS$_2$ interface, electrochemical data indicates significant changes to the chemical processes occurring on lithium insertion into the MoS$_2$ material. For pristine MoS$_2$ nanosheets, two subsequent reactions are observed, with the first one at $\sim$1.1 V and the second at $\sim$0.55 V versus Li/Li$^+$. (Fig. 3a,b) This is consistent with the known pathways for insertion of lithium into pristine MoS$_2$, which occurs first through an intercalation reaction (1.1 V) that follows

$$\text{MoS}_2 + x\text{Li}^+ + xe^- \rightarrow \text{Li}_x\text{MoS}_2$$  \hspace{1cm} (1)
where MoS$_2$ undergoes a transition from a semiconducting 2H phase to the metallic 1T phase due to strain-induced deformation of the crystal from lithium ion insertion. Following this transition, the MoS$_2$ can undergo a subsequent conversion reaction at lower voltages (0.55 V) that follows

\[
\text{Li}_x\text{MoS}_2 + 4\text{Li}^+ + 4e^- \rightarrow 2\text{Li}_2\text{S} + \text{Mo} + 3\text{Li}^+ \quad (2)
\]

In contrast to this, insertion of lithium into the vertically stacked C-MoS$_2$ nanosheets yields a chemical reaction evident at ~2.3 V versus Li/Li$^+$ based on both CV and differential capacity curves (Fig. 3c,d) which is close to the open-circuit voltage (OCV) of the device. This reaction proceeds in the absence of Li intercalation into MoS$_2$ and no significant signature of lithium insertion at lower voltages occurs such as in pristine MoS$_2$ nanosheet electrodes. This highlights the presence of a chemical storage process occurring in vertically stacked C-MoS$_2$ materials that is not observed in pristine MoS$_2$ materials (Fig. 4a) and that interface-induced strain can directly trigger chemical conversion at practical voltages. It is important to note that these results distinguish the stacked C-MoS$_2$ configuration from simple mixtures of carbon nanomaterials and MoS$_2$ nanosheets which have been reported previously$^{38-42}$, in two key ways, namely that the grown carbon layer induces interface strain not possible in pristine MoS$_2$ nanosheets, but the emergence of a distinct Raman peak at 746 cm$^{-1}$ is observed for the stacked C-MoS$_2$ nanosheets.

To address the effect of the C-MoS$_2$ interface on the electrochemical properties during lithium insertion, Raman spectroscopy of the electrophoretically assembled MoS$_2$-based electrodes at different cathodic potentials was carried out (Fig. 4b). This analysis is possible due to the preparation of electrodes in a manner that does not require binder materials often used in conventional battery electrodes that can overwhelm the desired Raman spectroscopic features. At OCV conditions, both electrode materials exhibit only the native Raman modes of the C and MoS$_2$ materials that can play a role in the origin of strain measured using these techniques. We also observe the lack of any electrochemical signature of lithium intercalation into the ultrathin carbon coating, implying that stacked C-MoS$_2$ nanosheets exhibit differences from pristine nanosheets that can be explained by compressive strain imposed on the 2D MoS$_2$ material.
A$_{1g}$ and E$_{2g}$ modes are observed as expected from conversion (Supplementary Fig. 8, Supplementary Note 6). This confirms that the high voltage $\sim 2.3$ V signature in the CV and differential capacity curves for vertically stacked C-MoS$_2$ nanosheets (Fig. 3c,d) is a chemical conversion process similar to that which is known to occur at low voltages ($0.55$ V) in pristine MoS$_2$. To further support this, cathodic scans were continued down to 0.01 V versus Li/Li$^+$ for the pristine MoS$_2$ electrode, where the signature of conversion is evident due to the presence of the Raman mode at 746 cm$^{-1}$. Despite the difference in voltage of the conversion reactions between MoS$_2$ and C-MoS$_2$, similar Raman spectroscopic signatures of the polysulfide conversion product and similar post-conversion redox energetics in both cases implies that the resulting chemical state of the material in both conversion reactions is the same. To further support this, we performed in situ electrochemical impedance spectroscopy (EIS, Supplementary Fig. 9, Supplementary Table 1), where EIS analysis was performed at the same voltages as those assessed using Raman spectroscopy. EIS studies elucidate a picture consistent with Raman spectroscopy results that indicates the electrochemical signature of conversion in different voltage regimes for the pristine MoS$_2$ and the stacked C-MoS$_2$, respectively (Supplementary Note 7).

**Discussion**

On the basis of the combined spectroscopic and electrochemical analysis, a picture emerges emphasizing the role of interface strain on lithium insertion in vertically stacked C-MoS$_2$ materials. In the pristine semiconducting 2H phase of MoS$_2$, conversion of MoS$_2$ nanosheets cannot occur at voltages above where intercalation occurs ($1.1$ V versus Li/Li$^+$) and can only proceed in a two-step chemical process following an intercalation reaction. As many researchers have discussed the promise of MoS$_2$ nanosheets for battery cathodes, the requirement of a conversion reaction that is near the reduction potential of lithium is highly impractical in full-cell architectures. In a vertically stacked C-MoS$_2$ nanosheet, the interface strain due to lattice mismatch in a carbon-MoS$_2$ solid–solid interface leads to an average $\sim 0.1$% compressive strain that propagates into the MoS$_2$ nanosheet lattice and enables control of the energetics of chemical conversion. In this regard, interface strain provides the appropriate energetic landscape to sustain direct conversion at voltages that enable pairing with conventional anode materials such as silicon or graphite which give promise to practical incorporation of this device in a full-cell battery configuration. This distinctive difference in the chemical pathways achieved during lithium insertion as a result of interface strain is illustrated in Fig. 4a, where the chemical state of the 2D materials is drastically different following a cathodic scan to 1 V.

The broader use of controlled interface mechanics to modify chemical pathways in low-dimensional materials presents an unexplored horizon for engineered low-dimensional nanostructures. This utilizes 2D materials as a framework to merge concepts of strain engineering with mechanochemistry to control the energetics of chemical processes relevant to energy storage, energy conversion, catalysis, and sensing applications. Building from our results showing that strained interfaces in vertically stacked C-MoS$_2$ nanosheets can modulate electrochemical reactivity, we envision a new paradigm for material design that exploits interface strain and mechanics as a versatile toolbox to modulate performance of designer 2D materials in diverse applications.

**Methods**

MoS$_2$ nanosheet synthesis. In all, 500 mg of bulk MoS$_2$ powder (Aldrich, particle size $\leq 2$ μm) was added to 50 ml of 1-methyl-2-pyrrolidinone (Aldrich, 99.9% anhydrous). The solution was sonicated in a bath sonicator for 12 h using 8 × 90 min intervals. After sonication, the solution was centrifuged at 2,000 r.p.m. for 40 min. The upper 2/3 of the supernatant was removed and subsequently
centrifuged for 1 h at 5,000 r.p.m. before the excess supernatant was removed and the accumulated nanosheets were placed under vacuum overnight to completely evaporate the solvent.

**Vertically stacked carbon-MoS2 nanosheet synthesis**. MoS2 nanosheets contained within an alumina boat were placed into a 1-inch tube furnace and the tube was evacuated to 2 mTorr. A gas mixture of 100 standard cubic centimeters per minute (scm) Ar and 20 scm H2 maintained at atmospheric pressure were introduced during ramping to a temperature 750 °C. At 750 °C, 2 scm of acetylene (C2H2) was introduced for 10 min followed by a temperature ramp to 850 °C and an additional 10 min soak, and a final ramp to 950 °C for 10 min. After this process, the acetylene was turned off and the furnace cooled back down under a flow of argon and hydrogen, where materials were removed.

**Electrophoretic deposition**. A total of 20 mg of vertically stacked C-MoS2 or pristine MoS2 nanosheets were suspended in 20 ml NMP and sonicated for 30 min. Following this, a stainless steel spacer was placed at 0.5 cm from a 1 cm × 1 cm stainless steel counter electrode. A voltage of 30 V was applied for 30 min before carefully removing the coated steel electrode from solution and placing this into a vacuum chamber overnight to dry the sample.

**Electrochemical device fabrication and testing**. Electrochemical half-cell devices were assembled in an argon glovebox using CR 2032 stainless steel coin cells purchased from MTI. The coated steel discs were separated from a lithium metal anode by a 2500 µm Celgard separator. 0.3 µL of a 1 M LiPF6 in 1 g per 1 ml solution of ethylene carbonate and diethyl carbonate. Cyclic voltammetry solution was electroplated onto the 1 -inch square MoS2/polyaniline and MoS2/C architectures for lithium-ion battery applications. ACS Appl. Mater. Inter. 6, 14464–14465 (2014).

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Author contributions
L.O. and C.L.P jointly conceived the project and designed the experiments. L.O. and T.H. performed material fabrication with insights from K.S., and L.O. carried out device testing and performance analysis. R.C. performed TEM imaging and analysis, and A.P.C. performed X-ray diffraction measurements and analysis. B.S. performed XPS measurements and analysis. L.O. and C.L.P. wrote the manuscript and all authors participated in discussion and reviewed the manuscript before submission.

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