MoSe$_2$ Nanosheets and Their Graphene Hybrids:

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Supporting Information
**Materials and Methods.**

*Synthesis and Preparation.* We report a facile way to prepared MoSe₂ and MoSe₂/RGO by hydrothermal reaction followed by low temperature crystallization annealing. All of the chemicals used in the present work were of analytical grade, and the reactions were carried out under open-air conditions using distilled water. Selenium (99.99%), Na₂MoO₄ (99.99%) and hydrazine hydrate (N₂H₄H₂O, 98%) solution were obtained from Sigma-Aldrich.

For the preparation of MoSe₂ nanosheets: 0.002 mol Na₂MoO₄ was dispersed in 50ml distilled water under constant stirring to form a clear solution. In a separate flask, the required amount of Se powder (0.004mol) was dissolved in hydrazine hydrate solution (10 ml) in open air. Instantly the colorless solution turns dark brown and remains unchanged under atmospheric conditions at least for one day. Then 10ml hydrazine hydrate-Se was added to 50ml Na₂MoO₄ slowly at room temperature. The mixture gives a clear orange-red solution with the final Mo: Se mole ration is about 1:2. Then the mixture was transferred to a 100 mL Teflon-lined autoclave and heated in an oven at 200°C for 10 h with no intentional control of ramping or cooling rate. The black precipitates was collected by centrifugation at 7000 rpm for 5 min, washed with DI water and recollected by centrifugation. The washing step was repeated for at least 3 times. Then product was dry-vacated overnight. Finally, the precipitates were annealed at 470 °C in flowing high-pure N₂ atmosphere for 10 h to yield final crystalline products.

For the preparation of MoSe₂ /RGO nanosheets: GO was made by a modified Hummers method. Then 0.1g GO was dispersed in 50ml distilled water with 0.0005 mol Na₂MoO₄ under constant sonication at room temperature for approximately 30 min until a clear and homogeneous solution was achieved. In a separate flask, 0.001mol Se powder was dissolved in hydrazine hydrate solution (10 ml) in open air. The following steps are similar to those of
preparation of MoSe2 nanosheets. For comparison, the other two MoSe2 /RGO hybrids with different graphene and MoSe2 ratios were prepared: One is with 0.001 mol Na2MoO4 and 0.002mol Se, and the hydrothermal reaction time maintained at 10h; and the other is with 0.00025mol Na2MoO4 and 0.0005mol Se, and the hydrothermal reaction time shortened to 6h.

**Characterizations.** Powder X-ray diffraction (XRD) measurements were carried out using a Philips X’Pert powder diffractometer with Cu KR radiation ($\lambda = 1.54056$ A $\circ$) with a scan step of 0.05 deg/s. To record the pattern, nanoparticle powder was coated on a glass plate. Scanning electron microscopy (SEM) images were recorded on a JSM 6300 (JEOL). Samples were prepared by drop-drying from an ethanol suspension of the hybrid onto Si wafers. Transmission electron micrographs (TEM), high-resolution transmission electron microscopy (HRTEM) images were recorded using a JEOL JEM-2010 electron microscope at 200 kV. Samples were prepared by drop-drying a diluted suspension of the samples in ethanol onto a 200 mesh holey carbon copper grid that was dried completely under ambient conditions before the measurements. X-ray photoelectron spectroscopy (XPS) spectrum was collected on PHI 5600 (Physical Electronics) XPS Spectrometer. Raman spectrum of powder samples were recorded on LabRAM HR Raman microscope with a laser excitation wavelength of 633 nm. Samples were dispersed on Si (100) wafer with Si Raman mode at 520 cm$^{-1}$ as reference.

**Electrochemical Studies.** The measurements process is similar to that of MoS2/graphene described detailed in the previous report$^5$ for comparison. MoSe2 and MoSe2/RGO electrode fabrication: 4mg catalysts(MoSe2 or MoSe2/RGO) was suspended in stock solution containing 0.8mL deionized $\text{H}_2\text{O}$, 0.2mL ethanol and 80 $\mu$L nafion solution (5%) by ultra-sonication for 30
min to form a homogeneous ink. Then 5 μl of the catalyst ink was drop-casted on rotating glassy carbon electrode of 2 mm in radius (loading ~ 0.16 mg/cm²) for air drying.

For testing durability, MoSe₂/RGO catalyst was loaded onto FTO electrode. The 11 μl of the catalyst ink was drop-casted onto 0.283cm² FTO electrode surface (loading ~ 0.156 mg/cm²), air-dried and subsequently dried in a vacuum oven for hours before use. By doing so, we obtained a MoSe₂/RGO/FTO electrode with a similar mass catalyst loading to that of the catalyst on carbon glassy electrode.

Electrochemical analysis was done using a CHI660B. Three electrodes configuration was employed. The working electrode was the glassy carbon electrode with MoSe₂ or MoSe₂/RGO on it (in stability test, the working electrode was FTO electrode with MoSe₂/RGO on it), the reference electrode was saturated calomel electrode and the counter electrode was a graphite rod. Linear sweep voltammetry (using the pontentiostat from CH Instruments) with scan rate of 5 mVs⁻¹ was conducted in 0.5 M H₂SO₄. In all measurements, we used saturated calomel electrode (SCE) as the reference. It was calibrated with respect to reversible hydrogen electrode (RHE). The calibration was performed in the high purity H₂ saturated electrolyte with a Pt wire as the working electrode. CVs were run at a scan rate of 1 mV s⁻¹, and the average of the two potentials at which the current crossed zero was taken to be the thermodynamic potential for the hydrogen electrode reactions. In 0.5 M H₂SO₄, E (RHE) = E (SCE) + 0.271 V. All the potentials reported in our manuscript are against RHE.
Figure S1. MoSe$_2$ nano-flowers before thermal annealing. (A) SEM image of the MoSe$_2$ nano-flowers. (B) TEM image showing that MoSe$_2$ nano-flowers are composed by ultra-thin nanosheets. (C) HRTEM image showing the side of nanosized MoSe$_2$ with few layers. The MoSe$_2$ nano-flowers are of partial crystallinity (as shown in white circle) with amorphous part
(in black circle). (D) HRTEM image showing the center of nano-size MoSe$_2$, which demonstrate typical folded edges with (002) plane of 2H-MoSe$_2$. (E) XRD pattern shows broad peaks with maxima approximately locating at (002), (004), (100) and (110) of 2H-MoSe$_2$. The broad peaks indicates it is of poor crystalline. (F) Raman spectrum of MoSe$_2$ nanosheets. A$_{1g}$ and E$_{2g}^1$ modes of 2H-MoSe$_2$, which should been in the range 240-290 cm$^{-1}$, cannot be detected, while replacing by a broad Raman mode peak. This indicates poor crystalline of MoSe$_2$.

Figure S2. XPS of MoSe$_2$ nanosheets before ( ) and after annealing ( ). (A) Survey spectrum. (B) High resolution C 1s spectrum. (C) High resolution Mo 3d spectrum. (D) High resolution Se 3d spectrum. The small amount of carbon in pure MoSe$_2$ is resulting from precursor or
contaminants during experiment process from environments. To the amorphous sample directly from hydrothermal reaction, the 3d peak of Se is not so well split and molybdenum is in its mix states.
Figure S3. MoSe$_2$/RGO hybrids (sample 2: C: Mo: Se=77:1:1.5) (A) SEM image of the MoSe$_2$/RGO hybrids. (B) TEM image showing the morphology of MoSe$_2$/RGO hybrids. (C) HRTEM image showing MoSe$_2$ nanosheets sparsely stacking on a RGO. (D) HRTEM image showing the density of MoSe$_2$ nanosheets is a little higher on the side of RGO. (E) XRD pattern and (F) Raman spectrum of the hybrid. No MoSe$_2$ XRD and Raman mode peak can be detected for its ultra-low content.
Figure S4. MoSe$_2$/RGO hybrids (sample 3: C: Mo: Se=5:1:2) (A) SEM image and (B) TEM image showing that three kinds of products: MoSe$_2$/RGO hybrids, free MoSe$_2$ nanoparticles and large hexagonal platelets. (C) TEM image of MoSe$_2$/RGO hybrids. Large MoSe$_2$ can be detected in white circle. (D) HRTEM image showing MoSe$_2$ basal plane on a RGO. (E) HRTEM image
showing the hexagonal MoSe$_2$ nanosheets are near to completely cover on surface of RGO. (F) TEM image of pure MoSe$_2$ nano-flowers. (G) HRTEM image showing ultra thin MoSe$_2$ nanosheets with folded edges. (H) HRTEM image showing the center of MoSe$_2$ nanoflowers which were also composed by few layers nanosheets. (I) TEM image of large MoSe$_2$ hexagonal nanoplatelets. (J) HRTEM image showing the side of MoSe$_2$ hexagonal platelets indicating that actually MoSe$_2$ still grows on RGO. Inset is the diffraction pattern which indicates that MoSe$_2$ are single crystal. (K) HRTEM image showing center of MoSe$_2$ nanoplatelets. Inset is the diffraction pattern which indicates it is high quality single crystal. (L) XRD pattern demonstrates it maintains 2H-MoSe$_2$. (M) Raman spectrum of the hybrid.
Figure S5. XPS of MoSe$_2$/RGO hybrids (C: Mo: Se = 13:1:2; C: Mo: Se = 5:1:2; C: Mo: Se = 77:1:1.5). (A) Survey spectrum. (B) High resolution C 1s spectrum. (C) High resolution Mo 3d spectrum. (D) High resolution Se 3d spectrum.

Fig S6. Electrochemical measurements in a cathodic potential window. (A) Polarization curves and (B) corresponding tafel plots recorded on glassy carbon electrodes with a catalysts loading of 0.16 mg/cm$^2$. Conditions: potential scan rate of 5 mV s$^{-1}$, electrode rotating rate of 2400 rpm.

Pure MoSe$_2$, MoSe$_2$/RGO (C: Mo: Se = 13:1:2), MoSe$_2$/RGO (C: Mo: Se = 77:1:1.5), MoSe$_2$/RGO (C: Mo: Se = 5:1:2)

In sharp contrast, MoSe$_2$/RGO hybrids (sample 1: C:Mo: Se = 13:1:2) exhibited even lower onset potential at 0.0.05 V vs. RHE with a tafel slope close to ~69 mV per dec. On one extreme, to the MoSe$_2$/RGO hybrids with C:Mo: Se =77:1:2, onset potential is a little increased to ~0.06 V and tafel slope to ~85 mV/decade; in the other extreme, to the final product with mole ratio C: Mo: Se =5:1:2, where the products include MoSe$_2$ grown on RGO, free MoSe$_2$ and large single crystal MoSe$_2$/RGO heterojunction platelets, the onset potential is increased to ~0.075 V vs. RHE and the tafel slope ~91 mV/decade, approaching those of the pure MoSe$_2$ nano-flowers.
The variance of HER properties of in MoSe$_2$/RGO hybrids are close related to their morphologies and structures and further decided by the growth mechanisms$^1$: At low supersaturations of precursor as sample 2, heterogeneous nucleation of MoSe$_2$ nanosheets on GO is predominant. The resulting MoSe$_2$ content is low, and only few nanoparticles formed on RGO with limited active edges contributing to hydrogen generation. When effective content increased, the nanosheets on RGO began to grow up with relative large size and the density was also increased, which all increase the amount of active edges and therefore contributing to overpotential and tafel slope. However, when the precursor content is further increased and at high supersaturations, the homogeneous nucleation, which is the up-limit of heterogeneous nucleation works together with heterogeneous nucleation. Pure MoSe$_2$ nanoparticles can form altogether with MoSe$_2$/RGO hybrid. And the HER property is close to pure MoSe$_2$. 

![Graphs showing HER properties of Pure MoSe$_2$, MoSe$_2$/RGO (C:Mo:Se=12:1:2), MoSe$_2$/RGO (C:Mo:Se=77:1:1.5), and MoSe$_2$/RGO (C:Mo:Se=5:1:2).]
Figure S7. Catalyst stability tests for MoSe$_2$ (A) and MoSe$_2$/RGO (B: C: Mo: Se=13:1:2; C: C: Mo: Se=77:1:1.5; D: C: Mo: Se=5:1:2), in which HER currents are maintained after 50 cycles in the cathodic potentials windows.

**Computational Methods**

The density functional theory calculations have been performed using RPBE2 functional as implemented in VASP package. The cutoff energy for the plane wave basis was 420 eV. All atoms were relaxed until the Hellmann-Feynman forces acting on them were below 0.02 eV/Å. A slab model is employed to calculate the hydrogen adsorption energies, which consisting of four Mo atoms in x-direction and six Mo atoms in y-direction based on previous study. The lattice constant of MoSe$_2$ has been determined to be 3.347Å and compares well with the experimental lattice constant of 3.299Å. The unit cell dimension in x-direction is 13.388 Å, in y-direction 25Å and in z-direction 18Å. A 4×1×1 Monkhorst-Pack k-point mesh is used for the Brillouin zone sampling. The stability of hydrogen can be described by the differential hydrogen adsorption energy $\Delta E_H$ which is calculated as follows:

$$
\Delta E_H = E(\text{MoSe}_2+n\text{H}) - E(\text{MoSe}_2+(n-1)\text{H}) - 1/2 E(\text{H}_2)
$$

Where $E(\text{MoSe}_2+n\text{H})$ is the total energy for the MoSe$_2$ slab system with $n$ hydrogen atoms adsorbed on the edge, $E(\text{MoSe}_2+(n-1)\text{H})$ is the total energy for $(n-1)$ hydrogen atoms adsorbed on the edge and $E(\text{H}_2)$ is the energy for a hydrogen molecule in the gas phase. The differential hydrogen binding energy describes the energy needed to increase the coverage by one hydrogen atom. The slab models with different hydrogen coverages 25% (S1), 50% (S2), 75% (S3) and 100% (S4) are shown in Figure S8. The differential binding energy is defined such that the value for 50% indicates, how much energy is required to increase the coverage from 25% to 50%, and similar for the other coverages. The calculated results show -0.646 eV for 25%, -0.613 eV for 50%, -0.389eV for 75% and 0.045eV for 100%. Based on these energies we calculate the Gibbs free energy for hydrogen adsorption as

$$
\Delta G_{H^0} = \Delta E_H + \Delta E_{ZPE} - T \Delta S_H
$$
Where \( \Delta E_H \) is the differential hydrogen chemisorption energy from formula (1), \( \Delta E_{ZPE} \) is the difference in zero point energy between the adsorbed state and the gas phase and \( \Delta S_H \) is the entropy difference between the adsorbed state and the gas phase. The entropy of hydrogen adsorption is taken as \( \Delta S_H \approx \frac{1}{2} S_{H_2}^0 \) where \( S_{H_2}^0 \) is the entropy of \( H_2 \) (2179.3 cm\(^{-1}\) for \( H_2 \) taken from Ref. 6.) in the gas phase at standard conditions. The calculated vibrational frequencies of \( H \) adsorbed on MoSe\(_2\) are 2283 cm\(^{-1}\), 406 cm\(^{-1}\) and 348 cm\(^{-1}\) for MoSe\(_2\) slab with 25% H coverage, 2263 cm\(^{-1}\), 532 cm\(^{-1}\) and 439 cm\(^{-1}\) for MoSe\(_2\) slab with 50% H coverage, 2182 cm\(^{-1}\), 436 cm\(^{-1}\) and 294 cm\(^{-1}\) for MoSe\(_2\) slab with 75% H coverage, 2161 cm\(^{-1}\), 559 cm\(^{-1}\) and 379 cm\(^{-1}\) for MoSe\(_2\) slab with 100% H coverage. Thus we obtain \( \Delta G_H^0 = \Delta E_H + 0.256 \text{ eV for 25\%,} +0.268 \text{ eV for 50\%,} +0.249 \text{ eV for 75\%,} +0.26 \text{ eV for 100\%.} \) After correction, the differential binding free energies are -0.39 eV for 25\%, -0.344 eV for 50\%, -0.14 eV for 75\% and 0.305 eV for 100\%. The free energy closest to thermoneutral is -0.14 eV, which describes the coverage at 75\%. It is most likely that the hydrogen evolution is mainly driven by hydrogen adsorption at these two coverages.

![Figure S8](image-url)  
Figure S8. The optimized geometry of MoSe\(_2\) slab system with different hydrogen coverages: 25\%(S1), 50\%(S2), 75\%(S3) and 100\%(S4). The H, Mo and Sn atoms are represented by the white, green and yellow balls, respectively.

To check the reliability of the above methods, test calculations have been performed for MoS\(_2\) system. The lattice constant of MoS\(_2\) has been determined to be 3.207 Å and compares well with the experimental lattice constant of 3.16 Å\(^4\) and calculated result 3.235 Å\(^3\). The differential hydrogen binding energies are -0.557 eV for 25\%, -0.475 eV for 50\%, 0.068 eV for 75\% and 0.66 eV for 100\%. After correction by equation (2), we obtain the differential binding
free energies -0.32eV for 25%, -0.231 eV for 50%, 0.307eV for 75% and 0.909 eV for 100%. The free energy closest to thermoneutral is -0.231 eV, which corresponds to coverage at 50%. Therefore, it is most likely that the hydrogen evolution is mainly driven by hydrogen adsorption at these two coverages. This is acceptable qualitative agreement with the literature [ref 3] which ensure the reliability of methods and results here.

The calculation results of MoSe$_2$ and MoS$_2$ using same methods provide us the opportunities to compare the HER catalytic activities. The Gibbs free energy for atomic hydrogen adsorption (DGH) on MoSe$_2$ edges is closer to thermoneutral than that of MoS$_2$, with an H coverage is about 75% on the edge under operating conditions, also higher than that of MoS$_2$ as reported before. The consistence of experiments and calculation indicate that MoSe$_2$ has potential to be a better HER catalyst than MoS$_2$.

Reference


