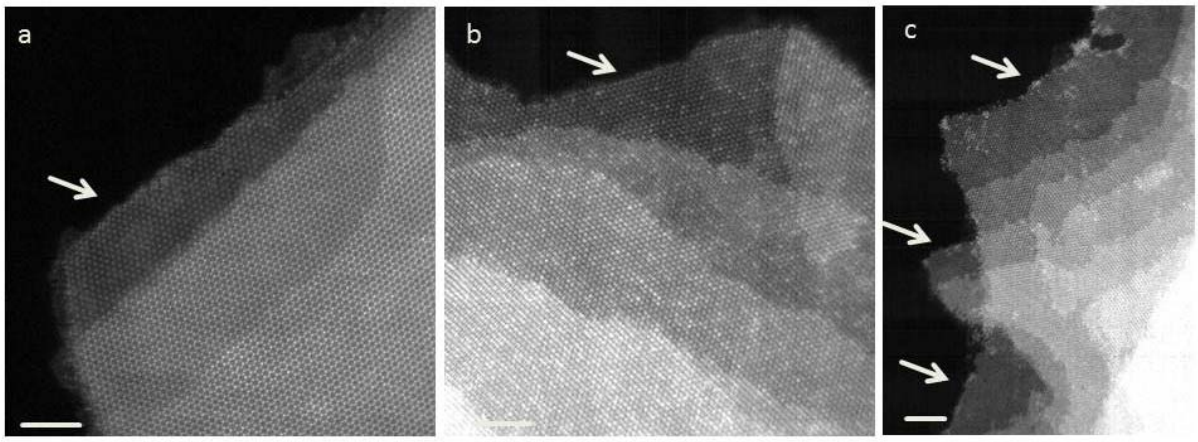
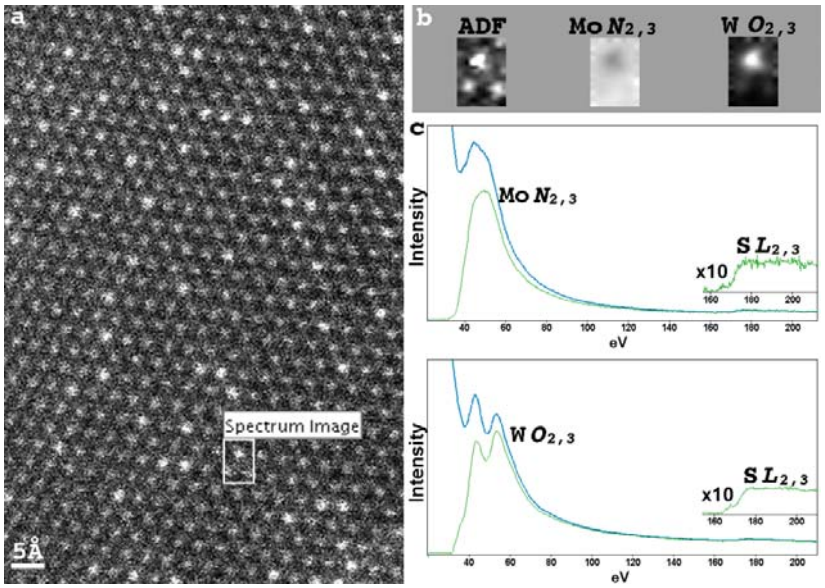
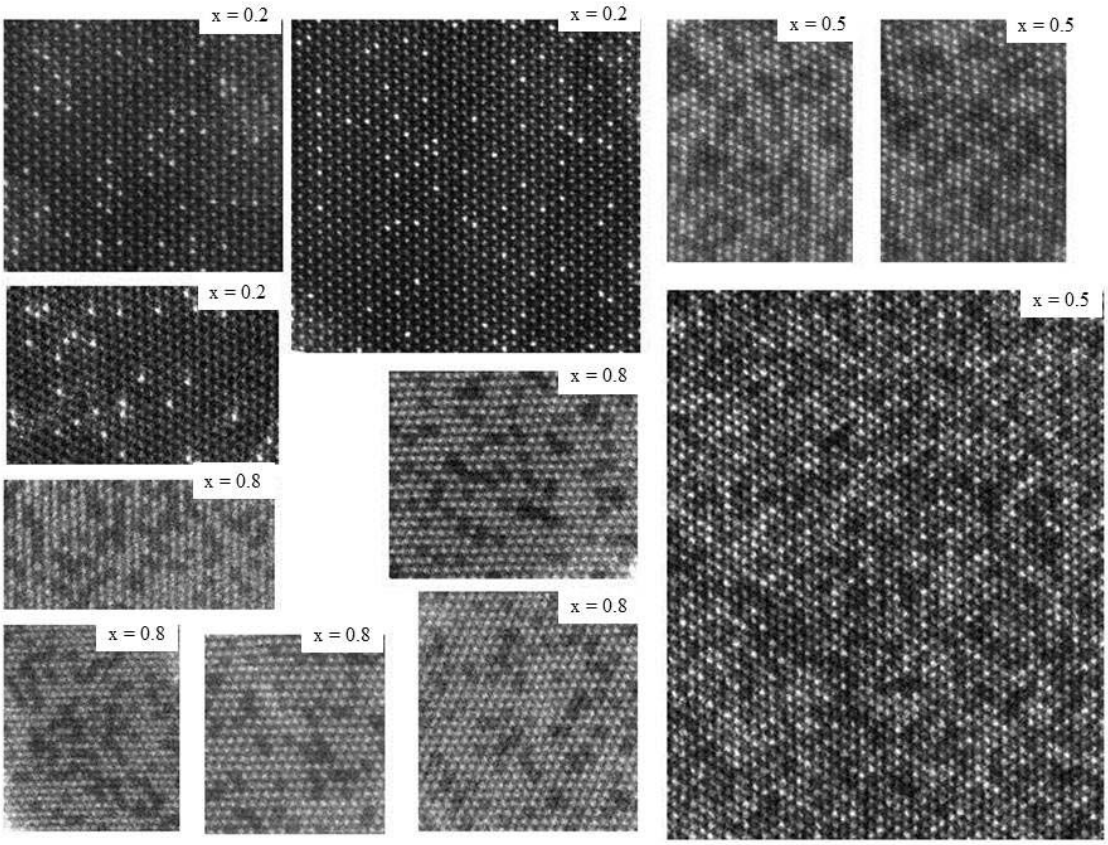
Supplementary Figures



Supplementary Figure S1. Cleaved $Mo_{1-x}W_xS_2$ specimens with single- to few-layered regions. (a, b, c) Examples of **scanning transmission electron microscope annular dark-field** images of mixed $Mo_{1-x}W_xS_2$ layers (x = 0, 0.2, and 1). x refers to the starting materials. The single-layer regions are marked with white arrows. Scale bars = 3 nm. Note that some regions with less contrast and no periodic structure are the amorphous carbon layers of inevitable contamination during the transfer process.



Supplementary Figure S2. Electron energy loss spectroscopy (EELS) analysis of a single layer of $Mo_{1-x}W_xS_2$ (x = 0.2). (a) annular dark-field (ADF) image shows a rectangular region from which the spectrum image was taken. (b) EELS chemical maps of Mo and W obtained simultaneously with the ADF image from the rectangle in (a). The energy dispersion was set to 0.25 eV with the binning 2. The acquisition time for each spectrum is ~0.05 sec. The W *O*-edge and Mo *N*-edge were extracted after a background subtraction. Blue and green lies show the spectra before and after the power-law background subtraction. They clearly show one W atom and two Mo atoms involved in the rectangular area. Because the two edges are overlapping together, the multiple linear least squares fitting was performed by using the low-loss spectra. (c) The reference spectra recorded from the pure MoS_2 and WS_2 layers, involving W $O_{2,3}$ edge and Mo $N_{2,3}$ edge. Note that the spectra should be carefully recorded from the single layer regions without any carbon contamination. A principal component analysis (PCA) was used to extract the chemical maps.



Supplementary Figure S3. Examples for unprocessed scanning transmission electron microscope annular dark-field images used for alloying quantifications (Fig. 3). The brighter spot corresponds to the W atom and less brighter to the Mo atom. The S atoms appear much darker and are not always visible. The neighbouring two transition atoms are separated at ~ 0.42 nm. The magnification is slightly different for all the images.

Supplementary Methods

Error bars in alloying degree calculations:

In our case for W atoms, taking into account total 6 neighbours for each atom, the formulas for alloying degree [32] can be transformed to:

$$P_{observed} = \frac{\sum_{i=0}^{6}(i \times N_{W-iMo})}{6 \times N_W},$$

$$P_{random} = \frac{N_{Mo}}{N_W + N_{Mo}},$$

where N_W and $N_{W\text{-}iMo}$ are the total number of W atoms and number of W atoms surrounded by i Mo atoms (i = 0 to 6), respectively. Thus,

$$J_W = \frac{P_{observed}}{P_{random}} \times 100\% = \frac{(N_W + N_{Mo})\sum_{i=0}^{6}(i \times N_{W-iMo})}{6 \times N_W \times N_{Mo}} = \frac{1}{6}\left(\frac{1}{N_W} + \frac{1}{N_{Mo}}\right)\sum_{i=0}^{6}(i \times N_{W-iMo}).$$

As a result for Mo atoms:

$$J_{Mo} = \frac{R_{observed}}{R_{random}} \times 100\% = \frac{1}{6}\left(\frac{1}{N_{Mo}} + \frac{1}{N_W}\right)\sum_{i=0}^{6}(i \times N_{Mo-iW}),$$

where R_{observed} is defined as the ratio of the averaged W coordination number to the total coordination number 6, and R_{random} is the atomic ratio of W in the examined layer.

The error bars for the content and alloying degree were calculated taking into consideration the statistical calculation of W and Mo atoms in a layer. The obtained result depends directly on a sample size (total population of atoms in a sample). The samples with smaller sample size used for the atoms counting show bigger error values for content and alloying degree calculations.