Composition- and Phase-Controlled Synthesis and Applications of Alloyed Phase Heterostructures of Transition Metal Disulphides

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Figure S1. (a) Typical TEM image showing the edge part of Mo$_{1-x}$W$_x$S$_2$ nanosheet consisting of a few atomic layers. (b) Brightness profile along the white line drawn in (a) revealing that the interlayer spacing varies, typically from 0.6 to 1.0 nm.
Figure S2. EDX spectrum of typical Mo_{1-\chi}W_{\chi}S_2 nanosheets synthesized at 220 °C, showing a W:Mo atomic ratio of ~1:11, or the $\chi$ value is ~0.08.

<table>
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<tr>
<th>Element</th>
<th>Weight %</th>
<th>Atomic %</th>
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<tbody>
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<td>N K</td>
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<td>12.32</td>
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<tr>
<td>O K</td>
<td>4.89</td>
<td>14.02</td>
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<tr>
<td>S K</td>
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<tr>
<td>Mo L</td>
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</tr>
<tr>
<td>Total</td>
<td>100.00</td>
<td>100.00</td>
</tr>
</tbody>
</table>

Figure S3. HR-STEM image of a typical Mo_{1-\chi}W_{\chi}S_2 nanosheet showing sulfur vacancies which are highlighted by yellow circles.
As shown in Figure S4a, the W, Mo, S and N elements can be detected in the full scan spectrum. The high resolution S 2p spectrum in Figure S4b can be deconvoluted to give two sets of doublet peaks, attributable to the S$^{2-}$ in the 1T (161.5 and 162.7 eV) and 2H (162.3 and 163.5 eV) structures, respectively.$^{1,2}$ In the high resolution Mo 3d spectrum (Figure S4c), two sets of doublet peaks can be assigned to Mo$^{4+}$ in the 1T (228.8 and 231.9 eV) and 2H (229.4 and 232.6 eV) structures, respectively.$^{1,3}$ The peak at 226.2 eV is attributed to S 2s.$^{1,3}$ The high resolution W 4f spectrum (Figure S4d) reveals three sets of doublet peaks for 1T W$^{4+}$ (32.2 and 34.2 eV), 2H W$^{4+}$ (32.8 and 34.9 eV), and W$^{6+}$ (36.0 and 38.3 eV), respectively.$^{4-6}$ It can be seen that compared to MoS$_2$, WS$_2$ is more prone to oxidation.$^7$ Besides, the W 5p (39.8 eV) and Mo 4p (36.9 eV) peaks can also be observed.$^{4,5}$ The high resolution N 1s spectrum (Figure S4e) can be deconvoluted to give three peaks, assignable to NH$_4^+$ (401.4 eV),$^8$ NH$_3$ (396.4 eV)$^8$ and Mo 3p (394.6 eV).$^9$
Figure S5. (a) DSC and (b) TGA results of 60% 1T Mo$_{0.92}$W$_{0.08}$S$_2$ nanosheets, showing two endothermic steps which correspond to the removal of NH$_3$ at around 75 °C and NH$_4^+$ ions at around 225 °C.

Figure S6. (a) HRTEM side-view of a typical 60% 1T Mo$_{0.92}$W$_{0.08}$S$_2$ nanosheet showing the randomly stacked layers with varied interlayer spacings. Some 1T and 2H domains are highlighted with blue and red rectangles, respectively. (b) Raman spectrum of the as-prepared Mo$_{0.92}$W$_{0.08}$S$_2$ nanosheets. (c) HR-STEM image of a typical 60% 1T Mo$_{0.92}$W$_{0.08}$S$_2$ nanosheet revealing the presence of 1T' domains.
The 30% 1T Mo$_{0.87}$W$_{0.13}$S$_2$ nanosheets show the flower-like morphology as shown in Figure S7a. The XRD peaks (Figure S7b) positioned at 8.9°, 14° and 33° can be assigned to (002)$_{\text{enlarged}}$, (002)$_{2H}$ and (100)$_{2H}$ planes, respectively. The EDX spectrum (Figure S7c) indicates the W : Mo atomic ratio of ~ 1 : 6.4, suggesting the formation of Mo$_{0.87}$W$_{0.13}$S$_2$. Raman spectrum (Figure S7d) shows three peaks at 403, 377 and 346 cm$^{-1}$ corresponding to the MoS$_2$/WS$_2$ A$_{1g}$, MoS$_2$-like E$_{12g}$ and WS$_2$-like E$_{12g}$ modes. The 1T’ phase Raman active modes (147 cm$^{-1}$, 224 cm$^{-1}$) in the lower frequency region can be observed as well. The small peak at 287 cm$^{-1}$ can be assigned to 2H phase. \[\text{Figure S7. (a) SEM image, (b) XRD pattern, (c) EDX spectrum and (d) Raman spectrum of 30\% 1T Mo}_{0.87}\text{W}_{0.13}\text{S}_2 \text{nanosheets prepared at 240 °C.}\]
Figure S8. XPS (a) Mo 3d, (b) S 2p and (c) W 4f spectra of as-prepared 30% 1T Mo$_{0.87}$W$_{0.13}$S$_2$ nanosheets synthesized at 240 °C.

In the high resolution Mo 3d spectrum (Figure S8a), three sets of doublet peaks for Mo$^{4+}$ with the 1T (228.6 and 231.7 eV) and 2H (229.2 and 232.4 eV) structures and Mo$^{6+}$ (235.9 and 233.12 eV) can be observed.$^{1,3}$ The peak at 226.2 eV is attributed to S 2s.$^{1,3}$ The high resolution S 2p spectrum in Figure S8b can be deconvoluted to give two sets of doublet peaks, attributable to the S$^{2-}$ in the 1T (161.2 and 162.3 eV) and 2H (162.1 and 163.3 eV) structures, respectively.$^{1,2}$ The high resolution W 4f spectrum (Figure S8c) reveals three sets of doublet peaks for 1T W$^{4+}$ (32.0 and 34.1 eV), 2H W$^{4+}$ (32.7 and 34.8 eV) and W$^{6+}$ (35.8 and 37.9 eV), respectively.$^{4,6}$ In addition, the W 5p (39.3 eV) and Mo 4p (36.9 eV) peaks can also be observed.$^{4,5}$
Figure S9. (a) SEM image, (b) XRD pattern, (c) EDX spectrum and (d) Raman analysis of 80% 1T Mo$_{0.96}$W$_{0.04}$S$_2$ nanosheets prepared at 200 ℃.

The 80% 1T Mo$_{0.96}$W$_{0.04}$S$_2$ nanosheets show the flower-like morphology as shown in Figure S9a. The XRD peaks (Figure S9b) positioned at 8.9°, 18° and 33° can be assigned to (002)$_{\text{enlarged}}$, (004)$_{\text{enlarged}}$ and (100) planes, respectively. The EDX spectrum (Figure S9c) indicates the W : Mo atomic ratio of ~1 : 20, or Mo$_{0.96}$W$_{0.04}$S$_2$ was obtained. Raman spectrum (Figure S9d) shows two dominant peaks at 403 and 377 cm$^{-1}$ corresponding to the A$_{\text{1g}}$ and MoS$_2$-like E$_{\text{12g}}$ bands and the distorted 1T phase Raman active modes (147 cm$^{-1}$, 224 cm$^{-1}$) in the lower frequency region can be observed as well. The small peak at 302 cm$^{-1}$ can be assigned to the 2H phase. Note that the WS$_2$-like E$_{\text{12g}}$ is not observed, probably because the doping concentration of W is too low at ~4%.
Figure S10. XPS (a) Mo 3d (b) S 2p and (c) W 4f spectra of as-prepared 80% 1T Mo$_{0.96}$W$_{0.04}$S$_2$ nanosheets prepared at 200 °C.

In the high resolution Mo 3d spectrum (Figure S10a), two sets of doublet peaks can be assigned to Mo$^{4+}$ in the 1T (228.6 and 231.7 eV) and 2H (229.2 and 232.4 eV) structures.$^{1,3}$ The peak at 226.2 eV is attributed to S 2s.$^{1,3}$ The high resolution S 2p spectrum in Figure S10b can be deconvoluted to give two sets of doublet peaks, attributable to the S$^{2-}$ in the 1T (161.2 and 162.3 eV) and 2H (162.1 and 163.3 eV) structures, respectively.$^{1,2}$ The high resolution W 4f spectrum (Figure S10c) reveals three sets of doublet peaks for 1T W$^{4+}$ (31.7 and 33.9 eV), 2H W$^{4+}$ (32.6 and 34.5 eV) and W$^{6+}$ (35.7 and 37.8 eV), respectively.$^{4-6}$ In addition, the W 5p (39.3 eV) and Mo 4p (36.6 eV) peaks can also be observed.$^{4,5}$
Figure S11. (a) SEM image, (b) XRD pattern, (c) Raman spectrum, (d) EDX spectrum, (e) XPS W 4f spectrum and (f) XPS S 2p spectrum of 80% 1T WS\textsubscript{2} nanosheets.

The 80% 1T WS\textsubscript{2} nanosheets show the flower-like morphology as shown in Figure S11a. The XRD peaks (Figure S11b) positioned at 8.9°, 18° and 33° can be assigned to (002)\textsubscript{enlarged}, (004)\textsubscript{enlarged} and (100) planes, respectively. Raman spectrum (Figure S11c) shows two peaks at 416 and 350 cm\textsuperscript{-1} corresponding to the A\textsubscript{1g}, E\textsubscript{12g} modes. Three small WS\textsubscript{2} peaks (171 cm\textsuperscript{-1}, 261 cm\textsuperscript{-1} and 317 cm\textsuperscript{-1}) can be observed in the lower frequency region which can be assigned to the 1T phase.\textsuperscript{13-15} The EDX spectrum (Figure S11d) indicates the W:S atomic ratio of \approx 1 : 2. The high resolution W 4f spectrum (Figure S11e) reveals three sets of doublet peaks for 1T W\textsuperscript{4+} (31.7 and 33.9 eV), 2H W\textsuperscript{4+} (32.6 and 34.5 eV) and W\textsuperscript{6+} (35.7 and 37.8 eV), respectively.\textsuperscript{4-6} The high resolution S 2p spectrum (Figure S11f) can be deconvoluted to give four peaks, attributable to the S\textsuperscript{2-} in the 1T (161.2 and 162.3 eV) and 2H (162.1 and 163.3 eV) structures, respectively.\textsuperscript{1,2}
Figure S12. (a) SEM image, (b) XRD pattern, (c) Raman spectrum, (d) EDX spectrum, (e) XPS Mo 3d spectra and (f) XPS S 2p spectra of 80% 1T MoS$_2$ nanosheets.

The 80% 1T MoS$_2$ nanosheets show the flower-like morphology as shown in Figure S12a. The XRD peaks (Figure S12b) positioned at 8.9°, 18° and 33° can be assigned to (002)$_{\text{enlarged}}$, (004)$_{\text{enlarged}}$ and (100) planes, respectively. Raman spectrum (Figure S12c) shows two peaks at 403 and 377 cm$^{-1}$ corresponding to the $A_{1g}$, $E_{12g}$ modes. The 1T’ phase Raman active modes (147 cm$^{-1}$, 336 cm$^{-1}$) in the lower frequency region can be observed as well. The small peak at 287 cm$^{-1}$ can be assigned to the 2H phase. The EDX spectrum (Figure S12d) indicates the Mo:S atomic ratio of ~1 : 2. The high resolution Mo 3d spectrum (Figure S12e) reveals two sets of double peaks, which can be assigned to Mo$^{4+}$ in the 1T (228.6 and 231.7 eV) structure and 2H (229.2 and 232.4 eV) structures, respectively. The peak at 226.2 eV is attributed to S 2s. The high resolution S 2p spectrum (Figure S12f) can be deconvoluted to give four peaks, attributable to the S$^{2-}$ in the 1T (161.2 and 162.3 eV) and 2H (162.1 and 163.3 eV) structures, respectively.
Figure S13. (a) Cyclic voltammetry (CV) measurements of different metal sulfide catalysts in presence of cupric sulfate. The sharp peaks correspond to the overpotential stripping and deposition, i.e. I_A and I_C, respectively. The broad peaks correspond to the underpotential regions, i.e. II_A and II_C, respectively. The bare glassy carbon electrode does not exhibit any underpotential deposition signal. The charge ratio for copper striping and hydrogen adsorption, i.e. Q_{Cu}/Q_{H}, reaches 2 at 505, 510 and 475 mV vs. RHE for (b) Mo_{0.92}W_{0.08}S_2 (60% 1T), (c) WS_2 (80% 1T) and (d) MoS_2 (80% 1T), respectively.

To compare the catalytic activity of MoS_2 (80% 1T), WS_2 (80% 1T) and alloyed Mo_{1-\chi}W_{\chi}S_2 nanosheets, we measured their density of active sites using the copper underpotential deposition method reported previously by Green et al.\textsuperscript{16} The cyclic voltammetry (CV) measurements of different catalysts were conducted in a solution containing 0.1 M H_2SO_4 and 2 mM CuSO_4 with scan rate of 2 mV/s using a saturated calomel electrode as the reference electrode (Figure S13a). The underpotential deposition (UPD, II_A) region, which is in the higher potential compared to the thermodynamic deposition potential (overpotential deposition, OPD, I_A) region, was thus located, for example, at ~400-660 mV for the 60% 1T Mo_{0.92}W_{0.08}S_2 based electrode. The amount of charge transferred during the UPD can be determined by conducting the following three-step process. Taking 60% 1T Mo_{0.92}W_{0.08}S_2 as
an example, first, in a 0.1 M of \( \text{H}_2\text{SO}_4 \) and 2 mM \( \text{CuSO}_4 \) solution, the electrode surface was electrochemically cleaned by applying a potential (e.g. 673 mV) higher than the UPD region for 120 s. Then, the deposition of copper was conducted at a constant potential in the range of 400-660 mV, for example 450 mV, for 100 s. After that, the voltage was gradually increased to 673 mV to oxidize the deposited copper at a scan rate of 2 mV/s, and the amount of charge transferred was recorded. Similar steps were performed for the same catalyst at the same deposition potential but in a 0.1 M of \( \text{H}_2\text{SO}_4 \) solution without the presence of \( \text{CuSO}_4 \), in order to obtain the amount of charge exchanged during the hydrogen adsorption. The charge ratio for copper stripping and hydrogen adsorption (i.e. \( \frac{Q_{\text{Cu}}}{Q_{\text{H}}} \)) at various deposition potentials were calculated and plotted in Figure S13b-d. It can be seen that the \( \frac{Q_{\text{Cu}}}{Q_{\text{H}}} \) ratio decreases with increasing the deposition potential. The \( \frac{Q_{\text{Cu}}}{Q_{\text{H}}} \) ratio of 2 is expected when the monolayer copper is deposited at the same site as that for hydrogen adsorption since copper stripping involves two electrons versus one for hydrogen adsorption. From Figure S13b-d, we can determine that the deposition potential to yield single-atomic layer deposition of copper is 505, 510 and 475 mV vs. RHE for \( \text{Mo}_{0.92}\text{W}_{0.08}\text{S}_2 \) (60% 1T), 1T WS\(_2\) (80% 1T) and 1T MoS\(_2\) (80% 1T), respectively. The mole number of the deposited copper (Equation 1), \( N_{\text{Cu}} \) (Equation 2) and the active site density (\( N_{\text{Cu}}/A_{\text{electrode}} \)) were calculated and listed in Figure 4d.

\[
n_{\text{Cu}} = \frac{Q_{\text{Cu}}(C)}{(96500C/e)(2e/Cu)} 
\]

\[
N_{\text{Cu}} = n_{\text{Cu}}(\text{mol})*L(\text{mol}^{-1}) 
\]
Figure S14. (a) Polarization curves of Pt-C (10 wt% of Pt), MoS$_2$ nanosheets (80% 1T), WS$_2$ nanosheets (80% 1T), Mo$_{0.96}$W$_{0.04}$S$_2$ nanosheets (80% 1T), Mo$_{0.92}$W$_{0.08}$S$_2$ nanosheets (60% 1T), Mo$_{0.92}$W$_{0.08}$S$_2$ nanosheets (annealed) and Mo$_{0.87}$W$_{0.13}$S$_2$ nanosheets (30% 1T). (b) Corresponding Tafel plots obtained from the polarization curves in (a). (c) List of Tafel slope values calculated from the Tafel plots in (b).

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<th>Sample</th>
<th>Tafel slope (mV decade$^{-1}$)</th>
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<tr>
<td>Pt-C</td>
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<tr>
<td>MoS$_2$ (80% 1T)</td>
<td>55.8</td>
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<tr>
<td>WS$_2$ (80% 1T)</td>
<td>45.4</td>
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<tr>
<td>Mo$<em>{0.96}$W$</em>{0.04}$S$_2$ (80% 1T)</td>
<td>45.9</td>
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<tr>
<td>Mo$<em>{0.92}$W$</em>{0.08}$S$_2$ (60% 1T)</td>
<td>43.8</td>
</tr>
<tr>
<td>Mo$<em>{0.87}$W$</em>{0.13}$S$_2$ (30% 1T)</td>
<td>69.7</td>
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<tr>
<td>Mo$<em>{0.92}$W$</em>{0.08}$S$_2$ (annealed)</td>
<td>250</td>
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10% 1T Mo$_{0.87}$W$_{0.13}$S$_2$ nanosheets prepared by heating the precursor solution at 200 °C for 24 h and then at 240 °C for 24 h.

The 10% 1T Mo$_{0.87}$W$_{0.13}$S$_2$ nanosheets also show the flower-like morphology as shown in Figure S15a. The deconvoluted XRD peaks (Figure S15b) positioned at 8.9°, 14° and 33° can be assigned to (002)$_{\text{enlarged}}$, (002)$_{2H}$ and (100)$_{2H}$ planes, respectively. The EDX spectrum (Figure S15c) indicates a the W : Mo atomic ratio of ~1 : 6.8, or Mo$_{0.87}$W$_{0.13}$S$_2$ was obtained. Raman spectrum (Figure S15d) shows two dominant peaks at 403 and 377 cm$^{-1}$ corresponding to the A$_{1g}$ and MoS$_2$-like E$_{12g}$ bands. The distorted 1T' phase Raman active modes (147 cm$^{-1}$, 224 cm$^{-1}$) in the lower frequency region can be observed as well.$^{10}$ The small peak at 287 cm$^{-1}$ can be assigned to the 2H structure.$^{11}$
Figure S16. XPS spectra of (a) Mo 3d (b) S 2p and (c) W 4f of as-prepared 10% 1T Mo$_{0.87}$W$_{0.13}$S$_2$ nanosheets.

In the high resolution Mo 3d spectrum (Figure S16a), three sets of doublet peaks for Mo$^{4+}$ in the 1T (228.6 and 231.7 eV) and 2H (229.2 and 232.4 eV) structures and Mo$^{6+}$ (235.9 and 233.12 eV) can be found.\textsuperscript{1,3} The peak at 226.2 eV is attributed to S 2s.\textsuperscript{1,3} The high resolution S 2p spectrum in Figure S16b can be deconvoluted to give two sets of doublet peaks, attributable to the S$^{2-}$ in the 1T (161.2 and 162.3 eV) and 2H (162.1 and 163.3 eV) structures, respectively.\textsuperscript{1,2} The high resolution W 4f spectrum (Figure S16c) reveals three sets of doublet peaks for 1T W$^{4+}$ (31.7 and 33.9 eV), 2H W$^{4+}$ (32.6 and 34.5 eV) and W$^{6+}$ (35.7 and 37.8 eV), respectively.\textsuperscript{4-6} Besides, the W 5p (39.3 eV) and Mo 4p (36.6 eV) peaks can also be observed.\textsuperscript{4,5}
Figure S17. (a) Dynamic sensing performance of a sensor based on Mo$_{0.87}$W$_{0.13}$S$_2$ (10% 1T) nanosheets towards acetone gas at different concentrations. (b) Linear fit of the response versus acetone concentration for 0-5 ppm acetone. The limit of detection (LOD) was calculated at a sensitivity of 3 times of signal to noise ratio, i.e. 0.002%, to be 0.7 ppm. Dynamic sensing performance of a sensor based on (c) annealed Mo$_{0.87}$W$_{0.13}$S$_2$ and (d) Mo$_{0.87}$W$_{0.13}$S$_2$ (30% 1T) towards acetone gas at different concentrations.

Figure S18. (a) $I_d$-$V_{ds}$ characteristics of a back-gated thin film FET based on as-prepared Mo$_{0.87}$W$_{0.13}$S$_2$ (30% 1T) nanosheets at $V_g = 0$ V, and (b) the $I_d$-$V_{ds}$ curves of the FET at various $V_g$ measured in vacuum ($5\times10^{-5}$ Torr) at 100 K.
Reference


