On-stack two-dimensional conversion of MoS$_2$ into MoO$_3$

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Abstract

Chemical transformation of existing two-dimensional (2D) materials can be crucial in further expanding the 2D crystal palette required to realize various functional heterostructures. In this work, we demonstrate a 2D ‘on-stack’ chemical conversion of single-layer crystalline MoS$_2$ into MoO$_3$ with a precise layer control that enables truly 2D MoO$_3$ and MoO$_3$/MoS$_2$ heterostructures. To minimize perturbation of the 2D morphology, a nonthermal oxidation using O$_2$ plasma was employed. The early stage of the reaction was characterized by a defect-induced Raman peak, drastic quenching of photoluminescence signals and sub-nm protrusions in atomic force microscopy images. As the reaction proceeded from the uppermost layer to the buried layers, PL and optical second harmonic generation signals showed characteristic modulations revealing a layer-by-layer conversion. The plasma-generated 2D oxides, confirmed as MoO$_3$ by x-ray photoelectron spectroscopy, were found to be amorphous but extremely flat with a surface roughness of 0.18 nm, comparable to that of 1L MoS$_2$. The rate of oxidation quantified by Raman spectroscopy decreased very rapidly for buried sulfide layers due to protection by the surface 2D oxides, exhibiting a pseudo-self-limiting behavior. As exemplified in this work, various on-stack chemical transformations can be applied to other 2D materials in forming otherwise unobtainable materials and complex heterostructures, thus expanding the palette of 2D material building blocks.

Since the first mechanical exfoliation of two-dimensional (2D) crystalline graphene [1, 2], various dielectric and semiconducting analogues represented by h-BN and MoS$_2$ have been isolated, revealing many new scientific phenomena and principles [3–9]. Despite being incompatible with mass production of large area samples, this simple exfoliation method can be applied to essentially any layered material with weak interlayer interactions [3], remaining one of the best methods for high quality crystals [10, 11]. Since most single layer (1L) transition metal dichalcogenides (MX$_2$, where M and X denote the metal and chalcogen, respectively) are predicted to be thermodynamically stable [12], the palette of 2D crystals can be filled with tens of metallic, semiconducting and insulating ‘colors’. In contrast to ‘top-down’ exfoliation, it was also shown that 2D crystals and their heterostructures can be constructed ‘bottom-up’ from appropriate building blocks via chemical routes as demonstrated by the vapor deposition of graphene and other crystals [13–17]. Alternatively, arbitrarily stacked extended 2D structures can be formed by physically stacking one 2D crystal on top of another, exploiting interplanar van der Waals (vdW) interactions [18]. Even with limited ‘colors’ available, there have already been interesting 2D heterostructure-related reports, such as tunable metal–insulator transitions [19], field effect tunneling transistors [20], and photodetectors [21].
Chemical transformation of existing 2D materials may also be useful in further expanding the 2D crystal palette required to realize various functional heterostructures. The top single, few or even all layers of supported 2D materials may be selectively transformed into another of a different chemical nature by choosing appropriate chemical reactions. Such ‘on-stack transformations’ may form 2D materials that are not readily generated via conventional synthetic routes or physical vdW stacking routes. This presents a challenge and opportunity for chemists and materials scientists to explore and develop various chemical reactions that can be applied to each type of 2D crystal. Considering the high aspect ratio (length-to-thickness) of 2D materials, precise control over the thickness of modified layers further requires a given reaction to be highly uniform across the basal planes. In addition, chemical reactions of 2D materials are also of fundamental significance and deserve systematic investigation since their unique geometric and electronic properties may lead to novel phenomena and findings characteristic of low dimensional materials. For example, the chemical reactivity of 1L graphene was shown to be much higher than few layer-thick graphene for facile out-of-plane distortion [22–24] or larger susceptibility towards external charge doping [25]. Even the edges of graphene are distinct from the inner area in terms of chemical reactivity [24] and electronic properties [26]. The presence of solid substrates, atomically rough in most cases, has profound effects on the geometric [10, 11, 27] and electronic structures [28], chemical reactivity [23] and wettability [29] of the supported graphene.

In this regard, chemical transformation between chalcogenides of transition metals can be a model reaction to explore the chemistry of 2D materials. While the disulfides and diselenides of molybdenum have a strong tendency towards oxidation [30], the resulting trioxides may also be reduced to dichalcogenides in an excess of chalcogen precursors at elevated temperatures [31, 32]. Atomically thin MoS2 has been well studied, drawing great interest for its direct-indirect bandgap transition [5, 7] depending on the number of layers, thus revealing rich photophysics [33] and allowing various optoelectronic applications [34]. MoO3, with a larger bandgap (>2.7 eV), is photochromic [35] and electrochromic [36], and has thus been actively investigated for its potential in displays and smart windows [37]. With a large work function of 6.7 eV, MoO3 films also serve as hole dopants as well as hole transport layers [38]. Due to its high dielectric constant, MoO3 may serve as an ideal gate dielectric [38] for atomically thin transistors based on 2D semiconductors [39]. Although there have been many studies on thin MoO3 films formed by thermal and sputter deposition [37], their surfaces exhibited a typical roughness larger than a few nm [40], far from the layer-by-layer precision that can be routinely achieved with various 2D crystals. Since atomically thin MoS2 layers of high crystallinity or large area can be prepared, respectively, by the exfoliation [3] or chemical vapor deposition (CVD) method [41], 2D oxides of atomic thickness may be generated by chemical transformation of the 2D sulﬁdes.

In this work, we demonstrate O2-plasma-based conversion of 2D MoS2 crystals into highly flat 2D MoO3 or MoO3/MoS2 heterostructures with layer-by-layer precision. As the plasma oxidation time increased, the Raman and photoluminescence (PL) intensity from MoS2 decreased, indicating loss of the sulﬁdes. X-ray photoelectron spectroscopy (XPS) showed that Mo6+ increased at the expense of Mo4+, conﬁrming the conversion. Optical second-harmonic generation (SHG) spectroscopy revealed a drastic alteration in intensity, which is explained by the breakage and recreation of inversion symmetry in the remaining crystalline sulﬁdes. The plasma-generated 2D oxides were highly flat, with a typical roughness of 0.18 nm. The thickness of a single layer oxide was 1.8 ± 0.1 nm, ~2.5 times the interlayer spacing of crystalline α-MoO3. Systematic Raman and atomic force microscopy (AFM) measurements also revealed that the oxidation proceeded from the top layer into the underlying layers, with the rate decaying rapidly due to the passivation effect of the surface oxide layers. Our study suggests that similar on-stack chemical transformations can be devised to convert one form of 2D chalcogenide into another or their heterostructures, which should expand the palette of 2D materials.

**Results and discussion**

**Raman spectroscopic characterization of 2D sulﬁdes and their oxidation**

Figures 1(a) and (b) show optical micrographs of 1L and 2L MoS2 (1LMS and 2LMS, respectively) obtained before and after a series of exposures to low-frequency O2 plasma (see methods for the details). The accumulated exposure time ($t_{ox}$) represents the total reaction time. The optical contrast of both samples significantly decreased at $t_{ox} ≥ 26$ s, and the ﬂake of 1LMS could be barely identiﬁed at $t_{ox} = 242$ s. The change in the optical contrast was attributed to the conversion to 1L MoO3 (1LMS) with negligible absorption in the visible range, as will be shown below. A similar contrast change was observed for nLMS ($n = 3–4$) (see figure S1). Figure 1(c) shows the Raman spectra of 1LMS obtained in the ambient conditions at various $t_{ox}$. Among the four Raman-active modes of bulk 2H-MoS2 (space group $D_{3h}^2$) [42], the in-plane $E_{2g}$ and out-of-plane $A_{1g}$ were shown to be useful in determining the number ($n$) of layers of thin MoS2 samples [6]. Although their symmetry representations vary depending on $n$ ($E'$ and $A'_1$ for odd-numbered nLMS belonging to the $D_{3h}^1$ space group; $E_2$ and $A_{1g}$ for even-numbered nLMS belonging to the $D_{3d}^2$ space group)
[43], the bulk-notations will be used for simplicity according to the original report for 1L [6]. The frequency difference ($\Delta \omega$) of the two Raman peaks was found to be 18.5 cm$^{-1}$, and their widths were comparable to those of the previous report [6], which confirms that the sample is single-layered. The lack of the defect-activated LA(M) peak also verifies its high structural quality (figure S2) [44]. As further direct evidence, atomically resolved transmission electron microscope (TEM) images and diffraction patterns were obtained for freestanding 1L samples (figure S3).

Oxidation induces a few distinctive changes in the Raman spectra. The in-plane Raman mode softened by $\sim$1 cm$^{-1}$ on the first exposure for 2 s and downshifted further with the other mode moving in the opposite direction when subjected to additional exposure ($t_{ox} = 8$ s). Since the newly evolving Raman peaks have both lower and higher peak frequencies than their pristine counterparts, their frequency difference, $\Delta \omega_{(NC)}$, is $\sim$5 cm$^{-1}$ larger than that of pristine 1L$_{\text{SSS}}$. Both peaks also broadened asymmetrically and displayed attenuated intensity. For $t_{ox} = 26$ s, when significant loss was observed in the optical contrast in figure 1(a), for example, the Raman intensities $I$(E$_{1g}^\text{ox}$) and $I$(A$_{1g}$) decreased to $\sim$5% of those for the pristine sample, with both peaks moving further away from each other and further broadening. The additional exposure ($t_{ox} = 80$ s) led to no detectible signal for both peaks, indicating complete loss of MoS$_2$. Within the phonon confinement model, the oxidation-induced downshift (upshift) of E$_{1g}$ (A$_{1g}$) can be explained by the relaxation of the fundamental Raman selection rule [45]. In essence, the defects confining phonons allow scattering of phonons with energies lower (higher) than E$_{1g}$ (A$_{1g}$) near the zone center. The low (high)-frequency shoulders of E$_{1g}$ (A$_{1g}$) that caused the asymmetric broadening are also due to the defects, which selectively allow scattering of the phonons near the M points in the double-resonance Raman scattering mechanism [46]. Indeed, the spectra of partially oxidized 1L and 2L (figures 1(c) and (d)) are well described by the five Voigt functions, including the defect-activated TO(M), LO(M) and ZO(M) [44, 45]. As discussed in detail below, plasma-generated reactive oxygen species create sub-oxide defects (MoS$_x$O$_{1-x}$) on the basal plane of MoS$_2$, essentially forming a nanocrystalline (NC) phase MoS$_2$ sheet.

The Raman spectra of multi-layered samples showed similar spectral changes with a layer-by-layer oxidation behavior. The in-plane mode of 2L$_{\text{SSS}}$ in figure 1(d), for example, showed a noticeable broadening due to the M-point phonons for $t_{ox} = 8$ s and became sharper with 40% attenuated intensity for $t_{ox} = 26$ s. Additional exposure ($t_{ox} = 80$ s) led to a further decrease in intensity and significant

![Figure 1. Raman spectroscopic characterization of plasma-oxidized MoS$_2$. (a) and (b) Optical micrographs of single and double-layer MoS$_2$ (1L$_{\text{SSS}}$ and 2L$_{\text{SSS}}$) obtained after O$_2$ plasma treatment for varying oxidation time ($t_{ox}$). When completely oxidized after 242 s, both samples became transparent, indicating formation of the corresponding 2D Mo oxides (1L$_{\text{Ox}}$ and 2L$_{\text{Ox}}$). (c) and (d) Raman spectra of 1L and 2L MoS$_2$, obtained with increasing $t_{ox}$, of (top to bottom) 0, 2, 8, 26, 80 and 242 s. The raw spectra (open circles and solid lines) were offset for clarity. The blue solid lines for $t_{ox} = 8$ s are cumulative fits of five Voigt functions representing the color-shaded Raman peaks: two violets for E$_{1g}$ and A$_{1g}$, one blue peak for TO(M), one wine for LO(M) and one olive for ZO(M) (see the text for their assignment).](image)
broadening. The NC-phase observed for $t_{\text{ox}} = 8$ s is formed on the top MoS$_2$ layer, with the bottom layer remaining intact. The disappearance of the NC-phase features for $t_{\text{ox}} = 26$ s can be attributed to complete oxidation of the top layer, which is only weakly coupled with the still pristine bottom layer responsible for the remaining half of the Raman signals. The second appearance of the broadening for $t_{\text{ox}} = 80$ s indicates that the oxidative attack reached the bottom layer, forming NC-phase domains. Additional exposure ($t_{\text{ox}} = 242$ s) led to a complete loss of Raman signal. These observations indicate that the oxidation proceeds in a layer-by-layer manner and is much slower for inner layers that are protected by the outer oxides.

**Symmetry characterization by SHG**

Since optical SHG requires a lack of inversion symmetry [47], it can serve as a sensitive symmetry probe for chemical modification occurring in thin MoS$_2$. As shown in figure 2(a), a strong SHG signal occurred at 400 nm when the fundamental 800 nm Ti:sapphire laser beam with a nominal pulse width of 140 fs was irradiated on non-centrosymmetric pristine 1L$_{\text{MS}}$ [48]. An input power dependence of the SHG peak intensity ($I_{\text{SHG}}$) confirmed the two-photon process (figure S4). The intensity of the SHG peak ($I_{\text{SHG}}$) indeed decreased with the plasma oxidation and finally reached zero for 1L$_{\text{MO}}$ ($t_{\text{ox}} = 20$ s), which correlates nicely with the Raman intensity variation of MoS$_2$ (figure 2(b)). Thus, the attenuation of $I_{\text{SHG}}$ can be attributed to the destruction of the 1L MoS$_2$ crystal. As shown in figures 2(a), 2L MoS$_2$ presents a striking contrast to the case of 1L. $I_{\text{SHG}}$(2L$_{\text{MS}}$) is ~60 times smaller than $I_{\text{SHG}}$(1L$_{\text{MS}}$) because even-number-layered MoS$_2$ crystals are centrosymmetric and thus do not support SHG. The residual signal of 2L$_{\text{MS}}$ is attributed to a minor interlayer asymmetry induced by the presence of the SiO$_2$/Si substrate [49]. A series of oxidation treatments, however, activated and then deactivated SHG by the 2L flake (figure 2(a)). Figure 2(b) reveals that $I_{\text{SHG}}$ intensity increased at the expense of the Raman signal represented by $I_{\text{A}_{1g}}$. Since $I_{\text{SHG}}$ reached its maximum at $t_{\text{ox}} = 30$ s, for which the Raman intensity is close to that of 1L$_{\text{MS}}$, the treated sample essentially corresponds to 1L$_{\text{MO}}$/1L$_{\text{MS}}$. This assignment is also supported by the fact that additional treatments led to a decrease in $I_{\text{SHG}}$, indicating oxidative degradation of the bottom sulfide layer. The lack of SHG signal from the completely oxidized layers (1L$_{\text{MO}}$ and 2L$_{\text{MO}}$) might be explained if the 2D oxides are a centrosymmetric crystal such as bulk $\alpha$-MoO$_3$ and belong to the space group of $D_{2h}^{19}$ [50]. As will be shown below, however, the 2D oxides are far from $\alpha$-MoO$_3$ and more likely to be amorphous and isotropic, thereby not generating SHG signals.
Despite the degradation of the crystalline lattice, the crystallographic orientation could still be determined for partially oxidized MoS\(_2\) since \(I_{\text{SHG}}\) is strongly dependent on the polarization angle \((\theta - \theta_0)\) between the fundamental polarization \((E_f)\) and armchair direction (\(\text{AC}\)), as defined in figure 2(c). For polarization-resolved SHG measurements, samples were rotated to vary \(\theta\), and the SHG signal parallel to the input polarization, \(I_{\text{SHG}}\) was collected using a polarizer located in front of the detector. The polar plot for 1L\(_{\text{MS}}\) in figure 2(d) revealed the 6-fold symmetry of \(I_{\text{SHG}} \propto \cos^3 3(\theta - \theta_0)\) [48], which also determined that \(\theta_0 = 15.0^\circ \pm 0.2^\circ\), the angle of \(\text{AC}\) with respect to a preset laboratory axis (LAB). When oxidized to give \(~0.4\) L\(_{\text{MS}}\), as judged from its Raman spectra \((t_{\text{ox}} = 15\) s), \(I_{\text{SHG}}\) decreased by \(~75\%\) but still showed the same angular dependence as the pristine 1L\(_{\text{MS}}\). The oxidation-induced modulation in \(I_{\text{SHG}}\) (figures 2(a) and (b)) and the robust \(\theta\)-dependence demonstrate that the SHG process can be utilized to characterize chemical changes in 2D materials.

Formation of ultraflat 2D oxides with single-layer precision

The on-stack transformation was found to proceed in a layer-by-layer manner and could be controlled with a high thickness resolution, even allowing formation of single-layer MoO\(_3\). To monitor morphological changes from the transformation, an amplitude-modulated, non-contact AFM was exploited. The height profile across the pristine 2L\(_{\text{MS}}\)-1L\(_{\text{MS}}\) area in figure 3(a) revealed a step with a height of \(0.70 \pm 0.1\) nm, which agrees well with the interlayer spacing \((0.62\) nm) of 2H-MoS\(_2\) [51]. Note that the height of the 1L\(_{\text{MS}}\)-SiO\(_2\) step varied over \(1.2-1.8\) nm from sample to sample due to the chemical and electrostatic contrast between dissimilar materials [52, 53] and interlayer molecular species trapped during the exfoliation. When 2L\(_{\text{MS}}\) was completely oxidized \((t_{\text{ox}} = 242\) s), the 2L\(_{\text{MO}}\)-1L\(_{\text{MO}}\) step height increased to \(1.8 \pm 0.1\) nm (figures 3(b) and (e)). As depicted in figure 3(f), the step height corresponds to the thickness of single-layer MoO\(_3\) and is \(~2.5\) times the interlayer spacing \((0.69\) nm) of \(\alpha\)-MoO\(_3\) [50]. A similar change was observed for the 2L\(_{\text{MS}}\)-1L\(_{\text{MS}}\) step of another sample when treated for \(t_{\text{ox}} = 242\) s (figures 3(c) and (d)). After the same treatment, however, the 3L\(_{\text{MS}}\)-2L\(_{\text{MS}}\) step height changed only by \(~0.2\) nm. In contrast to the 2L region, the Raman spectrum of the 3L region showed that \(~15\%\) of the lowermost layer remained intact (see figure S5 for Raman spectra obtained after each step of the sequential oxidations). Thus, the step height measured across the 3L-2L region corresponds to the thickness of the partially oxidized bottom layer.

Despite the increase in thickness, MoO\(_3\) layers were still highly flat, as seen in the AFM height images in figure 3. The change in the surface morphology of the 2D oxides was further quantified by the root-mean-square roughness \((R_{\text{qm}})\), or standard deviation of height distribution, shown in figure 3(c). The \(R_{\text{qm}}\) of 1L\(_{\text{MS}}\) was \(170 \pm 10\) pm, which is slightly higher than that of graphene [54] and equivalent to that of completely oxidized 1L\(_{\text{MO}}\), \(180 \pm 10\) pm for \(t_{\text{ox}} \geq 80\) s, as shown in figure S6. Notably, however, the surface roughness showed a spike of \(230 \pm 10\) pm for \(t_{\text{ox}} = 2\) s and a sharp decrease for \(t_{\text{ox}} = 8\) s. Similar spikes were also observed for 2L\(_{\text{MS}}\) and 3L\(_{\text{MS}}\) when treated for \(2\) s. The \(R_{\text{qm}}\) values of 2L\(_{\text{MO}}\) and 3L\(_{\text{MO}}\) (\(170 \pm 10\) pm) are also equivalent to those of their pristine counterparts. We attribute the roughness surge to clusters of partially oxidized MoS\(_2\), possibly molybdenum oxysulfides (MoS\(_{2}\)O\(_{y}\)) [55] that serve as nucleation sites during the plasma oxidation. This picture is also corroborated by the drastic PL quenching for \(t_{\text{ox}} = 2\) s, as will be shown below. However, the Raman spectra did not show a noticeable change (figures 1(c) and (d)) because the majority of the sample remained intact for the short reaction time.

Chemical nature of 2D oxides

The chemical transformation was revealed by XPS. While the probe size of the XPS instrument was larger than the typical size of the exfoliated samples (<\(20\) \(\mu\)m), large-area MoS\(_2\) films grown by the CVD were used (see methods for the details of preparation). While the effective thickness was found to be \(2\) L based on the peak difference \((\Delta\omega)\), their Raman intensity was lower than that of mechanically exfoliated samples, suggesting lower crystallinity (figure S7). Figure 4(a) presents the Mo 3d spectra obtained as a function of \(t_{\text{ox}}\). The pristine sample showed the strong doublet of Mo\(^{4+}\) arising from MoS\(_2\), with a binding energy \((E_B)\) of 229.5 eV (232.6 eV) for \(3d_{5/2}/3d_{3/2}\), which is consistent with the average literature value of \(E_B(3d_{5/2}) = 229.25\) eV for bulk MoS\(_2\) crystals [56]. The Mo\(^{6+}\) species of the pristine sample, responsible for the minor doublet with \(E_B = 232.7\) eV (235.7 eV) for \(3d_{5/2}/3d_{3/2}\), were attributed to residual MoO\(_3\) (<\(20\%\) of the total Mo species) formed before or after the CVD growth. Upon plasma treatment, the Mo\(^{6+}\) doublet grew significantly at the expense of the Mo\(^{4+}\) doublet, indicating the conversion to MoO\(_3\). The oxidation was also confirmed by the decrease in the intensities of the S 2s peak \((E_B = 226.7\) eV) in figure 4(a) and the S 2p doublet \((E_B = 161.9\) eV for \(2p_{3/2}\)) in figure 4(b). The current data cannot exclude the possibility that a small fraction of Mo\(^{6+}\) species \((E_B = 231.1\) eV for \(3d_{3/2}\)) [57], representing oxygen vacancy defects generated by incomplete oxidation, may be present.

To shed more light on the chemical transformation, we obtained optical absorption spectra using reflectance spectroscopy (figure S5, see methods for the details). For a very thin film (\(\text{thickness} \leq \lambda\)) supported on a thick transparent substrate with a
refractive index of $n_0$, the fractional change in reflectance ($\delta R$) is given as follows: $\delta R = \frac{R - R_0}{R_0} = 4n_0^{-1} A$, where $R$, $R_0$ and $A$ are the reflectance of the film, reflectance of the bare substrate, and absorbance [58]. Pristine 1L$_{\text{MS}}$–3L$_{\text{MS}}$ exfoliated on quartz substrates showed characteristic absorption peaks at 1.90, 2.05 and 2.85 eV, which were denoted, respectively, by A, B and C as per an earlier work [59]. The two former excitonic peaks originate from the direct-gap transitions between the valence and conduction bands at the K points in the Brillouin zone [5]. The high energy peak, C, arises from nearly degenerate multiple excitonic states [60] or transitions across nested valence and conduction bands [61]. All three peaks downshifted in energy with increasing thickness [5]. When the samples were treated for $t_{\text{ox}} = 80$ s, which is expected to oxidize $\sim$1.7L, the overall absorbance decreased significantly for all thicknesses. The A and B peaks of 1L, in particular, almost disappeared, with the major absorption edges relocated to $>2.7$ eV, which agrees well with the fact that MoO$_3$ is a wide-bandgap semiconductor [62]. The partially oxidized 2L exhibited downshifts of the A and B peaks but an upshift of the C peak, and 3L exhibited similar shifts but to a lesser degree. The spectral changes are attributed to the oxidation-induced defects and can be explained by the drastic changes in the electronic band structures of O-substituted MoS$_2$ [63]. To determine the optical bandgap of the 2D MoO$_3$, Tauc plot analysis was taken for the UV/Vis absorption spectra of CVD-grown large-area samples (figure S8). Despite some inconsistencies in the literature [64], it is generally accepted that an optical gap energy ($E_g$) of an amorphous semiconductor can be extrapolated using $(\alpha h\nu)^{2/m}$ $\propto$ $(h\nu - E_g)$ [65, 66], where $\alpha$, $h\nu$ and $m$ are, respectively, the absorption coefficient, photon energy and an exponent specifying the nature of the optical transition ($m = 2$ for an indirect allowed transition; $m = 1/2$ for a direct allowed transition). By choosing $m = 2$ for $\alpha$-MoO$_3$ as an indirect bandgap semiconductor [67], $E_g$ was determined to be $\sim3.0$ eV for 1L$_{\text{MoO}_3}$ and 2L$_{\text{MoO}_3}$. The resulting bandgap energies are in a good agreement with those of $\alpha$-MoO$_3$ crystals [62] and thermally deposited MoO$_3$ films [68, 69]. Despite the similar bandgap energies

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**Figure 3.** Layer-by-layer oxidation of few-layer MoS$_2$. (a) and (b) Non-contact AFM height images of a 1L$_{\text{MS}}$–2L$_{\text{MS}}$ sample obtained before and after oxidation ($t_{\text{ox}} = 242$ s). Height profiles across the red lines in (a) and (b) are also shown below the AFM images. (c) and (d) Non-contact AFM height images of another sample with 1L$_{\text{MS}}$, 2L$_{\text{MS}}$ and 3L$_{\text{MS}}$ regions before and after oxidation ($t_{\text{ox}} = 242$ s). Height profiles across the red lines in (c) and (d) are also shown below the AFM images. (e) Height histograms of the sample in (c) and (d) obtained for the 1L, 2L and 3L areas as a function of $t_{\text{ox}}$ at (top to bottom) 0, 2, 8, 26, 80 and 242 s. The mean height of 1L area was set to be zero. Root-mean-square roughness ($R_q$) of each area was determined by fitting the data with 3 color-shaded Gaussian functions as shown for the pristine sample (see figure S6 for the variation of the roughness induced by the oxidation). (f) Schematic diagram of ‘top-down’ layer-by-layer oxidation that converts MoS$_2$ into MoO$_3$. 
Figure 4. Elemental analysis of plasma-oxidized MoS$_2$. (a) Mo 3d XPS spectra of CVD-grown 2LMS samples oxidized for various $t_{\text{ox}}$ of (top to bottom) 0, 2, 8, 26, 80 and 242 s. The spectra were fitted with multiple mixed Lorentzian–Gaussian functions. The green shades correspond to Mo$^{4+}$ ($3d^5/2$) and Mo$^{4+}$ ($3d^3/2$) peaks and the violet shades to Mo$^{6+}$ ($3d^5/2$) and Mo$^{6+}$ ($3d^3/2$) peaks. At the binding energy of $\sim 227$ eV, the S 2s peak can be observed. (b) S 2p XPS spectra of the same samples shown in (a). The spectra were also fitted with two sub-peaks, $2p_1/2$ and $2p_3/2$. (c) The overall photoelectron intensity of Mo species and atomic fractions of Mo$^{4+}$ and Mo$^{6+}$ given as a function of $t_{\text{ox}}$.

Figure 5. The absorption spectra of 1L–3L MoS$_2$ exfoliated onto quartz substrates: (top) before and (bottom) after oxidation for $t_{\text{ox}} = 80$ s. The absorbance was determined from optical reflectance contrast measurements (see Methods for the details). See the text for the origins of the three prominent peaks denoted by A, B and C. For comparison with UV/Vis transmission measurements for CVD-grown samples and estimation of their optical bandgaps using Tauc plots, see figure S7.
and apparent layered structure of plasma-generated MoO$_3$, however, no Raman signal could be detected from the 2D oxides, possibly due to their amorphous nature. A careful Raman analysis in comparison with mechanically exfoliated thin $\alpha$-MoO$_3$ crystals set an upper bound for $\alpha$-MoO$_3$ content of $\sim 1\%$ (figure S9).

**PL intensity modulation**

The change in the PL spectra in figure 6 revealed further details of the chemical modifications occurring in 2D MoS$_2$. The PL spectrum of the pristine 1L$_{\text{MS}}$ mainly consists of the two exciton peaks A and B, respectively located at 1.84 and 2.00 eV, which is in good agreement with the absorption spectra. Both originate from the direct-gap transitions between the conduction and valence bands at the $K$ points in the Brillouin zone [5, 7]. First, we note that the PL is drastically quenched by the plasma treatments. After a 2 s exposure, for example, the intensity of A ($I_A$) decreased by $\sim 65\%$, although the Raman spectra in figure 1 show no significant change in $I(E_{2g}^{1})$ and $I(A_{1g})$. The quenching can be attributed to the plasma-generated defects that were confirmed by the defect-induced Raman peaks, as will be further discussed below. When further defects were introduced to form the NC phase ($t_{\text{ox}} = 8$ s), the PL intensity was only $\sim 10\%$ of the pristine value. The completely oxidized 1L$_{\text{MO}}$ gave no PL signal, which is consistent with the fact that its $E_g$ is larger than the excitation photon energy of 2.41 eV. 2L$_{\text{MS}}$ in figure 6(b) shows a similar defect-mediated PL quenching—$\sim 60\%$ decrease for $t_{\text{ox}} = 2$ s and almost zero PL signal for $t_{\text{ox}} = 8$ s, which introduced a significant number of defects judging from the Raman spectrum (figure 1(c)). Upon further oxidation ($t_{\text{ox}} = 26$ s), however, the PL intensity increased back to $\sim 30\%$ of that for the pristine 2L$_{\text{MS}}$.

We note that the Raman spectra showed that the top layer was almost completely oxidized with the bottom layer mostly intact (figure 1(d)). This suggests that the system essentially became a 1L$_{\text{MO}}$/1L$_{\text{MS}}$/SiO$_2$ sandwich, which further corroborates the layer-by-layer oxidation. Thicker samples showed a similar trend, but the PL intensity oscillation of $n$L$_{\text{MS}}$ could be seen only when $t_{\text{ox}}$ was selected in such a way that $(n - 1)$ L$_{\text{MO}}$/1L$_{\text{MS}}$ was nicely formed.

Structural defects in crystalline semiconductors have various modes of interaction with excited charge carriers, and their interactions become more significant in lower dimensional materials due to confined wave functions within a tighter space. For carbon nanotubes with low lying dark exciton states, sp$^3$-type defects form new sets of radiative energy levels granting an enhanced PL quantum yield [70]. Defects may trap excited free charge carriers and mediate ultrafast Auger decay of photoexcitation in quantum dots [71]. Excitons can be localized at defects and radiatively decay at lower energies, as shown for 1L MoS$_2$ irradiated with $\alpha$ particles [72] and 1L WS$_2$ treated with Ar plasma [73]. Defects in some 2D semiconductors have also been shown to serve as single photon emitters [74, 75]. Localization followed by non-radiative decay is one among various quenching routes of excitons, which also include exciton-exciton annihilation and electron–phonon interactions [76]. The PL quenching
observed at the very early stage of the oxidative conversion can be attributed to partially oxidized defects, including the nanometer scale protrusions that were responsible for the roughness spikes (figure S6). The higher defect-sensitivity of PL can be more clearly seen in the comparison between Raman and PL intensities given as a function of \( t_{ox} \) (figure S10).

Layer-by-layer conversion

The overall change can be summarized by the scheme for 3LMS with terraces of 2LMS and 1LMS presented in figure 3f. At the early stage of reactions (\( t_{ox} = 2 \) s), the top surface of 3LMS exposed to the gaseous oxidants undergoes partial oxidation forming nanometer-scale oxysulfides (MoS\(_2\)O\(_x\)) clusters that are responsible for the increased \( R_g \). At this stage, the average thickness of the top layer is not much different from that of pristine 1LMS or the interlayer spacing of 2H-MoS\(_2\) crystals. Although the Raman spectra reveal no significant change, the PL intensity of 3LMS drops significantly due to the lack of quenching sites within the remaining 2LMS. Further exposure will repeat the above reactions for the second top layer but with a greatly decreased reaction rate.

Although the Raman analysis suggests that the 2D oxides are amorphous, their high flatness and modulation in SHG and PL intensities indicate that the oxidation reaction proceeds in the layer-by-layer manner. Thus, it is likely that the oxides are also layered like \( \alpha \)-MoO\(_3\) crystals. Since the number density of Mo in a single \( \alpha \)-MoO\(_3\) layer [67] is 18% higher than that for 1LMS [51], a 2D conversion into the crystalline oxide would lead to a large tensile strain (~9%) when the areal density of Mo is maintained or generate voids requiring significant mass transport to compensate for the difference in the Mo densities. Moreover, the average thickness of 1L-MoO\(_3\) (figure 3) is 2.5 times the interlayer spacing of \( \alpha \)-MoO\(_3\). These facts suggest that the 2D oxides are much less dense than \( \alpha \)-MoO\(_3\). Despite the apparent flatness and lack of pits or cracks in the 2D oxides, these considerations lead us to conclude that there must be numerous structural irregularities, including fine voids, that cannot be detected by the AFM probes. Our results also showed that the plasma oxidation is highly effective for the topmost sulﬁde layer and increasingly slower for the next buried layers. Such voids may serve as a route for the oxidants required for the reactions underneath the top layer.

In summary, we demonstrated a model 2D chemical reaction that converts 1L sulfides into 1L oxides, thus allowing MoO\(_3\)/MoS\(_2\) heterostructures. Single and few-layer MoS\(_2\) prepared via micromechanical exfoliation of 2H-MoS\(_2\) crystals were treated with strong oxidants generated from O\(_2\) plasma. The early stage of the reaction was detected by defect-induced Raman peaks, drastic quenching of PL signals and sub-nm protrusions in AFM images. As the reaction proceeded from the uppermost layer to buried layers, PL and SHG signals showed characteristic modulations revealing a layer-by-layer conversion. The plasma-generated 2D oxides, confirmed as MoO\(_3\) by XPS, were found to be amorphous but highly flat with a surface roughness of 0.18 nm, comparable to that of 1L MoS\(_2\). The rate of oxidation quantified with Raman spectroscopy decreased very rapidly for buried sulﬁde layers due to protection by the surface 2D oxides. As exempliﬁed in this work, the on-stack chemical transformation can be applied to other 2D materials in forming otherwise unobtainable materials and complex heterostructures, thereby expanding the palette of 2D material building blocks.

Experimental section

Mechanical exfoliation

Single and few-layer MoS\(_2\) samples were prepared by mechanical exfoliation [3] of molybdeneite, a natural mineral of 2H-MoS\(_2\) (SPI). Silicon wafers with 285 nm thick SiO\(_2\) layers were used as substrates. Ultrathin layers of MoS\(_2\) were identiﬁed using an optical microscope, and their numbers of layers and quality were determined using Raman spectroscopy [6]. To prepare thin \( \alpha \)-MoO\(_3\) crystalline ﬂakes as a Raman standard (ﬁgure S9), a similar mechanical exfoliation was applied to a powder of MoO\(_3\) (Materion).

Growth of large-area samples by CVD

Two different CVD growth methods were used in synthesizing large area MoS\(_2\) films. In one approach for the samples used for XPS measurements, Mo metal of 0.5 nm for 2LMS was deposited on SiO\(_2\)/Si substrates by e-beam evaporation. The samples were positioned in a quartz tube furnace, which was then evacuated to a low vacuum. The samples were heated to 750 °C under a flow of Ar at 50 ml min\(^{-1}\). Since the surface of deposited Mo films usually oxidizes when exposed to ambient air during transfer to the furnace, H\(_2\) gas was briefly introduced at 750 °C to reduce the Mo oxides. After the pre-annealing and reduction processes, a H\(_2\)S/H\(_2\)/Ar gas mixture (1:5:50) was introduced for 15 min to sulfurize Mo ﬁlms into MoS\(_2\). The pressure in the furnace was maintained at 300 mTorr during the sulfurization step. To enhance the crystallinity of grown films, the samples were further annealed briefly at 1000 °C under a ﬂow of the H\(_2\)S/Ar gas mixture (1:50). In the approach for the samples used in UV/Vis measurements, 5–10 mg of MoO\(_3\) powder (Sigma-Aldrich) in a quartz boat was
placed at the center of the furnace, and quartz substrates were placed near and downstream of the boat. The furnace was heated to 600 °C at a rate of 20 °C min⁻¹ under Ar gas flow at a rate of 200 ml min⁻¹. At 600 °C, H₂S gas was introduced for 30 min at a rate of 1 ml min⁻¹ to sulfurize MoO₃ into MoS₂. Then, the samples were rapidly cooled to room temperature. The average thickness and quality of the grown films were characterized by their Raman and PL spectra.

Plasma oxidation
For oxidation, samples were treated with either of two low-frequency plasma instruments operated at 50 kHz, a commercial unit (Femto Science Inc., Cute-1MP) and a quartz-tube-type unit. The partial pressure of O₂ in the two plasma chambers was 540 and 300 mTorr, respectively. For oxidation reactions, oxygen plasma was maintained for a pre-specified period of 10 min at a rate of 1 ml min⁻¹. The apparent oxidation was ∼3 times faster for the former than the latter. Thus, t₁₀₀ given in this work has been corrected for the difference.

Raman and PL measurements
The Raman and PL spectra of the samples were obtained with a microscope-based (Nikon, Ti) Raman setup that is equivalent to that detailed elsewhere [77, 78]. Briefly, the 514 nm excitation beam from a solid state laser (Cobolt, Fangdango) was focused onto an ∼1 μm diameter spot using an objective lens (40X, numerical aperture = 0.60). The back-scattered signal was collected by the same objective and guided to a spectrograph (Princeton Instruments, SP2300) combined with a liquid nitrogen-cooled charge-coupled detector (CCD) (Princeton Instruments, PyLon). The spectral resolutions judged from the FWHM of the Rayleigh line were 3.0 and 12 cm⁻¹ for the Raman and PL spectra, respectively.

SHG measurements
A similar microscope-based spectroscopy setup was employed for the SHG detection. A train of 140 fs pulses from a Ti:Sapphire laser (Coherent, Chameleon) operated at 800 nm was focused onto a 1.6 μm spot in FWHM with an objective lens (40X, numerical aperture = 0.60). The backscattered SHG signal centered at 400 nm was collected and fed to a spectrograph (Andor, Shamrock 303i) equipped with a thermoelectrically cooled CCD (Andor, Newton). To vary the polarization angle of the fundamental laser with respect to the MoS₂ lattice vectors, samples were rotated in a rotational mount with an angular accuracy better than 0.2°. For polarized detection, the SHG signal was filtered with a polarizer located in front of the spectrograph.

AFM measurements
The topographic details of the samples were investigated using an atomic force microscope (Park Systems, XE-70). The height images were obtained in non-contact mode using Si tips with a nominal tip radius of 8 nm (MicroMasch, NSC-15). The AFM tip was driven to a free oscillation with an amplitude of 20 nm and engaged in amplitude-modulated scanning with an amplitude set-point of ∼14 nm.

XPS measurements
The elemental information of the CVD-grown samples was obtained using an x-ray photoelectron spectrometer (Thermo Scientific, K-Alpha™). XPS measurements were carried out with Al Kα line (1.4866 keV). The binding energy of the photoelectrons was calibrated with respect to Mo(IV) 3d₅/₂ (E₀ = 229.5 eV), which was more reliable than the C 1s peak (E₀ = 284.6 eV) originating from carbon residues on the samples.

Optical absorption measurements
For the samples exfoliated onto quartz substrates, fractional changes in reflectance were used to obtain absorption spectra. As a broadband Vis/NIR light source, the output of a tungsten-halogen lamp (iISIM Inc., Mighty Light Beam) was collected with a multimode optical fiber (core diameter of 50 μm) and guided to the micro-spectroscopy setup used for the SHG measurements. The FWHM of the focus spot was 0.8 and 2.0 μm in the visible and NIR ranges, respectively. For the samples CVD-grown on quartz substrates, the absorption spectra were obtained with a UV/visible spectrometer (Jasco, V-650).

TEM measurements
For TEM measurements, MoS₂ flakes exfoliated onto SiO₂/Si substrates were transferred to carbon-film grids with 2 μm holes (Quantifoil) using an isopropyl alcohol and KOH solution [79]. The samples were analyzed using an aberration-corrected FEI Titan Cubed TEM (FEI, Titan² G2 60-300), which was operated at 80 kV acceleration voltage with a monochromator. The microscope provides sub-angstrom resolution at 80 kV and −11 ± 0.5 μm of spherical aberration (Cₐ).

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