SUPPORTING INFORMATION

One-pot rapid synthesis of Mo(S,Se)$_2$ nanosheets on graphene for highly efficient hydrogen evolution

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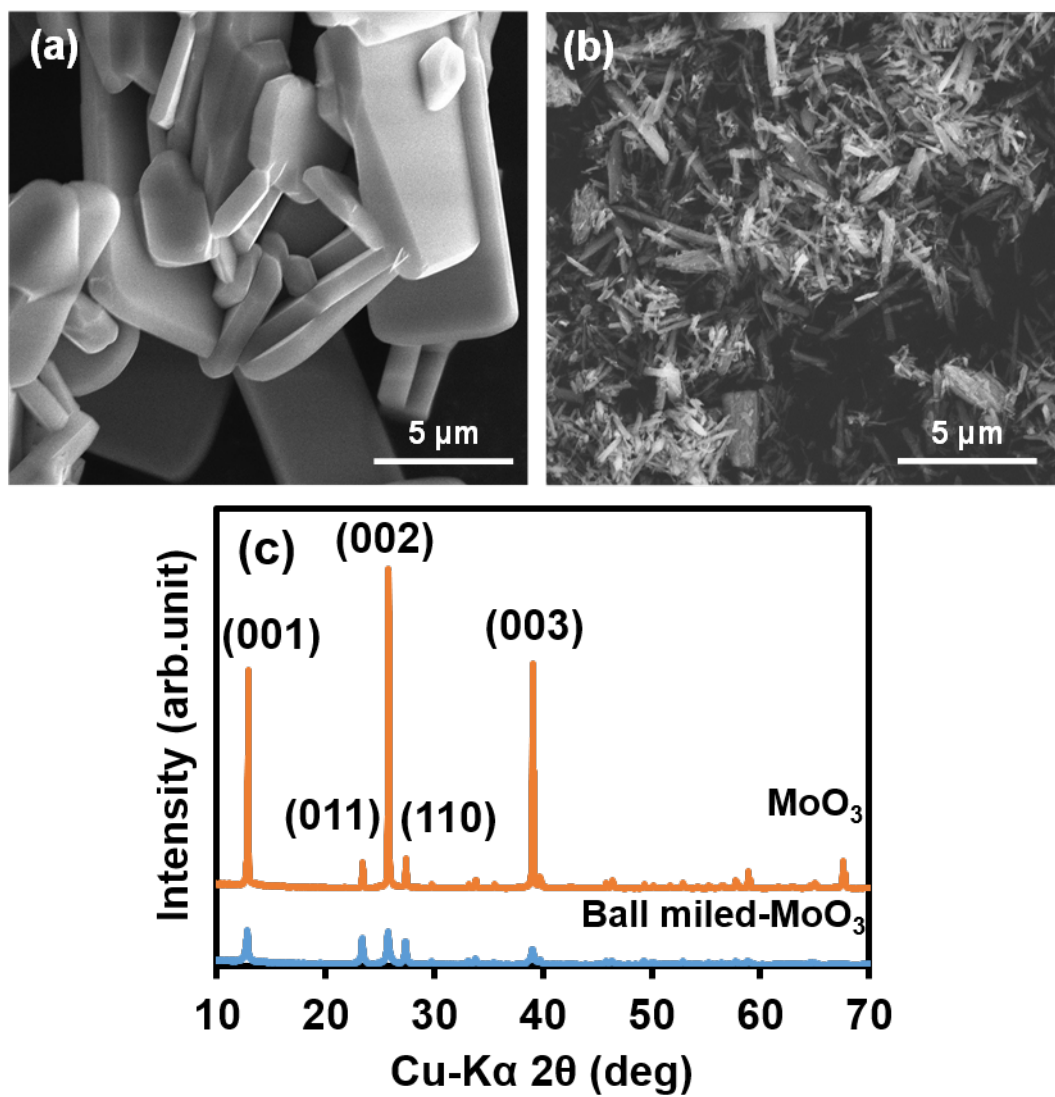Total number of tables: 1

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Fig. S1 SEM images of (a) pristine MoO_3 (b) Ball-milled MoO_3, (c) The XRD patterns of MoO_3 before and after the ball-milling
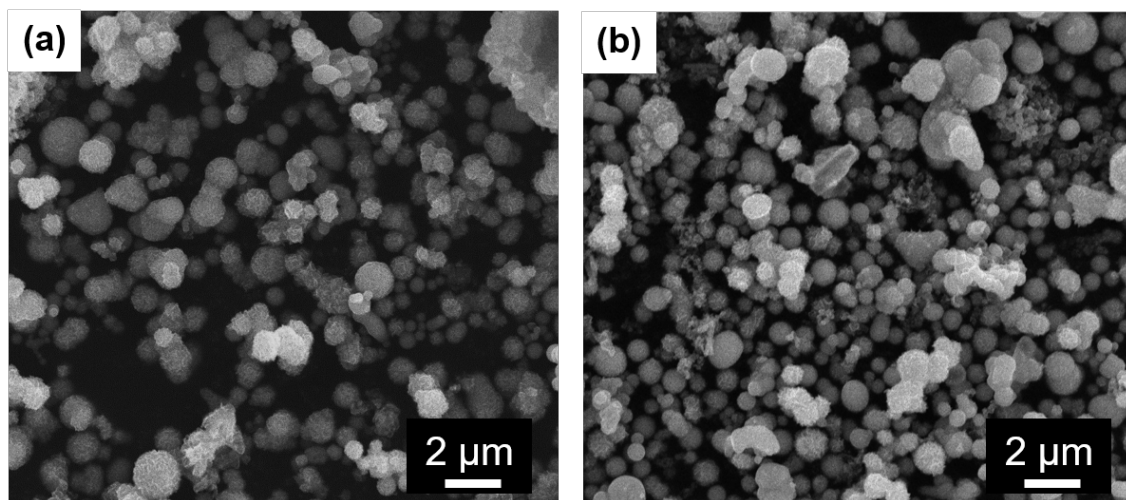
Fig. S2 Cooling-time dependence on the morphology of MoS_2 by SEM observation

(a) Rapid cooling (Put the reactor in water bath)

(b) Slow cooling (Leave the reactor in the air for 30 min)

Hansen solubility parameters between MoS$_2$ and SC EtOH

The solubility parameter used in the latest study is Hansen's solubility parameter (HSP),[1] which separates the contribution of dispersion (δ_D), polarity (δ_P), and hydrogen bond (δ_H). The closer the values of the solubility parameters of the solvent and solute are, the higher is the solubility. In order to obtain comprehensive solubility (δ_T), the following formula is used.

$$\delta_T{}^2 = \delta_D^2 + \delta_P^2 + \delta_H^2 \qquad (1)$$

To use HSP, the interaction radius (R_0) and distance (R_a) between HSPs are required. Generally, when determining the HSP of a substance, its solubility is examined using solvents (about 20 in number) whose HSPs are already known. When the HSPs of solvents that can dissolve the substance and of those that cannot dissolve the substance are plotted in a three-dimensional space, the solvents that can dissolve the substance collect in a similar region. A sphere can be drawn to encompass all the points representing solvents that can dissolve the substance while excluding all the points representing solvents that cannot dissolve the substance. The center of the sphere is defined as the HSP of the substance. The radius of the sphere is R_0, the interaction radius. A substance with a long radius R_0 can easily dissolve in a number of solvents, and one with a short radius dissolves in only a few solvents. The center coordinate of the sphere is defined as the HSP value of the substance. To calculate the distance (R_a) between the HSP value of a solvent and the HSP value of the substance, the following equation is used.

$$R_a^2 = 4\left(\delta_{D,\,S1} - \delta_{D,\,S2}\right)^2 + \left(\delta_{P,\,S1} - \delta_{P,\,S2}\right)^2 + \left(\delta_{H,\,S1} - \delta_{H,\,S2}\right)^2 \quad (2)$$

(S1: Solvent S2: Substance)

In general, however, HSP can only be applied under ambient conditions. Therefore, the HSP presently derived under supercritical conditions where physical properties fluctuate greatly depending on variations in temperature and pressure cannot be applied to SCFs. In 2004, a study to estimate the HSP of supercritical CO_2 was carried out, according to Ref. 2). The formula of HSP used in supercritical CO_2 is given below. To determine δ_D, δ_P and δ_T, (3), (4) and (5) were used for all SC EtOH in this study.

$$\frac{\delta_D}{\delta_{D,ref}} = \left(\frac{V_{ref}}{V}\right)^{1.25} \quad (3)$$

$$\frac{\delta_P}{\delta_{P,ref}} = \left(\frac{V_{ref}}{V}\right)^{0.5} \quad (4)$$

$$\frac{\delta_H}{\delta_{H,ref}} = \frac{1}{exp\left[-1.32 \times 10^{-3}\left(T_{ref} - T\right) - \ln\left(\frac{V_{ref}}{V}\right)^{0.5}\right]} \quad (5)$$

(V: Volume per molar, T: Temperature, ref: Each parameter at ambient conditions)
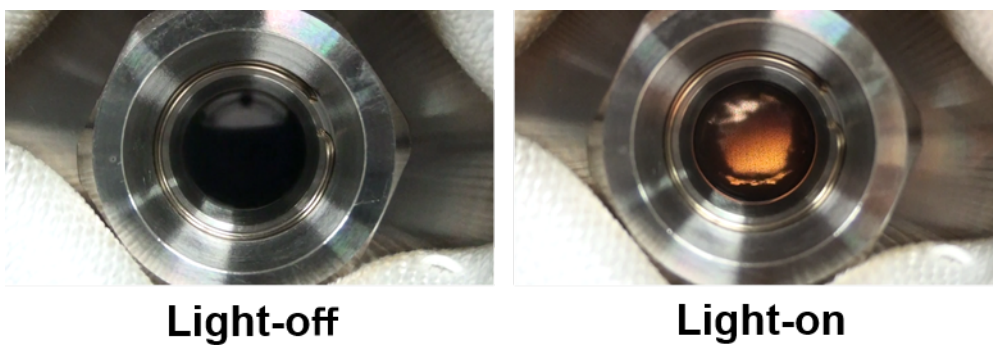
Light-off   **Light-on**

Fig.S3 Supercritical visualization reaction cell: SCF sulfurization of MoO_3 is demonstrated using 0.4 g/mL EtOH density (Light-on means illumination from behind the reaction cell.).
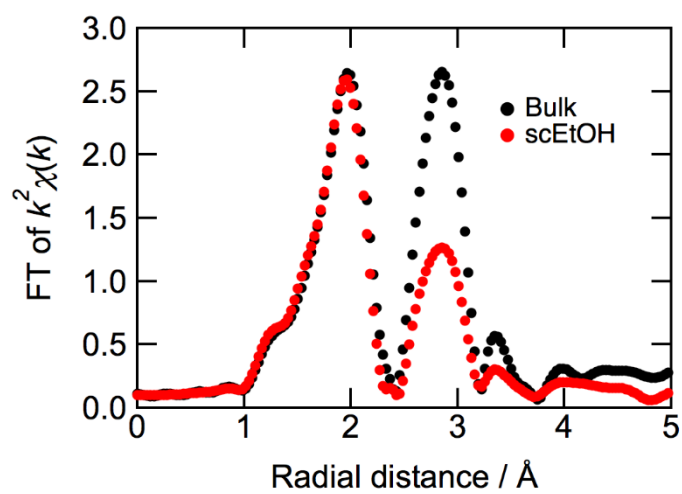
Fig.S4 The Fourier transformed k^2-weighted EXAFS plotted as a radial structure function.

Table S1 Detailed fitting parameters.

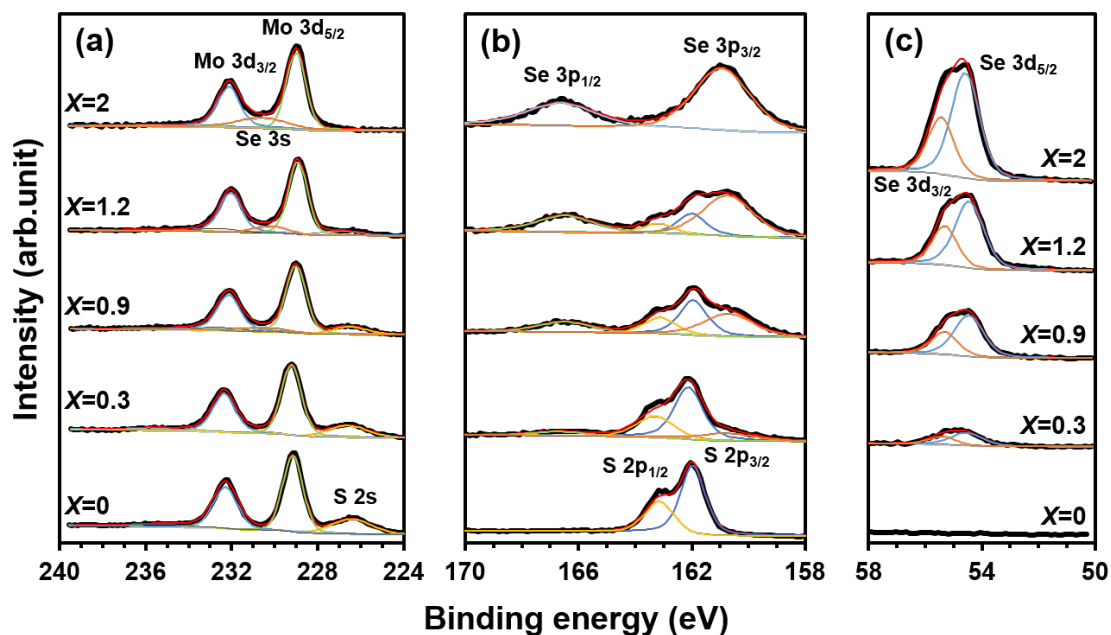|	amp$_{Mo-S}$	amp$_{Mo-Mo}$	ampS/ampMo	N_{Mo-S}/N_{Mo-Mo}	r$_{Mo-S}$	r$_{Mo-Mo}$	σ^2_{Mo-S}	σ^2_{Mo-Mo}	R-factor
Bulk	0.85(7)	1.2(1)	**0.7(1)**	1	**2.405(5)**	**3.170(4)**	0.0026(6)	0.0034(5)	0.0063
EtOH	0.88(5)	0.7(1)	**1.3(2)**	**1.8(4)**	**2.406(4)**	**3.167(4)**	0.0031(4)	0.0043(8)	0.0044

Fig.S5 The results of XPS for MoS$_{2-X}$Se$_X$ (a)Mo 3d, S 2s (b) S/Se 2p (c) Se 3d

The figures illustrate the Mo 3d, S/Se 2p, and Se 3d high resolution spectra of them. The Mo 3d peaks located at ~229 eV and ~232 eV can be attributed to the doublet of Mo 3d$_{5/2}$ and Mo 3d$_{3/2}$ and as the introduction of sulfur, the peak of S 2s gradually increases shown in Fig.S5(a). The binding energy for S 2p$_{3/2}$ and S 2p$_{1/2}$ are 162.0 eV and 163.3 eV, and the binding energies of Se 3p$_{3/2}$ and Se 3p$_{1/2}$ at 160.8 and 166.6 eV indicate the chemical oxidation state of Se^{2-}, shown in Fig. S5 (b). As the composition rate changes, the peaks shift to each other. The doublet peak of Se 3d$_{3/2}$ and Se 3d$_{5/2}$ is shown in Fig.S5(c). As the introduction of selenium, the peak intensity gradually increases.
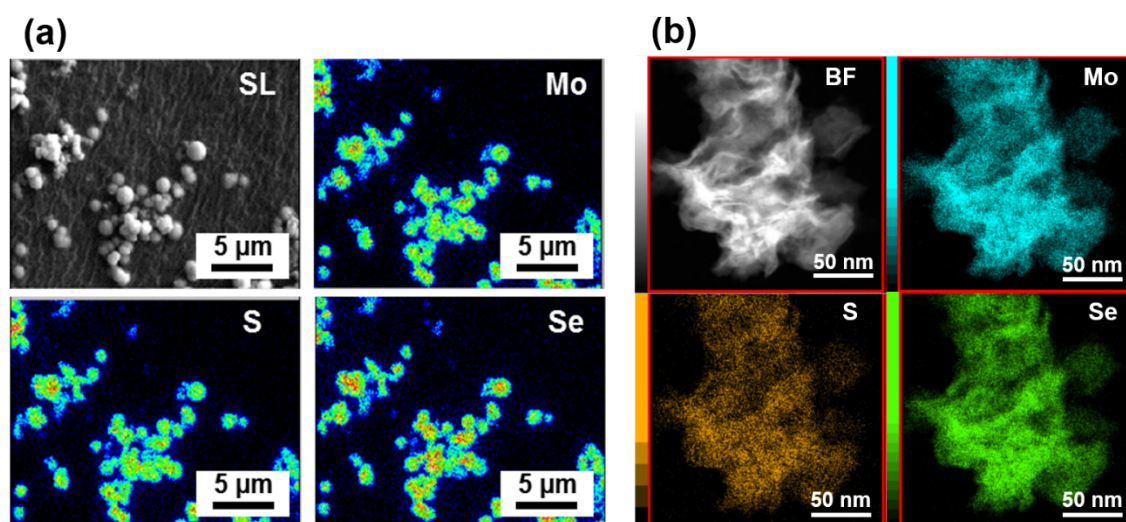
Fig.S6 The distribution of Mo, S and Se in $MoS_{1.1}Se_{0.9}$ with (a)SEM−WDS (b)
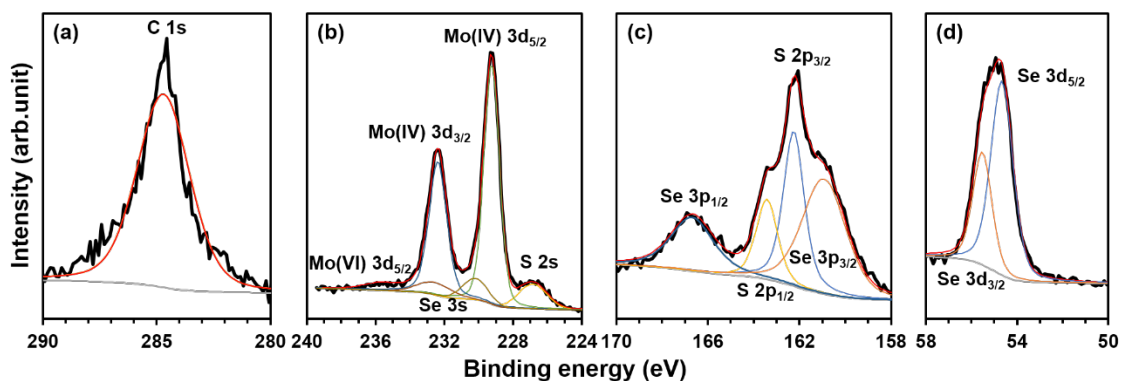
STEM−EDS

Fig.S7 The results of XPS for $MoS_{0.9}Se_{1.1}$/rGO

(a)C 1s (b)Mo 3d, S 2s (c) S/Se 2p (d) Se 3d

No peaks for hexavalent molybdenum derived from MoO_3 were observed. It is known that the degree of reduction of rGO can be determined from the C1s peak and the amount of functional carbon groups containing oxygen can be evaluated by the peak intensities of C−O (epoxy and alkoxy), C=O, and O−C=O functional groups, observed at 286.8, 287.3, and 289.4 eV, respectively.[3] We observed little peaks of them for the $MoS_{0.9}Se_{1.1}$/rGO sample, suggesting that sufficient reduction of GO occurred.

References

1) Hansen, C. M. The Three Dimensional Solubility Parameter. *J. Paint Technol*., **1967**, 39, 505.

2) Williams, L. L.; Rubin, J. B.; Edwards, H. W. Calculation of Hansen Solubility Parameter Values for a Range of Pressure and Temperature Conditions, Including the Supercritical Fluid Region. *Ind. Eng. Chem. Res.*, **2004**, 43, 4967–4972.

3) Jana, M.; Saha, S.; Khanra, P.; Murmu, N. C.; Srivastav, S. K.; Kuila, T.; Lee, J. H. Bio-Reduction of Graphene Oxide Using Drained Water from Soaked Mung Beans (Phaseolus aureus L.) and Its Application as Energy Storage Electrode Material. *Mater. Sci. Eng. B* **2014**, 186, 33–40.