# Scalable Fabrication of Molybdenum Disulfide Nanostructures and their Assembly 

Yun Huang, Kang Yu, Huaizhi Li, Kai Xu, Zexi Liang, Debora Walker, Paulo Ferreira, Peer Fischer, and Donglei (Emma) Fan*


#### Abstract

Molybdenum disulfide $\left(\mathrm{MoS}_{2}\right)$ is a multifunctional material that can be used for various applications. In the single-crystalline form, $\mathrm{MoS}_{2}$ shows superior electronic properties. It is also an exceptionally useful nanomaterial in its polycrystalline form with applications in catalysis, energy storage, water treatment, and gas sensing. Here, the scalable fabrication of longitudinal $\mathrm{MoS}_{2}$ nanostructures, i.e., nanoribbons, and their oxide hybrids with tunable dimensions in a rational and well-reproducible fashion, is reported. The nanoribbons, obtained at different reaction stages, that is, $\mathrm{MoO}_{3}$, $\mathrm{MoS}_{2} / \mathrm{MoO}_{2}$ hybrid, and $\mathrm{MoS}_{2}$, are fully characterized. The growth method presented herein has a high yield and is particularly robust. The $\mathrm{MoS}_{2}$ nanoribbons can readily be removed from its substrate and dispersed in solution. It is shown that functionalized $\mathrm{MoS}_{2}$ nanoribbons can be manipulated in solution and assembled in controlled patterns and directly on microelectrodes with UV-click-chemistry. Owing to the high chemical purity and polycrystalline nature, the $\mathrm{MoS}_{2}$ nanostructures demonstrate rapid optoelectronic response to wavelengths from 450 to 750 nm , and successfully remove mercury contaminants from water. The scalable fabrication and manipulation followed by light-directed assembly of $\mathrm{MoS}_{2}$ nanoribbons, and their unique properties, will be inspiring for device fabrication and applications of the transition metal dichalcogenides.


Transition metal dichalcogenides (TMD) have attracted immense research interest owing to their 2D stacking molecular structures and the resulted chemical and physical properties. ${ }^{[1]}$ Among various TMD materials, single-crystal molybdenum disulfide $\left(\mathrm{MoS}_{2}\right)$ nanoflakes in the 2 H -phase, which constitute the basic unit of various crystalline $\mathrm{MoS}_{2}$ nanostructures and bulk $\mathrm{MoS}_{2}$, possess edge sites and in plane sulfur vacancies which for instance show outstanding catalytic activity with an ultralow hydrogen adsorption Gibbs free energy-similar to that of the most efficient platinum and other noble metals. ${ }^{[2]}$ However, in contrast to platinum, $\mathrm{MoS}_{2}$ is much cheaper, and because it is a semiconductor, its electric conductivity can be readily tuned by the application of a voltage or light. This has been exploited in a variety of applications. For instance, $\mathrm{MoS}_{2}$ has been demonstrated as an optical and biochemical sensor material. ${ }^{[3]} \mathrm{MoS}_{2}$ fieldeffect transistors exhibit an on/off ratio as high as $\approx 10^{8}$ and near-ideal subthreshold
Y. Huang, Dr. K. Yu, H. Li, Z. Liang, Prof. P. Ferreira, Prof. D. Fan

Materials Science and Engineering Program
Texas Materials Institute
The University of Texas at Austin
Austin, TX 78712, USA
E-mail: dfan@austin.utexas.edu
Dr. K. Yu, Prof. P. Ferreira
The Department of Advanced Electron Microscopy
Imaging and Spectroscopy
International Iberian Nanotechnology Laboratory
Braga 4715-330, Portugal
Dr. K. Xu
Electrical and Computer Engineering
University of Illinois at Urbana-Champaign
Urbana, IL 61801, USA
Dr. D. Walker
School of Engineering and Applied Sciences
Harvard University
Cambridge, MA 02138, USA
(iD The ORCID identification number(s) for the author(s) of this article
can be found under https://doi.org/10.1002/adma.202003439.

Prof. P. Ferreira
Mechanical Engineering Department and IDMEC
Instituto Superior Técnico
University of Lisbon
Av. Rovisco Pais, Lisboa 1049-001, Portugal
Prof. P. Fischer
Max-Planck-Institute for Intelligent Systems Heisenbergstr. 3, Stuttgart 70569, Germany
Prof. P. Fischer
Institute of Physical Chemistry
University of Stuttgart
Pfaffenwaldring 55, Stuttgart 70569, Germany
Prof. D. Fan
Walker Department of Mechanical Engineering
The University of Texas at Austin
Austin, TX 78712, USA

DOI: 10.1002/adma. 202003439
swing of $\approx 65 \mathrm{mV} \mathrm{dec}{ }^{-1} \cdot{ }^{[4]}$ Flakes of $\mathrm{MoS}_{2}$ have been used for water treatment for the removal of mercury. ${ }^{[5]}$ Moreover, sizedependent effects, have been found when modulating dimensions of $\mathrm{MoS}_{2}$ nanostructures. ${ }^{[6,7]}$ Indeed, $\mathrm{MoS}_{2}$ emerges as a highly promising material that may impact many research fields, including electronics, ${ }^{[8]}$ catalysis, ${ }^{[9]}$ energy storage, ${ }^{[10]}$ water treatment, ${ }^{[11]}$ and gas sensing. ${ }^{[12]}$

To realize the full potential of $\mathrm{MoS}_{2}$, the first task is to find a convenient and robust means to scalably fabricate $\mathrm{MoS}_{2}$ with controllable dimensions. So far, various attempts have been made to synthesize $\mathrm{MoS}_{2}$ thin films and 3D composites via chemical vapor deposition (CVD) and hydrothermal growth. ${ }^{[13]}$ Tubular $\mathrm{MoS}_{2}$ or core-shell $\mathrm{MoS}_{2}$ /oxide nanostructures can be grown via a catalyzed transport reaction, ${ }^{[14]}$ sintering of $\left(\mathrm{NH}_{4}\right)_{2} \mathrm{MoS}_{4}$ in hydrogen/thiophene, ${ }^{[15]}$ and sulfurization of oxide nanobelts. ${ }^{[16]}$ Nevertheless, only modest dimensional control can be realized, and the quality is variable. It remains extremely challenging to synthesize $\mathrm{MoS}_{2}$ with a tunable geometry in larger volumes, which is imperative for applications and rational device integration. Only in a very recent report has it been shown that the dimensionality of thin $\mathrm{MoS}_{2}$ nanoribbons could be tuned when it is grown on phosphine pre-treated $\mathrm{Si}(001)$ surfaces. ${ }^{[7]}$ The nanoribbons are fabricated with a yield of $75 \%$, mixed with triangle nanosheets, and they exhibited optical properties that depended on their dimensionality. The as-obtained $\mathrm{MoS}_{2}$ nanoribbons are attached to the substrate in random positions and orientations. There is thus a notable technological gap between the unique properties of $\mathrm{MoS}_{2}$ and its applications due to the daunting task of fabricating $\mathrm{MoS}_{2}$ nanostructures of controlled and tunable dimensions with high yield, scalability and reproducibility.

Besides the demand in the fabrication of controlled $\mathrm{MoS}_{2}$ nanostructures, it is of great interest to be able to assemble them into different configurations for device characterization and integration. In reality, the majority of the state-of-the-art $\mathrm{MoS}_{2}$ nanodevices still rely on lithographic patterning of flakes of $\mathrm{MoS}_{2}$ that are exfoliated from bulk materials or grown via CVD. ${ }^{[17]}$ The device making process and assembly thus far is tedious due to the random dispersion of $\mathrm{MoS}_{2}$ flakes, and the required efforts in removing them from a substrate.

Here, we present a robust method of growing freely dispersible $\mathrm{MoS}_{2}$ nanostructures with tunable elongated morphologies, that is, nanoribbons, in relatively large quantities. Given the well-defined geometry of the $\mathrm{MoS}_{2}$ nanostructures, we are able to demonstrate their assembly into various designed configurations by utilizing a combined nanomanipulation and UVclick chemical reaction. Further tests show the rapid optoelectronic response of the nanoribbons and their effectiveness in the removal of mercury from water.

The fabrication of the $\mathrm{MoS}_{2}$ nanoribbons starts from the synthesis of $\mathrm{MoO}_{3}$ nanoribbon precursors via a hydrothermal reaction (Figure 1a-c). The growth method of the $\mathrm{MoO}_{3}$ nanoribbons is herein modified from the previously reported procedure such that large quantities can be obtained much more readily. ${ }^{[18]}$ In brief, a solution containing ammonium heptamolybdate tetrahydrate and nitric acid is heated and kept at $180^{\circ} \mathrm{C}$ for 20 h (Experimental Details in Supporting Information). After cooling and washing, the procedure yields a white powder of $\mathrm{MoO}_{3}$ nanoribbons, which can be collected and dried (Figure 1a-d). The length distribution is shown in Figure S1, Supporting Information. The $\mathrm{MoO}_{3}$ powder is placed in
a two-zone furnace (Mellen TC12) at $500{ }^{\circ} \mathrm{C}$, 25 cm from the opening inside a quartz tube sealed at one end ( 30 cm long and 18 mm in diameter) for 30 min , and 20 cm away from the sulfur powder inside an identical tube at $200^{\circ} \mathrm{C}$. A flow of argon gas at 50 sccm is introduced to carry the sulfur vapor such that it can react with the $\mathrm{MoO}_{3}$ nanoribbons. The reaction produces $\mathrm{MoS}_{2} /$ $\mathrm{MoO}_{2}$ hybrid nanoribbons (Figure 1b-e). Here, the temperature of $500^{\circ} \mathrm{C}$ is carefully chosen so that the sulfurization can proceed efficiently without changing the nanoribbon morphology. We found that at a temperature of $650{ }^{\circ} \mathrm{C}$ and higher, the $\mathrm{MoO}_{3}$ nanoribbons collapse to chains of nanoparticles (Figure S2, Supporting Information), which is perhaps not surprising as the melting temperature of bulk $\mathrm{MoO}_{3}$ is $795{ }^{\circ} \mathrm{C}$. ${ }^{[19]}$ The conversion of $\mathrm{MoO}_{3}$ into $\mathrm{MoS}_{2} / \mathrm{MoO}_{2}$ hybrid nanoribbons substantially increases the temperature stability, since the melting temperatures of $\mathrm{MoS}_{2}$ and $\mathrm{MoO}_{2}$ are as high as 2375 and $1100^{\circ} \mathrm{C}$, respectively. Finally, a second sulfurization process is carried out at $900^{\circ} \mathrm{C}$, which completely converts all hybrid $\mathrm{MoS}_{2} / \mathrm{MoO}_{2}$ nanoribbons to $\mathrm{MoS}_{2}$ nanoribbons in 30 min (Figure $1 \mathrm{c}-\mathrm{f}$ ). The process is carefully designed and has been reported for the first time to the best of our knowledge. We obtain a spatula full of $\mathrm{MoS}_{2}$ nanoribbons from one synthesis (Figure $1 f$ inset). However, the procedure can readily be scaled up to obtain even larger quantities.

With the above fabrication process, $\mathrm{MoO}_{3}$, hybrid $\mathrm{MoS}_{2} /$ $\mathrm{MoO}_{2}$, and $\mathrm{MoS}_{2}$ all form longitudinal nanostructures (Figure 1d-f). Atomic force microscopy analysis shows that these products are ribbon-like with notably different widths and thicknesses in their cross-sections (Figure S3a, Supporting Information). The chemistry and structures of the as-fabricated nanoribbons of $\mathrm{MoO}_{3}$ (Figure $1 \mathrm{~g}-\mathrm{j}$ ), $\mathrm{MoS}_{2} / \mathrm{MoO}_{2}$ (Figure $1 \mathrm{~h}-\mathrm{k}$ ), and $\mathrm{MoS}_{2}$ (Figure 1i-1) are determined by Raman spectroscopy and X-ray diffractometry (XRD). Note that the $\mathrm{MoO}_{3}$ nanoribbons serve as both fabrication guiding templates and as the reaction source, which allows us to grow $\mathrm{MoS}_{2}$ and $\mathrm{MoS}_{2} / \mathrm{MoO}_{2}$ nanoribbons with tunable dimensions by adjusting the dimensions of the $\mathrm{MoO}_{3}$ precursors.

Phase-contrast transmission electron microscopy (TEM), reveals that the obtained $\mathrm{MoO}_{3}$ nanoribbons are single crystals with an anisotropic orthorhombic layered structure (Figures S4 and S 5 , Supporting Information), which is consistent with a previous study. ${ }^{[20]}$ The ribbons grow along the [001] and [100] orientations along their length and width, respectively. Since the reaction energy depends on the acidity of the suspension, and is distinct along different crystalline orientations, we systematically increase the acidity of the reaction suspension to tune the growth anisotropy (with pH values ranging from 0.0 to -1.0 ). Indeed, it is found that the growth of the $\mathrm{MoO}_{3}$ nanoribbons along the [001] direction can be dramatically increased compared to that along the width ([100] direction), which permits the dimensions to be tuned. As shown in Figure 2, the length of $\mathrm{MoO}_{3}$ crystal structures can change from a few micrometers (Figure 2a,b) to $70 \mu \mathrm{~m}$ (Figure 2e,f). The distribution can be easily refined by a simple one-step filtration. As shown in Figure 2 g ,h and Figure S6, Supporting Information, long ( $>20 \mu \mathrm{~m}$ ) and short $(<20 \mu \mathrm{~m})$ ribbons synthesized as per the condition of Figure 2e can be easily separated by using a $40 \mu \mathrm{~m}$ filtration paper. For the longest ribbons, the width and thickness are around $1.2 \mu \mathrm{~m}$ and 64 nm , respectively (at $\mathrm{pH}=-1.0$, Figure S3b, Supporting Information). As a result, the $\mathrm{MoS}_{2}$ nanoribbons with lengths of up to tens of micrometers, for example, $35 \mu \mathrm{~m}$, can be obtained


Figure 1. a-c) Schematic of the fabrication process to obtain $\mathrm{MoS}_{2}$ nanoribbons in high yield from $\mathrm{MoO}_{3}$ nanoribbon precursors (a), via a two-step CVD process: b) reaction to generate hybrid $\mathrm{MoS}_{2} / \mathrm{MoS}_{2}$ nanoribbons and c) conversion to $\mathrm{MoS}_{2}$ nanoribbons. d-f) Scanning electron microscopy (SEM) images of the obtained $\mathrm{MoO}_{3}, \mathrm{MoS}_{2} / \mathrm{MoO}_{2}$ hybrid and $\mathrm{MoS}_{2}$ nanoribbons. Inset in (f): $\mathrm{MoS}_{2}$ nanoribbons synthesized in one batch; scale bar: 1 cm . g-i) Raman and j-I) XRD spectra of $\mathrm{MoO}_{3}, \mathrm{MoS}_{2} / \mathrm{MoO}_{2}$ hybrid and $\mathrm{MoS}_{2}$ nanoribbons, respectively.
with the tunable $\mathrm{MoO}_{3}$ as the guiding templates (Figure 2i). The corresponding Raman and XRD spectra of the long $\mathrm{MoS}_{2}$ nanoribbons are plotted in Figure 2j-k, respectively.

Next, we examine the transition process from $\mathrm{MoO}_{3}$ to $\mathrm{MoS}_{2}$ in the nanoribbons by controlling the sulfurization time. At the sulfurization temperature of $500{ }^{\circ} \mathrm{C}$, we find that the conversion of $\mathrm{MoO}_{3}$ to the $\mathrm{MoS}_{2} / \mathrm{MoO}_{2}$ hybrid occurs as early as in the first 2 min , when strong Raman and XRD spectra of $\mathrm{MoO}_{2}$ can be observed, and the $\mathrm{MoO}_{3}$ signals disappear (Note S1 and Figure S7, Supporting Information). After reacting for 5 min , the Raman signals of $\mathrm{MoS}_{2}$ and $\mathrm{MoO}_{2}$ are observed, while the XRD signals of $\mathrm{MoS}_{2}$ remain indistinguishable. This suggests that $\mathrm{MoS}_{2}$ starts the growth from the surface of the nanoribbons as early as in the first 2 min while it takes between 5 and 30 min to reach a sufficient amount distinguishable by XRD (conventional XRD does not detect low-content elements, e.g., $<1 \%$ ) ${ }^{[21]}$ After completing the 30 min sulfurization step, the Raman and XRD spectra present signals from both $\mathrm{MoO}_{2}$ (in blue) and $\mathrm{MoS}_{2}$ (in red) as shown in Figure 1h-k. ${ }^{[22]}$ Next, with a second sulfurization at $900^{\circ} \mathrm{C}$ for 30 min , only the peaks from the $\mathrm{MoS}_{2}$ remain (Figure 1i-1). Here, in addition to
supporting the Raman results, the XRD spectra (Figure 1j-1) indicate the crystalline nature of all the obtained nanoribbons.

As physical and chemical properties of these materials are closely correlated with their microstructures, it is highly desirable to examine the structures and distribution of elements of the nanoribbons, especially knowing that $\mathrm{MoS}_{2}$ and $\mathrm{MoO}_{2}$ exhibit distinct electronic properties. For instance, $\mathrm{MoS}_{2}$ in the 2 H -phase is a layered semiconductor with a bandgap varying from 1.2 to 1.8 eV as the thickness decreases. ${ }^{[6]}$ Meanwhile, $\mathrm{MoO}_{2}$ is known as a metallic oxide, and has been applied as electrode material in supercapacitors, ${ }^{[23]}$ lithium-ion batteries, ${ }^{[24]}$ and has been used for water splitting. ${ }^{[25]}$ The mixture of metallic $\mathrm{MoO}_{2}$ and layered $\mathrm{MoS}_{2}$ could be potentially interesting for various electronic and energy storage devices. Phase-contrast TEM images from the edge and center of $\mathrm{MoS}_{2} / \mathrm{MoO}_{2}$ hybrid ribbons both reveal the (0002) $\mathrm{MoS}_{2}$ planes with a distance of $\approx 0.626 \mathrm{~nm}$ (Figure 3a,b). After analyzing many TEM images of the $\mathrm{MoS}_{2} / \mathrm{MoO}_{2}$ nanoribbons (more provided in Figure S 8 , Supporting Information), it is found that the (0002) $\mathrm{MoS}_{2}$ planes dominate the edges of the nanoribbons with (011) $\mathrm{MoO}_{2}$ domains neighboring them. Inside the hybrid ribbons,


Figure 2. Tuning the dimensions of $\mathrm{MoS}_{2}$ nanoribbons by adjusting the acidity of the precursor solution. a-d) SEM images and the length distribution of: $\mathrm{a}, \mathrm{b}) \mathrm{MoO}_{3}$ nanoribbons synthesized with at $\mathrm{pH}=0.0\left(3.24 \times 10^{-3} \mathrm{M}\left(\mathrm{NH}_{4}\right)_{6} \mathrm{Mo}_{7} \mathrm{O}_{24} \cdot 4 \mathrm{H}_{2} \mathrm{O}\right.$ and $\left.0.573 \mathrm{~m} \mathrm{HNO}_{3}\right)$; c , d) $\mathrm{pH}=-0.32\left(3.24 \times 10^{-3} \mathrm{~m}\right.$ $\left(\mathrm{NH}_{4}\right)_{6} \mathrm{Mo}_{7} \mathrm{O}_{24} \cdot 4 \mathrm{H}_{2} \mathrm{O}$ and 1.15 M HNO 3 ); and e,f) $\mathrm{pH}=-1.0\left(3.24 \times 10^{-3} \mathrm{M}\left(\mathrm{NH}_{4}\right)_{6} \mathrm{Mo}_{7} \mathrm{O}_{24} \cdot 4 \mathrm{H}_{2} \mathrm{O}\right.$ and $\left.2.87 \mathrm{M} \mathrm{HNO}_{3}\right)$. a, c,e $) \mathrm{SEM}$ images show the general morphology of $\mathrm{MoO}_{3}$ nanoribbon. Multiple SEM images with higher magnification are used to characterize the length distribution in ( $b, \mathrm{~d}, \mathrm{f}$ ). The length distribution of the $\mathrm{MoO}_{3}$ nanoribbons synthesized at $\mathrm{pH}=-1.0$ can be further refined by a $40 \mu \mathrm{~m}$ pore size filtration paper. g) SEM image and h) length distribution of refined long and short $\mathrm{MoO}_{3}$ nanoribbons. i) $\mathrm{MoS}_{2}$ nanoribbons of tens of micrometers can be obtained with j,k) the corresponding Raman spectrum (j) and XRD spectrum (k), scale bar of inset: $10 \mu \mathrm{~m}$.
the (0002) $\mathrm{MoS}_{2}$ planes also appear amidst the $(\overline{1} 02) \mathrm{MoO}_{2}$ domains. A gradual lattice transition can be observed in the TEM image (Figure S8, Supporting Information). Across the entire length of the nanoribbons, $\mathrm{MoS}_{2}$ and $\mathrm{MoO}_{2}$ form largely alternating lamellar structures as shown in the high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) images and electron energy loss spectroscopy (EELS) mapping (Figure $3 \mathrm{c}-\mathrm{g}$ ). Correlated analysis indicates that the $\mathrm{MoO}_{2}$ and $\mathrm{MoS}_{2}$ are in the bright and grey areas in HAADF-STEM images, respectively. The $\mathrm{MoO}_{2}$ forms a continuous network, while $\mathrm{MoS}_{2}$ covers the surface and is distributed in long island structures inside the hybrid ribbon. Owing to its unique structure, metallic $\mathrm{MoO}_{2}$ could play an essential role in the electric conductivity of the hybrid ribbons. Our further characterization of the structure with energydispersive X-ray spectroscopy (EDS) supports the EELS analysis (Figure S9, Supporting Information).

After a second sulfurization at $900{ }^{\circ} \mathrm{C}$, all the $\mathrm{MoO}_{2}$ regions in the obtained $\mathrm{MoS}_{2} / \mathrm{MoO}_{2}$ hybrid nanoribbons convert into $\mathrm{MoS}_{2}$ (Figure 3h,i). In addition to the aforediscussed Raman and XRD studies (Figure 1), the chemistry of the $\mathrm{MoS}_{2}$ nanoribbons is further confirmed by phase-contrast TEM, EELS, and EDS mappings. No oxygen or its compound signal can be detected with the above techniques (Figure S10, Supporting Information). Moreover, the synthesized $\mathrm{MoS}_{2}$ nanoribbons exhibit high thermal stability as shown by the TEM images in

Figure 3 j of in situ heated TEM samples. No morphological change can be observed from the $\mathrm{MoS}_{2}$ nanoribbon even after the sample is subjected to a continuous heat treatment inside the TEM at $800^{\circ} \mathrm{C}$ for $80 \mathrm{~min}, 900^{\circ} \mathrm{C}$ for 20 min , and then $1000{ }^{\circ} \mathrm{C}$ for 20 min . This provides further evidence supporting the purity of the obtained $\mathrm{MoS}_{2}$ nanoribbons, considering the melting temperature of bulk $\mathrm{MoO}_{2}$ is only $1100^{\circ} \mathrm{C}$.

An advantage of the above growth procedure is not only that the nanoribbons can be obtained in large quantities, but that they can also be easily dispersed in a suspension. This is beneficial for applications of $\mathrm{MoS}_{2}$ in solution. We can therefore demonstrate that it is possible to select, manipulate, and assemble nanoribbons at designated positions.

Here we utilize a versatile electric manipulation technique to orient and position individual $\mathrm{MoS}_{2}$ nanoribbons in solution on a substrate. ${ }^{[26]}$ Then upon UV light exposure, a chemical click-reaction fixes the nanoribbon on the substrate with high accuracy in the position and angle. This could for instance be helpful to assemble a $\mathrm{MoS}_{2}$ device or to maneuver the nanostructures to pre-defined electrical contacts. Among the various nanomanipulation methods, which have made impressive contributions to the creation of artificial micro/nanoscale machines, ${ }^{[27]}$ electric manipulation has demonstrated a high degree of control and precision, particularly for the manipulation of longitudinal nanoparticles. ${ }^{[26]}$ More importantly, the technique can be applied to nanoparticles made of all materials,


Figure 3. a,b) Phase-contrast TEM of the edge (a) and center (b) regions of $\mathrm{MoS}_{2} / \mathrm{MoO}_{2}$ hybrid nanoribbon. c) HAADF-STEM image of $\mathrm{MoS}_{2} / \mathrm{MoO}_{2}$ hybrid nanoribbon and $\mathrm{d}-\mathrm{g}$ ) the corresponding EELS mapping of elements $\mathrm{Mo}(\mathrm{d}), \mathrm{O}(\mathrm{e}), \mathrm{S}(\mathrm{f})$, and mixture of O and $\mathrm{S}(\mathrm{g})$, showing the distribution of $\mathrm{MoS}_{2}$ in the hybrid ribbon. $h, i$ ) Phase-contrast TEM of the center ( h ) and edge (i) of $\mathrm{MoS}_{2}$ nanoribbon. j) In situ HAADF-STEM image of $\mathrm{MoS}_{2}$ nanoribbon at room temperature (I) and heated at $800^{\circ} \mathrm{C}$ for 30 min (II), at $800^{\circ} \mathrm{C}$ for 80 min (III), at $900^{\circ} \mathrm{C}$ for 20 min (IV), and at $1000{ }^{\circ} \mathrm{C}$ for $20 \mathrm{~min}(\mathrm{~V})$ continuously. No observable structural change can be found. Scale bar: 100 nm .


Figure 4. Assembly of $\mathrm{MoS}_{2}$ nanoribbons with thiol-yne "click-chemistry" onto a substrate. a) Overlapped snapshots of a MoS nanoribbon moving in a quadruple microelectrode along the prescribed trajectory to write "20." b) Top: Functionalization of $\mathrm{MoS}_{2}$ nanoribbons and a glass substrate with thiol-PEG-alkyne and silane-PEG-thiol, respectively. Bottom: Immobilization of $\mathrm{MoS}_{2}$ ribbons by UV-triggered thiol-yne click chemistry. c) Schematic shows the assembly process with controlled position and orientations before the chemical assembly. Inset: optical microscopy image of a $\mathrm{MoS}_{2}$ nanoribbon directly assembled to a pair of prepatterned microelectrodes. Scale bar: $20 \mu \mathrm{~m}$. d-f) Multiple $\mathrm{MoS}_{2}$ nanoribbons assembled into different configurations after "click" chemical reaction.
including metals, semiconductors, and insulators, which suggests its suitability to manipulate $\mathrm{MoS}_{2}$ nanostructures. The working principle of the electric manipulation has been described previously. ${ }^{[28]}$ Briefly, uniform DC and AC electric fields are used in the manipulation. A longitudinal nanostructure, which naturally carries surface charges, can be moved in the direction of the DC field due to Coulomb interactions. The AC field can be used to exert a torque, which allows the angular orientation. ${ }^{[29,30]}$ The transport and alignment are thus independently controlled. In the experiment, we disperse the $\mathrm{MoS}_{2}$ nanoribbons at the center ( $500 \mu \mathrm{~m} \times 500 \mu \mathrm{~m}$ ) of a patterned quadrupole microelectrode as shown in Figure 4a. Applying the combined DC and AC electric fields with feedback control, the nanoribbons instantly move along the X and Y directions alternatively, tracing a designed 2D trajectory as shown in Movie S1, Supporting Information. Snapshots are overlapped and shown in Figure 4a. With this manipulation, a nanoribbon can be selected and transported to a designated position and aligned.

It is then possible to fix the position of nanoribbons. Since the $\mathrm{MoS}_{2}$ nanoribbons are sulfur-rich with clear edges and grain boundaries, as shown by the TEM results in Figure 3h,
many unsaturated sulfur sites are available to react with molecular thiol groups. ${ }^{[31]}$ For this we exploit a light-triggered thiol-yne click-reaction to covalently fix the nanoribbon once it reaches a designated position. ${ }^{[32]}$ The scheme of the thiolyne click chemistry is implemented by conjugating the $\mathrm{MoS}_{2}$ nanoribbons with the thiol groups of thiol-PEG-alkyne molecules, leaving the active alkyne groups on the outer surface, and terminating the surface of a glass substrate with thiol groups by conjugating with silane-PEG-thiol molecules (as illustrated in Figure 4b, details in Supporting Information). When a functionalized $\mathrm{MoS}_{2}$ nanoribbon has been directed to a designated position, a short exposure with UV light, initiates the "click" reaction between the thiol and the alkyne groups (Figure 4c). The assembly of a $\mathrm{MoS}_{2}$ nanoribbon occurs in $5-10 \mathrm{~s}$ "at the press of a light button". The reaction and assembly process is well reproducible. We have demonstrated the transport, orientation, and positioning of multiple $\mathrm{MoS}_{2}$ nanoribbons next to each other into various patterns (Figure 4d-f and Movie S2, Supporting Information). With this technique, the $\mathrm{MoS}_{2}$ nanoribbons also can be directly assembled to a pair of prepatterned microelectrodes (inset of Figure 4c and Movie S3, Supporting

Information). The precision in position and orientation is determined as $144 \pm 601$ and $111 \pm 268 \mathrm{~nm}$ for the $X$, Y position and $-1.85 \pm 3.21^{\circ}$ for the angle, respectively. The polycrystalline nature of the synthesized $\mathrm{MoS}_{2}$ nanoribbons contributes to the robust and rapid assembly, because it is expected to show more reactive sulfur defects compared to the single-crystalline counterparts. To support this analysis, control experiments are carried by testing the assembly of functionalized $\mathrm{Au}-\mathrm{SiO}_{2}$ coreshell nanowires (counterpart of glass) on single-crystal $\mathrm{MoS}_{2}$ nanoflakes (counterpart of our polycrystalline $\mathrm{MoS}_{2}$ ). As shown in Movie S4, Supporting Information, functionalized $\mathrm{Au}-\mathrm{SiO}_{2}$ core-shell nanowires cannot fix on to the $\mathrm{MoS}_{2}$ nanoflakes even after a continuous 40 s UV exposure. However, all the functionalized $\mathrm{MoS}_{2}$ nanoribbons can quickly assemble on glass in around 10 s of UV illumination (Movie S5, Supporting Information). In these experiments, the conditions are controlled to be the same. We expect this assembly strategy could also be useful for assembling devices and for other TMD materials.

An important first step toward obtaining functional nanodevices is to reproducibly fabricate nanostructures with controlled composition, dimension, and chemistry. ${ }^{[33]}$ Due to the layered crystal structure, it is challenging to synthesize 2D TMD materials with dimensional control, particularly into a longitudinal structure. We herein present a robust and scalable approach to synthesize $\mathrm{MoS}_{2}$ nanoribbons with tunable dimensions and demonstrate their transfer, manipulation, and assembly "at the press of a light button." Compared to previous report, ${ }^{[7]}$ the obtained $\mathrm{MoS}_{2}$ nanoribbons are not adherent, and thus can be readily collected after growth. They can be dispersed in
water where they can be moved along defined trajectoriespositioned, oriented, and assembled in 2D patterns. The $\mathrm{MoS}_{2}$ nanoribbons are rich in reactive sulfur sites which are an enabling factor in their chemical functionalization and the subsequent rapid assembly to a substrate with a light-triggered "click" reaction. Overall, the fabrication and assembly of $\mathrm{MoS}_{2}$ nanoribbons demonstrated in our work might provide a new pathway to alleviate the roadblocks of applications of 2D materials. For instance, as demonstrated earlier, the $\mathrm{MoS}_{2}$ nanoribbon can be directly assembled to a pair of prepatterned electrodes with controlled position and alignment (Figure 4 and Movie S3, Supporting Information). However, every coin has two sides. Compared to those single-crystalline $\mathrm{MoS}_{2}$ structures made by exfoliated flakes and the recently reported $\mathrm{MoS}_{2}$ nanostructures obtained by substrate assisted fabrication, ${ }^{[7]}$ our $\mathrm{MoS}_{2}$ nanoribbons exhibit polycrystalline features. For applications in electronic devices, this may not be ideal as a controlled number of layers in single-crystal $\mathrm{MoS}_{2}$ can be used to tune its bandgap. The low defect density of a few-layer single-crystal structure also provides enhanced performance for optoelectronics. ${ }^{[8]}$ However, the intrinsic semiconductor properties of $\mathrm{MoS}_{2}$ can still be exploited for the utilization relevant to electronics, particularly given the merit of low-cost, scalable, and dimension-controlled synthesis. Here we study the optoelectronic performance of the fabricated $\mathrm{MoS}_{2}$ nanoribbons on $\mathrm{SiO}_{2} / \mathrm{Si}$ substrates to demonstrate its potential as photodetectors. As shown in Figure 5, the device shows a fast response to light with a wavelength from 450 to 750 nm , the performance of which is similar to that of single-crystal $\mathrm{MoS}_{2}$ but at a lower increase in magnitude. ${ }^{[34]}$


Figure 5. Optoelectronic performance of the $\mathrm{MoS}_{2}$ nanoribbons. a) Optical microscopy image and b) $I-V$ curve of the $\mathrm{MoS}_{2}$ device fabricated on a $\mathrm{SiO}_{2} /$ Si substrate. c) Photoresponse of the $\mathrm{MoS}_{2}$ nanoribbon with a bias voltage of 5 V to light with wavelengths from 450 to 750 nm . d) Rapid photoresponse of the $\mathrm{MoS}_{2}$ nanoribbon under 700 nm laser illumination. The rise time and decay time are $\approx 8$ and 16 ms , respectively.

Moreover, a large array of theoretical and experimental research points out that $\mathrm{MoS}_{2}$ exhibits excellent catalytic activities and is much cheaper than catalysts formed from precious metals. This is attributed to the edges and points to the defects in $\mathrm{MoS}_{2}$ nanostructures. ${ }^{[35]}$ For a similar reason, the as-obtained $\mathrm{MoS}_{2}$ nanoribbons demonstrate effective removal of mercury for water purification (Figure S11, Supporting Information). Overall, the structural tunable fabrication of $\mathrm{MoS}_{2}$ nanoribbons with high yield and dispersibility, low-cost, as well as their lighttriggered precision assembly may inspire the future fabrication and assembly of 2D TMD materials in various applications. Owing to the attributes of semiconductor and polycrystalline nature, the $\mathrm{MoS}_{2}$ materials also show useful properties for optoelectronics and water purification.

## Experimental Section

The details of the materials synthesis, functionalization and assembly process can be found in the Supporting Information.

The morphology of the ribbons synthesized at different stages were characterized using a scanning electron microscope (SEM, Hitach S-5500) in a secondary electron scattering mode at 20 kV and a JEOL 2010 TEM operated at 200 kV . The composition of the samples was characterized by XRD (Rigaku MiniFlex 600), Raman spectrum (Alpha 300, excited by 475 nm laser), as well as EELS and EDS mapping in a double-corrected TEM/STEM FEI Titan G3 Cubed Themis at the International Iberian Nanotechnology Laboratory, Braga, Portugal.

## Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

## Acknowledgements

The authors thank the support by the Welch Foundation (F-1734), National Science Foundation (CMMI- 1563382, EECS-1710922, and EECS-1930649). D.F. and Y.H. thank the travel support from the UT Austin-Portugal program. This work was also supported by FCT, through IDMEC, under LAETA, project UIDB/50022/2020.

## Conflict of Interest

The authors declare no conflict of interest.

## Keywords

assembly, click chemistry, manipulation, $\mathrm{MoS}_{2}$, transition metal dichalcogenides

Received: May 19, 2020
Revised: July 30, 2020
Published online: September 21, 2020

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