High Throughput Printing of Two-Dimensional Materials into Wafer-scale Three-dimensional Architectures

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Abstract

Architected materials that actively respond to external stimuli hold tantalizing prospects for applications in energy storage, harvesting, wearable electronics and bioengineering. Transition metal dichalcogenides (TMDs) which represent the three-atom-thick, two-dimensional (2D) building blocks, are excellent candidates but have found limited success compared to metallic, inorganic, and organic counterparts due to the lack of up-scalable manufacturing. Here we report the high-throughput printing of 2D TMDs into wafer-scale 3D architectures with structural hierarchy across seven orders of magnitude between critical feature sizes. Anode made of 3D MoS₂ architectures comprises the concentric vortex-like intricacy that unites technological merits from architecture, mechanical engineering, and electrochemistry not found in its bulk or exfoliated/epitaxy counterparts. The result is, contrary to expectation, the high-rate, high-capacity, and high-loading lithium (Li)-storage, surpassing those state-of-the-art anode designs while the technique offers an evaporation-like simplicity for industrial scalability.

Main Text

Architected materials, e.g., materials with three-dimensional (3D) architectures at the micro- and nanoscale, hold tantalizing prospects for widespread applications, ranging from photonic devices to energy storage and conversion systems, mechanical reinforcement, wearable electronics, and biomedical devices.^{1–6} Transition metal dichalcogenides (TMDs) which represent three-atom-thick 2D building blocks, have an intrinsic hierarchy of structure features, such as phase heterojunctions, grain boundaries between crystalline domains of sizes ranging from millimeters down to micrometers, dislocations at the nanoscale, and point defects such as S vacancies on the atomic scale.^{7,8} Despite the presence of innate structural hierarchies in tandem with the earth abundance and ease of solution processability, development of 3D architected TMDs remains at an early stage compared to their metallic, inorganic or even organic counterparts. Current manufacturing routes usually give rise to simple geometries of mesoporous and fractal-like features that recur only within two orders of magnitude, thus preventing researchers from combining TMDs' intrinsically attractive features with desirable material properties that are extrinsic to them. Indeed, the field of architected materials has been almost exclusively focused on metallic and inorganic materials, and the detailed mechanistic insights have shed light on many guidelines for inducing the “stronger-yet-ductile”⁹, “lightweight-and-flaw-tolerable”¹, “electrochemically reconfigurable”⁴, and “brittle-to-ductile” transitions. Developing such understanding for 3D architected TMDs shall open new inroads for a myriad of applications where new properties and functionalities arise from the deliberate, multiscale architecting of 2D atomic crystals.

Here, we report the wafer-scale printing of 2D monolayer MoS₂ into 3D architected MoS₂ that comprises multiple levels of structural hierarchy, comparably contribute to the overall material properties. We demonstrated an instability induced manufacturing scheme that enables the deliberate structuring of 2D exfoliated MoS₂ sheets into 3D hierarchically organized entities with extended control over structure-property relationships, delivering greatly enhanced mechanical and electrochemical properties purely by

rational design without the change in chemical compositions. Advanced imaging, theoretical modeling, and comprehensive spectroscopic characterizations collectively reveal the intricate but well-organized 3D topological frameworks with spatially connected vortical truss unit cells that can be directly and continuously printed on the target substrate (4-inch-wafer scale) even at a relatively high loading mass ($> 3.0 \text{ mg/cm}^2$). These characteristics enabled the fabrication of 3D architected MoS_2 anode that, contrary to the prevailing prediction, delivers lithium (Li)-ion charge storage capacity on par with the state-of-the-art layered black phosphorus (BP)¹⁰, silicon (Si)^{11,12}, Si-graphene¹³ and mesoporous graphene particle anodes¹⁴.

Our synthetic scheme is presented in **Figure 1a**. Bulk MoS_2 is chemically exfoliated into monolayered sheets, namely chemically exfoliated MoS_2 (ce- MoS_2), and then dispersed in a mixture of deionized water and isopropyl alcohol (DI- H_2O : IPA=7:3, v/v).¹⁵ The formation of 3D architected MoS_2 was driven by the spontaneous phase segregation which confines the dispersed ce- MoS_2 sheets to the area between drying patches.¹⁶ This leads to the formation of a localized network of micropores similar to cellular foam as schematically represented in **Fig. 1b** and experimentally observed in **Figs. 1c-d**. Although a detailed mechanism for this foam-like pattern formation is yet to be explored and maybe rather complicated, an elegant insight is readily gained from the experimental observation and simple predictive model: The nucleation sites of drying patches seem to be closely linked to the local thickness of retreating liquid thin film which can be empirically associated with the critical thickness [T_c , $T_c = 2k^{-1} \sin (q/2)$], where k^{-1} and q are capillary length and contact angle of H_2O (**Supplementary discussion and scheme 1**).¹⁷ This sheds light on the possibility of creating ordered arrays of patterns and the concomitant porosity if the local thickness of liquid thin film can be spatially regulated during dewetting. A very convenient approach for spatially controlling the local thickness of the liquid thin film is electrohydrodynamic printing as schematically illustrated in **Fig. 1a**.

In electrohydrodynamic printing, the outcome of extruding liquid meniscus, including continuous liquid jets, ultrafine droplets, or the combination of both, is determined by the electric field and the sequence can be programmed sequentially. In this light, we programmed the printing scheme as follows, (i) jetting mode for creating a ce- MoS_2 containing liquid thin film below T_c ; (ii) spraying mode for generating ultrafine and electrostatically charged droplets with a narrow distribution of diameters; and (iii) creating drying patterns upon bombarding the liquid thin film surface and simultaneously regulating the randomly dispersed 2D ce- MoS_2 into an orderly 3D architected assembly.¹⁸ When the dewetting patterns are set, emergence of truss unit cells depletes the solvents at the truss-air contact line, which in turn creates a swirling force to guide the successive deposition of ce- MoS_2 containing droplets. During this step, ce- MoS_2 are continuously carried off the droplets at the truss-air contact line and preferentially deposited along with the 3D porous framework, thus enabling the continuous production of new layers of rings and struts reminiscent of additive manufacturing.

This engineering feat is particularly appealing because of the ability to join the evaporation-like simplicity of geometric patterns to the complexity of hierarchical architectures in a scalable fashion.³ Previous demonstrations of 3D architected TMDs have been constrained by either the scalability of manufacturing routes, 3D features with limited orders of magnitude, or the dimensions of scaffolds.^{19,20} On the contrary, the multiscale structural features of 3D architected MoS₂ were found to distribute ubiquitously and uniformly in both lateral (4-inch wafer) and vertical directions (thickness >100 μm) as shown in **Figs. 1c-d**. From **Fig. 1e**, the truss unit cell comprises layers of alternating rings and struts tapering down toward the bottom of the copper (Cu) substrate. These nanoscale struts made of intertwined and folded ce-MoS₂ sheets (**Figs 1f-g**) serve as crucial elements that structurally interconnect between layers of concentric rings, forming vertically stacked and ring-shaped viaducts.²¹ These viaducts naturally define abundant transverse pores (pore size in the range of ~200 nm) on the sidewalls of these vortical truss unit cells as revealed in **Fig. 1f**. A further closeup view of these struts (**Fig. 1h**) shows a high density of tears and holes on the order of 5-20 nm highlighted by the dotted white lines. **Fig. 1i** features a high percentage of atomically resolved defects, such as S-vacancies, derived from the harsh Li intercalation reaction as shown in the high-angle annular dark-field (HAADF) and aberration-corrected scanning transmission electron microscopy (STEM).

To further examine the ubiquity and uniformity of multiscale structure features in the lateral direction, a series of scanning electron microscopy (SEM) images arranged in a radial-line-graphed manner were taken from different perspectives with respect to the center truss unit cell. From **Supplementary Fig. 1a**, it is clear that all the truss unit cells that are false colored in light orange and separated by 90°, comprise at least five layers of alternating rings and struts shaped down toward the Cu substrate. Meanwhile, tilted angle SEM images further reveal the uniform thickness and ordered arrangement of struts in tandem with the narrow size distribution of nanopores. 3D architected MoS₂ is found to strongly attached to the underlying Cu substrate and can only be made free-standing through dissolving the Cu substrate in ammonium persulfate solution. The difficulty of removing 3D architected MoS₂ from the underlying Cu substrate underscores the strong adhesion that ensures establishment of uninterrupted conductive pathways. Further, a close examination of surface morphology from the back side of 3D architected MoS₂ enables us to correlate the predictive model with experimental observation. As suggested in **Supplementary Fig. 1b**, the advent of vortical truss unit cells confirms the formation of dewetting patterns in the initial stage. Note that a wide distribution in pore sizes in the backside may stem from the occasional appearance of large pendant droplet during the initial deposition (areal loading less than 0.5 mg/cm²). Truss unit cells begin to tessellate and then propagate vertically when the areal loading exceeds 0.5 mg/cm², as shown in the SEM. These morphological characterizations collectively attest to the scalable uniformity of the dewetting-assisted manufacturing route to create architected patterns with multiscale structural features in all directions over the entire substrate. Other characterizations, including binding energies from X-ray photoelectron spectroscopy (XPS), characteristic peaks from X-ray diffraction (XRD), signatures from Raman spectra and energy dispersive X-ray spectroscopy (EDS) mapping of

relevant elements in a single truss unit cell as well as within the 3D networks, again prove the structural continuity and chemical coherence of 3D architected MoS₂ (**Supplementary Figs. 1c-e and 2**).

The characteristic failure and post yield deformation of 3D architected MoS₂ were observed through a programmable nanoindentation experiment that incorporated three stages in each cycle as follows, (1) compressing the same point to the displacement of 50% of the total thickness in 10 s; (2) holding for 10 s; and (3) release the loading in 10 s. The post-yield deformation behavior of 3D architected MoS₂ was characterized by a ductile-like behavior with the continuous serrated flow (**Figure 2a**). Catastrophic failure was attenuated by a combination of elastic ring buckling, shell buckling in individual struts, sliding between stacked sheets, and microcracking at nodes.²² This is manifested in the substantial recovery of 3D architected MoS₂ (up to 85% of their original height, 100 μ m as determined by the cross-sectional SEM) after compressions exceeding 50% strain. Failure in the 3D hierarchically structured MoS₂ carried out and localized primarily in the densification of individually protruded vortical truss cells. Puckering of these interconnected vortical truss cells creates an adaptable region in the higher-order networks that accommodate most of the ensuing displacement (inset in **Fig. 2a**). Upon unloading, the majority of the vortical truss cells within the 3D porous networks, in both vertical and lateral directions, remained intact by virtue of the global recovery. The result is the excellent adaptability of 3D architected MoS₂ that may be translated to withstand the continuous volume change commonly seen during the charging/discharging process. By contrast, the reference crystalline bulk, and restacked wrinkled films display a nearly zero recovery and complete fracture when loads exceed 100 μ N while the crumpled balls of MoS₂ show the strain-hardening effect (**Supplementary Fig. 3**). This difference in mechanical adaptability underlines the critical role of the 3D hierarchy in facilitating load dissipation and structural resilience.

In addition to the preserved structural integrity, another appealing feature of 3D architected MoS₂ is the inherently strained structure that provides a new degree of freedom to manipulate the intrinsic activities of 2D MoS₂ building blocks, such as diffusion barrier, adsorption and conductivity. **Fig. 2b** features a 2-inch Cu substrate printed with MoS₂ in dissimilar morphologies, including crumples (top), architected MoS₂ (middle), and wrinkles (bottom right), made possible by the programable printing. The strain-charge doping (ϵ -n) map derived from the linear relationship between biaxial strain/charge doping and Raman shifts provides an index for quantifying the strain load (characterized to shift by ~ 1.7 cm⁻¹ per % strain) and surface electron densities. Note that $\Delta\epsilon > 0$ is indicative of tensile strain and Δn can be used to compare the relative electron densities.²³ **Fig. 2c** shows that 3D architected MoS₂ is substantially strained ($\sim 1.75 \pm 0.15\%$ vs. $3.2 \pm 0.37\%$ of tensile strain in crumples, on the basis of the redshift magnitudes of the Raman E_{2g} and A_{1g} peaks) and displays a relatively higher electron density than that of the wrinkled counterpart. These results agree well with the previous reports and have profound implications on activating the 3D architected MoS₂ with the significantly decreased ion diffusion barrier with ~ 0.2 eV for Li, and greatly improved conductivity of 4.66 S/m relative to that of pristine 2H-MoS₂ bulk (0.42 eV for Li-ion diffusion barrier and conductivity of 0.0576 S/m, **Supplementary Fig. 4**). In

addition, strain-induced upshift of Mo *d* states towards Fermi level gives rise to a stronger interaction with metal ions, indicating that the storage capability could be directly tailored at the atomic level.²⁴

This is surprising given that MoS₂ is characterized by a 2H phase crystal structure where its metal atoms are coordinated in a trigonal prismatic manner.⁷ The result is a monolayer semi-insulator with a sizeable bandgap of ~1.9 eV, inferior electrical conductivity of ~0.03 S/m, relatively high diffusion barrier (0.42 eV) compared to BP (0.08 eV),²⁵ silicon (Si, 0.37-0.54 eV)²⁶ and graphite (0.37 eV),²⁷ and therefore not immediately attractive as an electrode material for any metal-ion battery. Furthermore, electrochemically driven dimensional changes in the randomly restacked MoS₂ electrodes lead to mechanical stress buildup at a charge-discharge current density of >5 A/g, ultimately resulting in fatigue and thus capacity fading after only few tenths of cycles. Indeed, it is widely deemed impractical and only a handful of studies have described the Li-ion storage properties of electrodes consisting of single- and multi-layered MoS₂ nanosheets. In contrast, the combination of manufacturing scalability, 3D hierarchically porous and spatially interconnected networks, multiscale architectural features, and strain-engineered ion diffusion barriers and conductivity suggests that 3D architected MoS₂ may be an ideal anode alternative with high-rate, high-capacity, high-mass-loading storage and long-term cyclability.⁴ **Figure 3a** schematically correlates these appealing features with the formation of hierarchical structures within 3D architected MoS₂.

To this end, the printed 3D architected MoS₂ (1.25 mg/cm², containing 0 wt % additives, Supplementary information) was first analyzed by using the finite element methods (FEM) program, the COMSOLTM package. Here, the state-of-charge (SOC) of the 3D pristine architected MoS₂ is defined by the degree of lithiation, e.g., SOC of 100% can be translated into fully lithiated/charged 3D architected MoS₂ where pristine or un-lithiated 3D architected MoS₂ is defined as SOC of 0%. The boundary conditions and other details of numerical modeling for an electro-chemo-mechanical modeling for a battery electrode can be found in the published work by Qaiser et. al.²⁸ **Fig. 3b** features the spatial distribution of Li-ions at various stages of SOC. The corresponding volume expansion is recorded in **Fig. 3c**. From the FEM results, it becomes apparent that the spatially connected vortical truss unit cells help dissipate localized strain over the entirety of 3D architected MoS₂, limiting the volumetric expansion and thus preserving the structural integrity. A short clip that snapshots the volumetric expansion (%) of 3D architected MoS₂ as a function of lithiation can be found in the **Supplementary information video 1**. In parallel, numerical calculations in **Supplementary Fig. 5** show that, at a fully lithiated state (SOC of 100%), the evolved von Mises stress distribution remains very low (~few MPa), confirming the efficacy of the 3D architected MoS₂.²⁹ Indeed, the superior electrochemical performance of 3D architected MoS₂ validates the theoretical prediction. 3D architected MoS₂ anodes can be obtained from disc-punching the wafer-scale batch printing with a high yield and a low variability. 100 anodes derived from the 4-inch-wafer-scale fabrication of 3D architected MoS₂ at different batches showed a high yield of 99% with averaged reversible discharge capacity of 1575 mAh/g at the 2nd cycle with an initial Coulombic efficiency of more than 95% (left panel, **Fig. 3d**).

Meanwhile, the charge/discharge profiles measured at various cycles (right panel, **Fig. 3d**) show plateaus at 1.4 V and 0.9 V in discharging process, respectively. These two plateaus remain discernable at increased current densities (0.2-10 A/g), indicating excellent reaction kinetics between Li^+ and 3D architected MoS_2 . However, none of these two plateaus is characteristic of the pristine MoS_2 nanosheets that typically undergo an intercalation reaction (1.1 V) and an ensuing conversion reaction at lower voltages (0.55 V). The absence of both intercalation and conversion reactions points to the presence of new electrochemical storage kinetics. Specifically, the emergence of characteristic 2H peaks in ex-situ Raman and X-ray photoelectron spectroscopy (XPS) spectra collectively ruled out the 2H to 1T phase transition, commonly observed in pristine MoS_2 bulk or stacked nanosheets (**Supplementary Fig. 6**). To probe the dominant electrochemical charge storage kinetics in 3D architected MoS_2 , it is necessary to verify the capacity contribution from the diffusion-controlled and the capacitive processes as shown in **Supplementary Fig. 7**. The pseudocapacitive process contributes a significant fraction of the overall capacity at low rates ($\sim 82.8\%$ capacitive at 1 mV s^{-1}) and predominates at high rates ($>99\%$ capacitive at 5 mV s^{-1}), making it possible for high-power operation.³⁰

The greatly enhanced electrochemical performance can be attributed to the two recognizably different characteristics that effectively suppresses the rampant formation of solid electrolyte interphase (SEI), thus increasing the Coulombic efficiency and the cycling stability.^{11,12} Firstly, the spatially uniform and vertically vortical networks of truss unit cells retain the structural integrity while facilitating the stabilization of SEI. After 200 deep cycles, the hierarchically structured morphology remains intact and is coated with a thin yet uniform layer of SEI ($\sim 100 \text{ nm}$, **Supplementary Fig. 8a**). Statistical analyses of both channel dimensions and nanopore diameters (**Supplementary Fig. 8b**) reveal a less than 10% increase, crucial for stable capacity retention in high mass loading cells. By contrast, random and disordered packing of MoS_2 sheets resulted in the rampant growth of SEI and therefore congestion of transport pathways (**Supplementary Figs 8c-e**). Secondly, the structural hierarchy that spans multiple orders of magnitude spatially confines the SEI formation and quantitatively decreases the SEI thickness, closely resembling the double-walled Si nanotubes and the pomegranate-inspired design strategy. **Fig. 3e** demonstrates the retention of a specific capacity at a high charge-discharge current density beyond 5 A/g and electrochemical stability at a mass loading of 1.25 mg/cm^2 . The 3D architected MoS_2 anode delivered a reversible capacity of 1092 mAh/g after cycling at 5 A/g for 2000 cycles, and a reversible capacity of 773 mAh/g after cycling at 10 A/g for 2000 cycles, respectively. The energy density is around 2385 Wh/kg and power density is $\sim 9540 \text{ W/kg}$ under 5 A/g current density. Under 10 A/g current density, energy density is 2106 Wh/kg and the power density reaches 20963 W/kg. Notably, the fast-charging capability of 3D architected MoS_2 anode could deliver a short refueling time of no more than 10 minutes and a cell level energy density of no less than 350 Wh/kg.

The spectroscopic characterization of *operando* Mo K-edge X-ray absorption near edge structure (XANES) corroborates the electrochemical redox (pseudocapacitive) reaction of 3D architected MoS_2 anode. **Figure 4a** shows the Mo K-edge XANES spectra of the architected 3D MoS_2 anode during

the first discharging (lithiation) and charging (delithiation) processes at a scan rate of 0.3 mV s^{-1} . It is worth noting that the absorption edge does not shift discernably during the first cycle. This indicates that the oxidation state of Mo does not change significantly. To further understand the oxidation state change of Mo ions, the XANES spectra for the first cycle with the potentials at an open-circuit voltage (OCV), the first full lithiation (0.01 V), the first full delithiation (3 V), and the references (MoO_3 and Mo metal foil) are displayed in **Fig. 4b**. The position of absorption edge of the 3D architected MoS_2 anode slightly shifts to a lower energy during the discharging (lithiation) process and then reverts back during the charging (delithiation) process. The changes in edge energies and shifts in absorption edges collectively suggest that part of the reversible capacity is contributed by the redox reaction of Mo ions. However, the edge energy for all lithiation/delithiation spectra are within only c.a. 1 eV of the 3D architected MoS_2 anode, which may be due to the anion–cation redox interactions between the Mo and S ions as observed in the literature.^{31,32}

In addition, the fingerprint feature of metallic Mo at c.a. 20016 eV was not observed in the fully lithiated electrode (0.01 V), demonstrating that the metallic Mo was not formed during lithiation process. This shows that the conversion reaction did not occur during the lithiation process, thus giving rise to excellent cycling stability. This result is different from the commercial micrometer-sized MoS_2 electrode where the metallic Mo was detected in the Mo K-edge XANES spectrum of the lithiated electrode.³³ Moreover, the large capacity of up to 1500 mAh g^{-1} is mainly the result of the surface-limited capacitive mechanism. **Figs. 4c** and **4d** display the CV curve and the energy shift of the X-ray absorption edge ΔE_{edge} during the first cycle, where ΔE_{edge} is defined by the energy difference between the second inflection points of OCV (c.a. 20018 eV) and certain potentials. It becomes clear that the edge energy decreases steeply from 2 V to 0.9 V vs. Li/Li^+ during the discharging process and increases sharply from 1 V to 3 V vs. Li/Li^+ during the charging process. These potential ranges bear a close resemblance to the peaks on the CV curve. Moreover, these peaks on CV curve still can be recognized even at high scan rate of 10 mV s^{-1} (**Supplementary Fig. 8**), revealing fast redox reactions. As a result, those redox couples are mainly contributed by the pseudocapacitive reactions of Mo ions, and the rest current is contributed by electrical double layer capacitive reactions. The surmise that hierarchical structuring 2D ce- MoS_2 into 3D architected MoS_2 shall greatly enhance Li-ion electrochemical activity is thus grounded in the emergence of pseudocapacitive mechanism of 3D architected MoS_2 .

Another advantageous feature of 3D architected MoS_2 anode is the superior reversible capacity relative to other MoS_2 -based anodes in dissimilar forms, such as crumples, wrinkles, and bulks, in both static and dynamic conditions (**Supplementary discussion 2 and Supplementary Figs. 9**). Also, the ability to continuously print out new layers of rings and struts that concurrently establish effective charge transport networks and ion transport pathways is manifested in overcoming the areal capacity–areal mass loading dilemma. **Figure 5a** provides both the cross-sectional and close-up views of 3D architected MoS_2 anode with an aerial mass loading of 3.5 mg/cm^2 , displaying the spatially connected yet hierarchically structured 3D networks throughout the entirety of the specimens regardless of the increased aerial mass

loadings. We then conducted the electrical impedance spectroscopy (EIS) study, and compared results with those control anodes, such as bulks, wrinkles, and crumples on an equal footing with areal loadings of 3.5 mg/cm^2 , respectively. The derived Li^+ diffusion coefficients (D_{Li}) in 3D architected MoS_2 are two to three orders of magnitude higher than that in MoS_2 bulks (**Supplementary Fig. 10**). Ohmic (R_s), solid electrolyte interface (R_{SEI}) and charge transfer resistance (R_{ct}) can be extrapolated from intercept, and diameters of the semicircles from the Nyquist plots as shown in **Fig. 5b** and recorded in **Supplementary Table 1**.

Following the initial deep cycling of 0.05 mA/cm^2 (1st to 3rd cycle) and the subsequent high rate of 1 mA/cm^2 (4th to 150th cycle), 3D architected MoS_2 anodes with areal loadings of 1.0 mg/cm^2 and 2.2 mg/cm^2 can achieve 150 cycles without noticeable degradation of areal capacity. Remarkably, increasing the areal loading to 3.5 mg/cm^2 results in the reversible areal capacity of 3.45 mAh/cm^2 and remains above 3 mAh/cm^2 after 100 cycles (**Fig. 5c**), comparing favorably than the capacity in a commercial Li-ion battery. Finally, we calculated the volumetric capacity of the 3D architected MoS_2 anodes with an overall packing density of $0.95 \pm 0.05 \text{ g/cm}^3$. Note that such an overall pack density is only slightly lower than that of the standard graphite anodes ($\sim 1.0 \text{ g/cm}^3$). By combining gravimetric capacity and electrode packing density, we benchmarked the performance with those of known high-rate anodes made of conventional graphite, emerging BP, Nb_2O_5 , Si and pristine MoS_2 (**Fig. 5d**, and **Supplementary Table S2-3**). The 3D architected MoS_2 anode exhibits a volumetric capacity of 1152.6 Ah/Liter at 4.5 mA/cm^2 after 1000 cycles and 500 Ah/Liter at 15 mA/cm^2 , exceeding most of the above-mentioned anodes and comparing favorably to the 2D BP benchmark with the similar performance if not better. **Supplementary Fig. 11** showcases the electrochemical performance of a prototypical full cell made of an architected MoS_2 anode and a LiFePO_4 (LFP) cathode.

Finally, we note that the dewetting-based printing, demonstrated here for 3D architected MoS_2 , is compatible with a wide variety of “2D inks”. The approach thus enables reduced graphene oxide (rGO)³⁴ and titanium carbide ($\text{Ti}_3\text{C}_2\text{T}_x$, metallically conductive MXene),³⁵ to be easily printed into 3D architected structures with precise control over structural hierarchy, multiscale porosity, conductive pathways, and spatial connectivity at wafer-scale as shown in **Supplementary Figs. 12-16** and **Table 4**. Additionally, our methodology represents a very visible nexus to merge emerging concepts in 2D layered materials, such as contact resistance³⁶, Janus and van der Waals (vdW) heterostructure³⁷, phase engineering³⁸ and defect tailoring^{36,39,40}, at successive length scales, producing new interfaces and properties not seen in both bulk materials or atomically thin nanosheets. Our work thus has profound implications for enabling applications beyond Li-ion batteries and for integrating materials beyond MoS_2 .

Methods

Characterizations. A ZEISS ULTRA-55 scanning electron microscopy (SEM) equipped with a Quantax EDX (Xflash® 6|100) was utilized to provide morphological views operating at 5 kV. Raman and

photoluminescence (PL) spectra on 3D architected MoS₂ were collected using a Witec alpha 300 confocal Raman microscope equipped with a RayShield coupler. A 532-nm solid-state laser as the excitation source. The excitation light with a power of 2.5 mW was focused onto the sample by a 100X objective lens (N.A. = 0.9). The signal was collected by the same objective lens, analyzed by a 0.75-m monochromator and detected by a liquid-nitrogen-cooled CCD camera. HR-TEM imaging was conducted using a Thermofisher USA (former FEI) Titan Themis Z transmission electron microscope (TEM) equipped with a double Cs (spherical aberration) corrector operating at 300 kV.

Conductivity measurement. The electronic conductivity of the samples was measured by four-probe method. In a typical measurement, powder sample with ~0.23g in mass was assembled in a Swagelok cell with an inner diameter of 13mm. The assembled cell was then loaded for 50 Mpa pressure for 3 minutes to achieve the pellets. The pellet samples were then measured employing a four-probe method (JANDEL Model RM 3000).

Mechanical measurement. Nanoindentation experiments were conducted on a Bruker Hysitron TI 950 Premier nanomechanical test platform. A Berkovich diamond nanoindenter Xprobe 2D with an included angle of 142.35° and a radius of 150 nm was used to locate and image the 3D architected MoS₂ and perform the indentation test.

X-ray absorption near edge structure (XANES). The *operando* Mo K-edge X-ray absorption near edge structure (XANES) was measured through a CR2032 coin cell with a hole, which was covered with Kapton using the fluorescent mode at beamline TPS44A at National Synchrotron Radiation Research Center (NSRRC) in Taiwan. The XANES spectra were calibrated and normalized by the Athena (version 0.8.056)/IFEFFIT (version 1.2.11) software.

Numerical Modeling. We used a numerical analysis to calculate the Li concentration gradients and corresponding stress. The diffusion of Li ions was taken as a time dependent process and was governed by Fick's second law. In COMSOL™, the module of transport of diluted species was utilized to model the diffusion process. The flux of Li ions was controlled by specifying the constant current density. We defined the full lithiation, i.e., SOC = 100%, when the structure attains the maximum theoretical capacity ($C_{\max}$) of MoS₂. To calculate the corresponding stress, Structural Mechanics module of COMSOL™ was utilized. The governing equations of identical modeling were previously described in details for other electrode materials, and will be shown briefly here.²⁸ For our case, when Li progresses, host material experiences the elastic strain ($d\epsilon_{ij}^e$) and lithiated-induced strain ($d\epsilon_{ij}^l$) i.e. thus the total strain becomes $d\epsilon_{ij}^t = d\epsilon_{ij}^e + d\epsilon_{ij}^l$ that linearly changes with Li concentration into MoS₂ structure. The relation between stress and strain can be established using the Hook's law as followings:

$$d\varepsilon_{ij}^e = d \left\{ \frac{1}{E} [(1 + \vartheta)\sigma_{ij} - \vartheta\sigma_{kk}\delta_{ij}] \right\} \quad (1)$$

where ϑ is Poisson's ratio, and E is elastic modulus of MoS₂, and σ_{ij} is the evolved stress

For $i = j$, $\delta_{ij} = 1$; otherwise $\delta_{ij} = 0$.

The bottom end of the structure was taken as fixed, while other areas were free to expand replicating the experimental conditions of lithiations. Thermal-strain approach was utilized to calculate the evolved stress during Li progression i.e., an arbitrary thermal expansion coefficient equivalent to the partial molar volume of MoS₂ was incorporated. For instance, $d\varepsilon_{ij}^l = \alpha\Delta T\delta_{ij}$, where α is equivalent to partial molar volume and ΔT represents the Δc . The diffusion coefficient, partial molar volume (molar mass/density), $C_{\max}$, E (elastic modulus) and ϑ (Poisson's ratio) were taken to be as 9×10^{-16} m²/s, 3.16×10^{-5} mol/m³, 31610 mol/m³, 2 GPa and 0.125 , respectively. The parameters of structure were comparable to the sizes taken by SEM images of fabricated structure. As the structure experiences the huge volume expansion, the non-linear or large deformation were employed in COMSOL™. The element size of mesh was taken small enough to ensure the solution convergence.

Data availability:

The data from this study are available from the corresponding author on reasonable request.

Declarations

Acknowledgement:

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Author statements:

X.W., and V.T. conceived and designed the project. X.W., Y.C., J.H.F., and Y.H.C. performed the synthesis of ce-MoS₂, rGO and MXene. X.W., C.-C.L., Y.-H.C., and W.Z. carried out the electrochemical characterizations. L.D., O.S.A., and W.X., reviewed the electrohydrodynamic printing. A.Y.L., and J.K. measured the strain-

doping profile. X.W. and C.-C.L. calculated the pseudocapacitive process. N.Q. performed the numerical modeling. All the authors discussed and contributed to the results. J.K., H.-Y.C., and V.T. wrote the paper.

Competing interests:

The authors declare no competing interests.

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Figures

Figure 1

Printing 3D architected MoS_2 through dewetting-driven destabilization. a, The manufacturing scheme illustrates the (i) exfoliation of 2D ce- MoS_2 inks; (ii) printing of ce- MoS_2 containing liquid thin films with the controlled thickness; and (iii) dewetting induced formation of vortical truss unit cell. b, Schematic of the resultant 3D architected MoS_2 . c, Demonstration of up-scalable printing of 3D architected MoS_2 on a 4-inch copper (Cu) substrate that comprises structural hierarchies over six orders of magnitude, including (d) interconnected 3D porous networks, (e) vortical truss unit cell, (f) nanopores and struts, (g) intertwined MoS_2 sheets, (h) tears and holes on the basal plane, and (i) strained-S vacancies.

Figure 2

Compression experiments on 3D architected MoS₂. a, SEM images of pre- (left panel) and post-compression (right panel) to 50% of displacement show an excellent recovery behavior. Load and displacement curve (center panel) displays a ductile-like feature with continuous serrated flow indicated by the gray arrows. b, Optical image of a 2-inch Cu substrate printed with conformationally dissimilar

MoS2 made possible by the programable, dewetting-driven destabilization assisted printing. c, Raman-derived strain-charge doping (ϵ -n) map.

Figure 3

COMSOL Simulation of the 3D architected MoS2. a, Schematic illustration showcases figures of merit of the vortical truss unit cell for the use of anode in Li-ion battery. b, Li-ion diffusion, and the associated concentration distribution within the architected MoS2 at different state-of-charge (SOC). The highest

concentration of scale bar at SOC=100% is calculated from the theoretical capacity of pristine MoS₂. c, Volume expansion at various SOC. d, Galvano-static discharge and charge profiles measured at constant and different current densities. e, Cycling performance of architected MoS₂ anodes measured at current densities of 5 A/g and 10 A/g, respectively.

Figure 4

In situ XANES tracking of electrochemical redox (pseudocapacitive) reaction of architected MoS₂ anode. a, Normalized operando Mo K-edge XANES spectra of 3D architected MoS₂ electrode measured at different potentials (blue: the discharging process; red: the charging process). b, Normalized operando Mo K-edge XANES spectra for the first cycle at OCV (2.86 V), the first fully discharge (0.01 V), and the first fully charge (3 V) of MoS₂, compared with MoO₃ and Mo metal foil reference materials. c, The cyclic voltammograms of 3D architected MoS₂ anode at a scan rate of 0.3 mV s⁻¹ and (d) the corresponding absorption edge energy shift (ΔE_{edge}) of 3D architected MoS₂ at different potentials (as labeled in the cyclic voltammograms).

Figure 5

High mass loadings of 3D architected MoS₂. a, High-resolution scanning electron microscope (HRSEM) images provide both cross-sectional and close-up views of 3D architected MoS₂ with increased mass loadings. b, Nyquist plots of architected MoS₂ (blue), crumples (green), wrinkles (orange) and bulks (gray). c, High aerial mass loading test (up to 3.5 mg cm⁻² active material) of 3D architected MoS₂

anodes. d, Volumetric capacity of architected MoS₂ outperforms various state-of-the-art anodes and compares favorably to the current benchmark of 2D BP composite anodes.

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