Preparation of Single-Layer MoS$_{2x}$Se$_{2(1-x)}$ and Mo$_x$W$_{1-x}$S$_2$ Nanosheets with High-Concentration Metallic 1T Phase

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Single- and few-layer transition metal dichalcogenide (TMD) nanosheets, such as MoS$_2$, WS$_2$, MoSe$_2$, etc., have attracted increasing attention in the past few years due to their unique chemical and electronic properties[1–5] as well as various promising applications in electronic/optoelectronic devices,[6,7] electrocatalysis,[8,9] sensors,[10–12] energy storage,[13,14] and biomedicine.[15,16] Ultrathin 2D ternary TMD nanosheets, such as MoS$_2$:Se$_{2(1−x)}$ and Mo$_x$W$_{1−x}$S$_2$, are also receiving much attention.[17–25] The ternary structure of ultrathin 2D TMD nanosheets enables them with some appealing properties or functions, such as tunable band gaps[18–22] and enhanced catalytic activity for hydrogen generation.[23,25] Currently, single- or few-layer ternary TMD nanosheets, such as MoS$_2$:Se$_{2(1−x)}$ and Mo$_x$W$_{1−x}$S$_2$, are normally prepared by mechanical exfoliation[17,18] and chemical vapor deposition.[19–22] However, few-layer ternary TMD flakes can be prepared by sonication-assisted exfoliation[23,24] and wet-chemical synthesis methods.[25] Therefore, it still remains a big challenge for the high-yield and large-scale preparation of single-layer ternary TMD nanosheets in solution.

Generally, ultrathin 2D TMD nanosheets have a 2H crystal phase (for example, MoS$_2$, WS$_2$, and MoSe$_2$), rendering them semiconducting properties with large band gaps of 1–2 eV and thus appealing for electronics/optoelectronics.[1–2] However, their low intrinsic electrical conductivity limited their potentials for some specific applications, such as electrodes for electrocatalysis and electrochemical supercapacitors, and low-resistance contact transistors.[1–2] Recently, it has been demonstrated that the phase engineering of ultrathin 2D TMD nanosheets from semiconducting 2H phase to metallic 1T phase is an effective approach to improve the conductivity of TMD nanosheets[26] and thus to achieve much enhanced performance in electrocatalytic hydrogen evolution.[27–29] electrochemical supercapacitors,[30] and low-resistance contact transistors.[31,32] Normally, the phase engineering of 2D TMD nanosheets can be achieved by the Li-intercalation with n-butyllithium,[27,28,30,31,33] laser irradiation,[32] electron beam irradiation,[34] and gate-controlled Li-intercalation.[35] Recently, the metallic 1T TMD nanosheets (for example, WS$_2$) can also be directly synthesized by the wet-chemical method.[36] Here, we use our recently developed electrochemical Li-intercalation and exfoliation method[37] to prepare the high-yield and scalable production of single-layer ternary TMD nanosheets with high-concentration metallic 1T phase (~66%), including MoS$_{2x}$:Se$_{2(1−x)}$ and Mo$_x$W$_{1−x}$S$_2$, from their 2H-phase layered bulk crystals (Scheme 1). As a proof-of-concept application, a thin film of the exfoliated MoS$_{2x}$:Se$_{2(1−x)}$ nanosheets with high concentration of metallic 1T phase is coated on a fluorine-doped tin oxide (FTO) substrate by simple drop-coating method, which is then used as an efficient electrocatalyst on counter electrode (CE) for the tri-iodide reduction in a dye-sensitized solar cell (DSSC).

Micrometer-sized 2H-phase layered bulk crystals of MoS$_{2x}$:Se$_{2(1−x)}$ and Mo$_x$W$_{1−x}$S$_2$ were synthesized from their elementary powders via the chemical vapor transport method (see the Experimental Section in the Supporting Information).
for details) (Figures S1 and S2, Supporting Information). Based on the energy-dispersive X-ray spectroscopy (EDS) analyses (Figures S1c and S2e, Supporting Information), the chemical formulae of MoS$_2$Se$_{2(1-x)}$ and Mo$_x$W$_{1-x}$S$_2$ crystals are determined to be MoS$_{1.35}$Se$_{0.65}$ and Mo$_{0.65}$W$_{0.35}$S$_2$, respectively. The as-prepared bulk crystals were then used as the sources to produce single-layer ternary nanosheets by using our recently developed electrochemical Li-intercalation and the exfoliation method. Note that MoS$_{2x}$Se$_{(2x+1)}$ is used as an example in this scheme.

Furthermore, the presence of high-concentration metallic 1T crystal phase in the exfoliated MoS$_2$Se$_{2(1-x)}$ nanosheets was confirmed by X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, and UV–vis absorption spectroscopy. In order to quantitatively calculate the concentration of 1T phase, XPS was used to study the phase compositions in the bulk crystal of MoS$_2$Se$_{2(1-x)}$, and the exfoliated nanosheets of MoS$_2$Se$_{2(1-x)}$ before and after annealing at 300 °C under Ar (Figure 2b,c and Figure S6, Supporting Information). The Mo 3d spectrum of bulk crystal gives peaks at around 229.0 and 232.1 eV (Figure 2b), assignable to Mo$^{4+}$ 3d$_{3/2}$ and Mo$^{4+}$ 3d$_{5/2}$ of 2H-phase MoS$_2$Se$_{(1-x)}$, respectively. The deconvolution of Mo 3d spectrum of exfoliated nanosheets indicates that the two main peaks shifted to lower binding energy by ~0.8 eV (228.2 and 231.3 eV) with respect to the position of 2H MoS$_2$Se$_{(1-x)}$ peaks (229.0 and 232.1 eV) (Figure 2b). Moreover, the additional peaks at 161.2 and 162.4 eV (or 53.5 and 54.5 eV) appeared besides the known peaks of 2H phase MoS$_2$Se$_{(1-x)}$ at 161.9 and 163.1 eV (or 54.2 and 55.2 eV) in the S 2p (or Se 2d) spectra (Figure 2c and Figure S6, Supporting Information). All the analyses of XPS Mo 3d, S 2p, and Se 2d spectra prove the presence of 1T phase in the exfoliated MoS$_2$Se$_{(1-x)}$ nanosheets, which is similar to that of chemically exfoliated 1T MoS$_2$ nanosheets.$^{33,34}$

Figure 1. Schematic illustration of preparation of single-layer ternary TMD nanosheets with high-concentration metallic 1T phase from their 2H-phase layered bulk crystals by using the electrochemical Li-intercalation and the exfoliation method. Note that MoS$_{2x}$Se$_{(2x+1)}$ is used as an example in this scheme.
Supporting Information.\textsuperscript{[40]} Only the exfoliated MoS\textsubscript{x}Se\textsubscript{2(1−x)} nanosheet exhibits small peaks, around 140 and 300 cm\textsuperscript{−1}, in the lower frequency region (Figure S7, Supporting Information), corresponding to the distorted 1T phase Raman active modes, \(J_1\) and \(J_3\), respectively, which are similar to the chemically exfoliated 1T MoS\textsubscript{2} nanosheets.\textsuperscript{[33]} The presence of 1T phase in exfoliated MoS\textsubscript{x}Se\textsubscript{2(1−x)} nanosheets was also evidenced by the absorption spectra (Figure 2d). No obvious characteristic peaks of 2H MoS\textsubscript{x}Se\textsubscript{2(1−x)} can be observed in the exfoliated MoS\textsubscript{x}Se\textsubscript{2(1−x)} nanosheet film, except a small peak at around 380 nm (Figure 2d). In contrast, after annealing of the exfoliated MoS\textsubscript{x}Se\textsubscript{2(1−x)} film at 300 °C, the characteristic A and B excitonic peaks of 2H MoS\textsubscript{x}Se\textsubscript{2(1−x)} at 650 and 715 nm, respectively, and the convoluted C and D excitonic peaks at around 443 nm were clearly observed (Figure 2d), suggesting the restoration of 2H phase.\textsuperscript{[33]}

Similarly, the single-layer ternary Mo\textsubscript{x}W\textsubscript{1−x}S\textsubscript{2} nanosheets with high-concentration metallic 1T phase can also be prepared by exfoliation of its bulk crystal using the same method (Figure 3).\textsuperscript{[37]} and the stable colloidal suspension of Mo\textsubscript{x}W\textsubscript{1−x}S\textsubscript{2} nanosheets was obtained (inset in Figure 3a). The well-dispersed Mo\textsubscript{x}W\textsubscript{1−x}S\textsubscript{2} nanosheets with size similar to MoS\textsubscript{x}Se\textsubscript{2(1−x)} nanosheets were confirmed by the SEM, AFM, and low-magnification TEM images (Figure 3a–c). The typical thickness of Mo\textsubscript{x}W\textsubscript{1−x}S\textsubscript{2} nanosheets is 0.9–1.2 nm (Figure 3b and Figure S8, Supporting Information), proving their single-layer nature. The hexagonal diffraction spots can be observed from the SAED pattern of a typical Mo\textsubscript{x}W\textsubscript{1−x}S\textsubscript{2} nanosheet (Figure 3d,e). The outside and inner six spots at the SAED pattern are corresponding to the (110) and (100) planes of the Mo\textsubscript{x}W\textsubscript{1−x}S\textsubscript{2} nanosheet, respectively. The HRTEM image reveals the continuous lattice fringe with a lattice spacing of 0.275 nm (Figure 3f).
of ≈ 0.272 nm (Figure 3f), assignable to the (100) planes of the Mo₅W₁₋ₓS₂ crystal. The EDS spectrum of a typical Mo₅W₁₋ₓS₂ nanosheet gives strong signals of Mo, W, and S (Figure S9, Supporting Information) and these elements are homogeneously distributed in the ternary nanosheet (Figure S10, Supporting Information). Moreover, the STEM was used to visualize the distribution of Mo and W atoms in the single-layer Mo₅W₁₋ₓS₂ nanosheet. The atomic STEM image shows that the W and Mo atoms are randomly distributed in the single-layer nanosheet, forming a hexagonal lattice arrangement. Due to the greater Z number of W atom, it shows brighter contrast than does the Mo atoms (Figure S11, Supporting Information).

In addition, the XPS analyses of three Mo₅W₁₋ₓS₂ samples give similar results with the three MoS₂Se₂(1−x) samples, respectively. The exfoliated Mo₅W₁₋ₓS₂ nanosheets show obvious shift to lower binding energy in comparison with the 2H bulk crystal in the Mo 3d, S 2p, and W 4f spectra, and the quenching of the 1T phase peaks can be observed after annealing (Figure 3g–i). The calculated concentration of metallic 1T phase is also as high as ≈ 66% for the exfoliated Mo₅W₁₋ₓS₂ based on the Mo 3d spectrum (Figure 3g). Similarly, all the three Mo₅W₁₋ₓS₂ samples show three prominent peaks at 407, 380, and 357 cm⁻¹ (Figure S12, Supporting Information), corresponding to the MoS₂-like A₁g, E₁²g, and WS₂-like E₂g modes of 2H Mo₅W₁₋ₓS₂, respectively. The distorted 1T phase Raman active modes (J₁: 150 cm⁻¹ and J₂: 215 cm⁻¹) in the lower frequency region can be observed in the exfoliated Mo₅W₁₋ₓS₂ nanosheets (Figure S12, Supporting Information). The UV–vis absorption spectra give similar results to the MoS₂Se₂(1−x) nanosheet films, revealing the metallic 1T phase in the exfoliated Mo₅W₁₋ₓS₂ nanosheets and the restoration of 2H phase after the exfoliated Mo₅W₁₋ₓS₂ nanosheets were annealed at 300 °C (Figure S13, Supporting Information).

As known, the single-layer MoS₂ nanosheets with high concentration of metallic 1T phase were prepared by exfoliating its bulk crystal via our Li-intercalation and exfoliation method. The detailed characterizations of bulk crystal of MoS₂, and exfoliated and annealed MoS₂ nanosheets by SEM, AFM, TEM, XPS, Raman spectroscopy, and UV–vis spectroscopy are shown in Figures S14–S18 (Supporting Information). All these results indicate that the exfoliated MoS₂ nanosheets also contain a high concentration of metallic 1T phase (≈ 67%) (Figure S15a, Supporting Information). It proved the coexistence of 2H and 1T phases in the single-layer MoS₂ nanosheets. In this work, we have successfully used our electrochemical Li-intercalation and exfoliation
method to prepare single-layer ternary TMD nanosheets with high concentration of metallic 1T phase with the layered 2H-phase bulk crystals as the source. The phase transformation from the semiconducting 2H phase to metallic 1T phase occurs during the electrochemical Li-intercalation. Alternatively, in the previously reported intercalation of TMD bulk materials with n-butyllithium,\cite{26,33} it is believed that the electron transfer from the butyl to TMDs occurs, which destabilizes the pristine 2H phase and thus to induce the phase transformation to obtain TMD nanosheets with high-concentration metallic 1T phase.\cite{43,44} However, in our study, the electrons can be donated from the Li foil to TMD crystals (i.e., MoS$_2$, MoS$_2$Se$_{1-x-1}$, and Mo$_x$W$_{1-x}$S$_2$) during the discharge process (Scheme 1)\cite{43,44} thus leading to the phase transformation to obtain TMD nanosheets with high-concentration metallic 1T phase. We believe that our method can also be used to effectively exfoliate other TMD materials and induce the phase transformation in the obtained single- or few-layer TMD nanosheets.
As known, TMD nanomaterials, such as MoS\(_2\) and WS\(_2\) particles\(^{[25]}\) and few-layer MoSe\(_2\) nanosheets\(^{[46]}\) can be used as cost-effective electrocatalysts in the CEs of DSSCs, which show good photovoltaic performance. Here, as a proof-of-concept application, a thin film of single-layer MoS\(_2\)\(\cdot\)Se\(_2\)\((1-x)\) nanosheets with \(\approx 66\%\) of metallic 1T phase drop-casted on an FTO substrate was used as the electrocatalyst for the triiodide reduction in I\(^{-}\)/I\(^{3-}\) redox electrolyte in a DSSC, which exhibits higher electrocatalytic activity compared with the thin films of 2H-phase single-layer MoS\(_2\)\(\cdot\)Se\(_2\)\((1-x)\) nanosheets and the single-layer MoS\(_2\) nanosheets with \(\approx 67\%\) of metallic 1T phase. In a typical experiment, the exfoliated single-layer MoS\(_2\)\(\cdot\)Se\(_2\)\((1-x)\) nanosheets, referred to as FTO-exfoliated-MoS\(_2\)\(\cdot\)Se\(_2\)\((1-x)\), by simple drop-casting method was used as the CE in a DSSC, in which an N719 dye-sensitized mesoporous TiO\(_2\) electrode was used as the photoanode.\(^{[47]}\) The schematic illustration of DSSC device is shown in Figure 4a. The deposited MoS\(_2\)\(\cdot\)Se\(_2\)\((1-x)\) nanosheet film has a thickness of \(\approx 50\) nm (Figure S19, Supporting Information). The 2H-phase MoS\(_2\)\(\cdot\)Se\(_2\)\((1-x)\) nanosheet film on FTO, referred to as FTO-Annealed-MoS\(_2\)\(\cdot\)Se\(_2\)\((1-x)\), was obtained by annealing the FTO-exfoliated-MoS\(_2\)\(\cdot\)Se\(_2\)\((1-x)\) under Ar atmosphere at 300 °C for 1 h. Figure 4b illustrates the photocurrent density–voltage (\(J–V\)) characteristic curves of DSSCs with three different CEs. The detailed photovoltaic parameters are summarized in Table 1. In a control experiment, the DSSC using the Pt-decorated FTO, referred to as FTO-Pt, as CE has an open-circuit voltage \(\left(V_{oc}\right)\) of 0.80 V, short-circuit current density \(\left(J_{sc}\right)\) of 12.82 mA cm\(^{-2}\), fill factor (FF) of 0.69, and power conversion efficiency (PCE) of 7.00%. When the FTO-exfoliated-MoS\(_2\)\(\cdot\)Se\(_2\)\((1-x)\) was used as CE, the photovoltaic parameters, \(V_{oc}\), \(J_{sc}\), FF, and PCE are 0.75 V, 13.40 mA cm\(^{-2}\), 0.65, and 6.5%, respectively. Although the FTO-Pt CE exhibits a little higher \(V_{oc}\) and FF, the FTO-exfoliated-MoS\(_2\)\(\cdot\)Se\(_2\)\((1-x)\) gives a little higher \(J_{sc}\). Therefore, their photovoltaic performance is comparable. In contrast, when the FTO-Annealed-MoS\(_2\)\(\cdot\)Se\(_2\)\((1-x)\) was used as CE, the PCE is only 5.4% with \(V_{oc}\) = 0.76 V, \(J_{sc}\) = 13.52 mA cm\(^{-2}\), and FF = 0.52. Although the changes of \(V_{oc}\) and \(J_{sc}\) are quite small, its FF shows a notable decrease compared with the other two CEs. For comparison, the photovoltaic performance of exfoliated MoS\(_2\) nanosheets with \(\approx 67\%\) of metallic 1T phase and annealed MoS\(_2\) nanosheets with 2H phase deposited on FTO electrodes, referred to as FTO-exfoliated-MoS\(_2\) and FTO-Annealed-MoS\(_2\), respectively, were also measured. Note that the MoS\(_2\) nanosheet thin film has the similar thickness with the MoS\(_2\)\(\cdot\)Se\(_2\)\((1-x)\) nanosheet thin film based on the preparation method (see the Experimental Section in the Supporting Information for details). Similarly, the FTO-exfoliated-MoS\(_2\) also gives a higher FF (0.65) and PEC (6.0%) compared with the FTO-Annealed-MoS\(_2\) (FF = 0.58 and PCE = 5.1%) (Figure S20 and Table S1, Supporting Information). Based on the aforementioned results, both of the exfoliated MoS\(_2\)\(\cdot\)Se\(_2\)\((1-x)\) and MoS\(_2\) nanosheets with high concentration

Figure 4. DSSCs based on MoS\(_2\)\(\cdot\)Se\(_2\)\((1-x)\) nanosheets. a) Schematic illustration of a typical assembled DSSC with N719 dye-sensitized TiO\(_2\) photoanode and FTO-exfoliated-MoS\(_2\)\(\cdot\)Se\(_2\)\((1-x)\) CEs. b) \(J–V\) curves of DSSCs with FTO-exfoliated-MoS\(_2\)\(\cdot\)Se\(_2\)\((1-x)\), FTO-Annealed-MoS\(_2\)\(\cdot\)Se\(_2\)\((1-x)\), and FTO-Pt used as CEs measured under simulated sunlight 100 mW cm\(^{-2}\) (AM 1.5). c) CV curves of FTO-exfoliated-MoS\(_2\)\(\cdot\)Se\(_2\)\((1-x)\), FTO-Annealed-MoS\(_2\)\(\cdot\)Se\(_2\)\((1-x)\), and FTO-Pt CEs in the acetonitrile solution containing 10 mM of LiI, 1 mM of I\(_2\), and 0.1 M of LiClO\(_4\) (supporting electrolyte). d) Nyquist plots of a symmetric dummy cell with configuration of two identical FTO-exfoliated-MoS\(_2\)\(\cdot\)Se\(_2\)\((1-x)\), FTO-Annealed-MoS\(_2\)\(\cdot\)Se\(_2\)\((1-x)\), or FTO-Pt electrodes (inset: a fitting equivalent circuit).
Table 1. Photovoltaic parameters of DSSCs with different counter electrodes and simulated data from the fitted EIS curves.

<table>
<thead>
<tr>
<th>Counter electrode</th>
<th>Vsc [V]</th>
<th>Jsc [mA cm⁻²]</th>
<th>FF</th>
<th>PCE [%]</th>
<th>Rct [Ω cm²]</th>
<th>Rct [Ω cm²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>FTO-Pt</td>
<td>0.80</td>
<td>12.82</td>
<td>6.9</td>
<td>7.0</td>
<td>27.07</td>
<td>2.28</td>
</tr>
<tr>
<td>FTO-exfoliated-MoS₂Se₂₁−ₓ</td>
<td>0.75</td>
<td>13.40</td>
<td>6.5</td>
<td>6.5</td>
<td>28.40</td>
<td>4.60</td>
</tr>
<tr>
<td>FTO-Annealed-MoS₂Se₂₁−ₓ</td>
<td>0.76</td>
<td>13.52</td>
<td>5.2</td>
<td>5.4</td>
<td>27.92</td>
<td>23.25</td>
</tr>
</tbody>
</table>

of 1T phase display better photovoltaic performance compared with the 2H ones after annealing.

The higher photovoltaic performance of exfoliated MoS₂Se₂₁−ₓ should be ascribed to its higher electrocatalytic activity toward the tri-iodide reduction in comparison with the annealed one, which is supported by the cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The CV curves in Figure 4c give two typical pairs of redox peaks for both FTO-exfoliated-MoS₂Se₂₁−ₓ and FTO-Pt CEs, indicating the Pt-like electrocatalytic activity of exfoliated MoS₂Se₂₁−ₓ nanosheets in the tri-iodide reduction. The two peaks correspond to the two-step reversible redox reaction in the I°/I⁻ electrolyte solution, i.e., the left pair (Ox-1 and Red-1): I°⁻ + 2e⁻ ↔ 3I⁻, and the right pair (Ox-2 and Red-2): 3I⁻ + 2e⁻ ↔ 2I⁻. However, one of the anodic peaks (Ox-2) could not be observed in the FTO-Annealed-MoS₂Se₂₁−ₓ CE. Moreover, the cathodic peak density of Red-1 in FTO-exfoliated-MoS₂Se₂₁−ₓ is higher than that of the FTO-Annealed-MoS₂Se₂₁−ₓ suggesting a faster redox reaction on FTO-exfoliated-MoS₂Se₂₁−ₓ CE.[48] Therefore, from the CV analysis, the FTO-exfoliated-MoS₂Se₂₁−ₓ CE exhibits better electrocatalytic activity compared with FTO-Annealed-MoS₂Se₂₁−ₓ CE. Similarly, the CV curves of FTO-exfoliated-MoS₂ and FTO-Annealed-MoS₂ CEs were also obtained and compared in Figure S19a (Supporting Information), further demonstrating the higher electrocatalytic activity of the exfoliated nanosheets compared with the one after annealing.

Furthermore, the electron transport process at the CE/electrolyte interface was studied by the EIS measurement in a symmetric dummy cell consisting of two identical CEs. Figure 4d shows the Nyquist plots for the MoS₂Se₂₁−ₓ samples obtained in the dark without bias potential, which are fitted with the equivalent circuit (inset in Figure 4d).[49] The semicircle in the high-frequency region presents the charge transfer resistance (Rct) and the corresponding constant phase angle element at the CE/electrolyte interface. The arc in the low-frequency region indicates the diffusion resistance (Zr) of the redox couple in the electrolyte. The intercept on the real axis is defined as the ohmic series resistance (R0). In these parameters, Rct and R0 are highly related to the electrocatalytic activity of CEs for the tri-iodide reduction. The obtained Rct and R0 for two MoS₂Se₂₁−ₓ CEs are summarized in Table 1. Obviously, the FTO-Annealed-MoS₂Se₂₁−ₓ has a slightly lower Rct (27.92 Ω cm²) compared with the FTO-exfoliated-MoS₂Se₂₁−ₓ (28.40 Ω cm²), which might arise from the enhanced adhesion between the electrocatalyst layer (i.e., MoS₂Se₂₁−ₓ film) and the FTO substrate after the thermal annealing.[49] However, compared with FTO-Annealed-MoS₂Se₂₁−ₓ with Rct of 23.25 Ω cm², the FTO-exfoliated-MoS₂Se₂₁−ₓ gives much lower Rct (4.60 Ω cm²), close to that of FTO-Pt CE (2.28 Ω cm²), suggesting its higher electrocatalytic activity. Based on the previous report on the equivalent circuit model for DSSCs,[50] the FF is inversely proportional to the sum of Rct and R0.

Due to the small difference of Rct for FTO-exfoliated-MoS₂Se₂₁−ₓ and FTO-Annealed-MoS₂Se₂₁−ₓ, the higher FF (0.65) because of its much lower Rct (19.60 Ω cm²) compared with the FTO-Annealed-MoS₂ (FF = 0.58 and Rct = 121.1 Ω cm²) (Figure S21a and Table S1, Supporting Information), indicating the higher electrocatalytic activity of the exfoliated MoS₂Se₂₁−ₓ nanosheets compared with those after annealing. Impressively, the FTO-exfoliated-MoS₂Se₂₁−ₓ gives Rct of 4.60 Ω cm², much lower than that of the FTO-exfoliated-MoS₂ with Rct of 19.60 Ω cm² (Figure S21b, Supporting Information). The much lower Rct of exfoliated MoS₂Se₂₁−ₓ compared with the exfoliated MoS₂ with similar concentration of 1T phase can be ascribed to higher conductivity of the semiconducting 2H-phase MoS₂Se₂₁−ₓ after annealing of the exfoliated-MoS₂Se₂₁−ₓ, which induces the sluggish electron transfer process. In contrast, the high concentration of metallic 1T phase in the FTO-exfoliated-MoS₂Se₂₁−ₓ (+66%) renders its higher conductivity, which can facilitate the electron transport from the CE surface to the redox electrolyte for the tri-iodide reduction. Similarly, the FTO-exfoliated-MoS₂ also gives a higher FF (0.65) because of its much lower Rct (19.60 Ω cm²) compared with the FTO-Annealed-MoS₂ (FF = 0.58 and Rct = 121.1 Ω cm²) (Figure S21a and Table S1, Supporting Information). In summary, single-layer ternary TMD nanosheets with high concentration of metallic 1T phase, including MoS₂Se₂₁−ₓ and Mo₇W₁₋ₓS₄, have been prepared in high-yield and large amount from their 2H-phase layered bulk crystals via our recently developed electrochemical Li-intercalation and exfoliation method. To the best of our knowledge, it is the first time to realize the preparation of single-layer ternary TMD nanosheets with high concentration of metallic 1T phase (~66%) at high-yield and large scale. The exfoliated ternary...
MoS$_2$Se$_{2(1-x)}$ nanosheets can be easily coated on an FTO to form a thin film by simple drop-coating method, and then directly used as an efficient electrocatalyst for the tri-iodide reduction on the CE in a DSSC. Moreover, this nanosheet could also be promising supported by the U.S. Department of Energy under contract no. 2015CB921000 and No. 2014CB932500) and the National Science Foundation of China (Grants No. 2014CB933800). This research is conducted by the National Research Foundation, Prime Minister’s Office, Singapore. Z.F. and C.H.J. acknowledge the financial support by the National Basic Research Program of China (Grants No. 2014CB932500 and No. 2015CB921000) and the National Science Foundation of China (Grants No. 51222022 and No. 51472215). This work made use of the resources of the Center of Electron Microscopy of Zhejiang University. The experiments performed at the Molecular Foundry, Lawrence Berkeley National Laboratory were supported by the U.S. Department of Energy under contract no. DE-AC02-05CH11231.


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