Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information for

Polymer-confined Growth of Perforated $MoSe_2$ Single-crystals on N-doped Graphene toward Enhanced Hydrogen Evolution

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Materials Preparation and Characterization

Chemicals Graphite (Grafguard with the average particle size of 350 mm) was expanded by microwave before use. $K_2S_2O_8$, P_2O_5, Concentrated H_2SO_4 (98%), $KMnO_4$, H_2O_2, acrylamide (AM), $(NH_4)_6Mo_7O_{24}$, Selenium powder (99.99%), 2-propanol, Nafion, 2-hydroxy-2-methylpropiophenone (photo initiator, PI) were all purchased from Sigma-Aldrich with analytical grade and used without further purification. Throughout the whole process, deionized (DI) water was used.

Preparation of macroscopic graphene oxide (GO) The graphene oxide was prepared by a modified Hummers method, which was reported by our previous work.[1] In brief, firstly, 30 mL concentrated sulfuric acid was added to a flask containing 1 g graphite, 5 g $K_2S_2O_8$ and 5 g P_2O_5, reacted at 90℃ for 4.5 h. Then the product was filtered through a 0.2 micron Nylon Millipore filter and washed with excess DI until the pH is around 5.5. After drying the sample at 60℃ for 3 h, 150 mL concentrated sulfuric acid and 30 g $KMnO_4$ were added slowly into a 250 mL flack at 0℃, then reacted at 35℃ for 4 h. Thirdly, add the mixture to 1 L DI water, stirring for another 2 h. Finally, 50 mL 30% H_2O_2 was added to the solution slowly until the solution turns bright yellow. The solution was stirred for another 2 h, and then settled for 24 h. After discarding the supernatant, 1 L of 10% HCl solution and excess deionized water were used to wash the product until the pH is ~7.

Synthesis of PAM grafted macroscopic GO (GO-PAM) The PAM modified GO was prepared following our recent work.[2] Briefly, the freshly prepared GO (25 mg), acrylamide (AM) (50 mg), and 2-hydroxy-2-methylpropiophenone (50 μl) were mixed in 30 ml DI water and stirred for 30 min to disperse homogeneously. The resultant mixture was deoxygenated by bubbling high purity N_2 for 30 min and then exposed under UV light (365 nm, 1.350 W cm^{-2}) for 10 min. After UV-assisted polymerization, the functionalized GO was purified by cycling centrifugation/DI re-dispersion for three times.

Preparation of low, medium and high density of $MoSe_2$ nanosheets on N-doped graphene (Pristine $MoSe_2$/NG) and the control samples (Graphene, N-doped graphene and bulk $MoSe_2$) For the high density of pristine $MoSe_2$/NG, first add 15 mg $(NH_4)_6Mo_7O_{24}$ into the as-prepared aqueous solution containing 40 mg GO-PAM, stirring overnight to reach adsorption equilibrium, then purified by cycling centrifugation/DI water re-dispersion for three times. After freeze drying, we can get the yellow powder(GO-PAM-$(NH_4)_6Mo_7O_{24}$), then annealing in the furnace at 300℃ in 100 sccm Ar condition for 60 min to obtain the black powder (MoO_3/NG, here "NG" denotes nitrogen doped graphene). 20 mg MoO_3/NG and 20 mg Se powder were placed in the silica tube (*note that MoO_3/NG was placed at the open side of tube, and the Se was put at the closed end of tube, as seen in Scheme 1 in the main text*), then heat up from room temperature to 750℃ by 25℃/min and keep for 60 min, 50 sccm Ar and 10 sccm H_2 were applied as growth environment, then cool down naturally to obtain black powder (Pristine $MoSe_2$/NG). Low and medium density of pristine $MoSe_2$/NG were obtained by controlling $(NH_4)_6Mo_7O_{24}$ input in the first step, *i.e.* 5 mg for the low density, 10 mg for the medium density of pristine $MoSe_2$/NG. For fair comparison, we also annealed the pristine $MoSe_2$/NG at 900℃ in Ar gas but without H_2. For the control samples, we calcined GO-PAM and GO in the same condition to obtain N-doped graphene (NG) and graphene (G), respectively. For the bulk $MoSe_2$, we replaced the MoO_3/NG by pure MoO_3 powder, repeated the same selenidation process to obtain flower-like bulk $MoSe_2$ particles.

Preparation of H_2-etched $MoSe_2$ nanosheets on N-doped graphene (Perforated $MoSe_2$/NG) Briefly, 20 mg prepared pristine $MoSe_2$/NG powder was placed in the furnace, heat up to 900℃ by 25℃/min and keep for 30 min, 100 sccm Ar and 40 sccm H_2 were applied as etching environment, then cool down naturally to obtain perforated

$MoSe_2$/NG.

Electrode preparation and electrochemical measurement In order to remove the insecure and exposed metal particles, all the synthesized products were pretreated in 0.5 M H_2SO_4 for 5h followed by filter washing and freeze drying process. Electrochemical measurements were performed with an electrochemical workstation (CHI 760C, CH Instruments Inc.) in a 0.5 M H_2SO_4 aqueous solution. Ag/AgCl electrode (saturated KCl) and a platinum wire were used as the reference and counter electrode, respectively. Typically, 10 mg of the catalyst powders was dispersed in 2.5 mL of a 4:1 (v:v) water/2-propanol mixed solvents along with 10μL of Nafion solution, and the mixture was sonicated for 60min. Then, 25μL of the above solution was drop-cast onto the surface of a glassy carbon (GC) disk electrode at a catalyst loading of 0.5 mg/cm^2. For the other control samples, like graphene, N-doped graphene and bulk $MoSe_2$, the mass loading was kept as same as 0.5 mg/cm^2. Polarization curves were acquired by sweeping the potential from -0.1 to -0.6 V (vs Ag/AgCl) at a potential sweep rate of 10 mV/s. All polarization curves were iR-corrected. Accelerated stability tests were performed in 0.5 M H_2SO_4 at room temperature by potential cycling between -0.1 to -0.6 V (vs Ag/AgCl) at a potential sweep rate of 100 mV/s for a given number of cycles. Current−time responses were operated by chronoamperometric measurements. The pH durability of catalyst was processed in different electrolyte media (0.5M H_2SO_4, 1M PBS and 1M KOH). In all measurements, the Ag/AgCl reference electrode was calibrated with respect to a reversible hydrogen electrode (RHE). The electrochemical impedance spectroscopy (EIS) was carried out in the range from 100 K to 0.01 Hz with an AC amplitude of 10 mV. All the experiments were processed at room temperature.

Characterization High-resolution transmission electron microscopy (TEM, JEOL 2010) and Scanning Electron Microscope (SEM, JEOL 6390) were applied to characterize the overall morphology and distribution of catalyst. The chemical composition and elemental valence states were characterized by X-ray photoelectron spectroscopy (XPS, PHI 5600). To characterize the crystal structure, XRD (PW1830, Philips) with Cu Karadiation (λ=1.5406 Å) is used. The Raman spectrum was recorded with a Renishaw Raman RM3000 scope using a 514 nm excitation argon laser. Inductively coupled plasma-optical emission spectrometer (ICP-OES, Varian 725-ES). Thermogravimetric analysis (TGA) was processed in air from room temperature to 700℃ with heating speed of 10℃/min.

Turnover frequency (TOF) calculation For $MoSe_2$/NG sample, here firstly we ignore the HER activity of N-doped graphene and regard the edge of $MoSe_2$ nanosheets as the main sites for HER. The exchange current per site was determined by the slope of the linear curve of exchange current density ($\mu A/cm^2_{geometric}$) versus edge length ($\mu m_{MoSe2\text{-}edge}/\mu m^2_{geometric}$) from Figure 5f in the main text, resulting 1.70×10^{-16} $A/nm_{MoSe2\text{-}edge}$ and R^2 value of 0.97. The Mo-Mo and Se-Se distance in $MoSe_2$ are 0.546 nm,[3] which means (1/0.546) site/$nm_{MoSe2\text{-}edge}$. This yields 9.20×10^{-17} A/site. This value was multiplied by the site density of Pt (1.50×10^{15} sites/cm^2) for fair comparison, results in 0.138 A/cm^2. In our case, we drop-casted $MoSe_2$/NG on the glass carbon electrode, the mass density of $MoSe_2$/NG is 4.67 g/cm^3, and the mass loading is 0.5 mg/cm^2, so the average thickness is around 107 μm, assume that each $MoSe_2$/NG layer is ~100 nm and each $MoSe_2$ domain has ~10 layers sheets of $MoSe_2$ single crystals. So that for each single layer $MoSe_2$, the current density should be $0.138/(107000/100)/10 = 1.29 \times 10^{-6}$ A/cm^2 as i_0. Then the TOF is calculated by using the following formula[4]:

$TOF_{MoSe2}\ (s^{-1}) = (i_0,\ A/cm^2) / [(1.5\times10^{15}\ sites/cm^2)\ (1.602 \times 10^{-19}\ C/e^-)\ (2\ e^-/H_2)]$

Table S1. Selected summary of the HER performance of $MoSe_2$-based electrocatalysts in 0.5 M H_2SO_4, and compared with our work.

Catalyst	***Synthesis Method***	***Current Density j (mA cm^{-2})***	***Overpotential at j (mV)***	***Tafel slope (mV dec^{-1})***	***Exchange Current Density (μA cm^{-2})***	***Ref.***
HD-p$MoSe_2$/NG	**Wet-chemical & CVD**	**-10**	**106**	**57**	**127.4**	***Our work***
		-20	**126**			
		-50	**165**			
		-100	**197**			
$MoSe_2$ film	Wet-chemical	-10	~250	80	0.01	*ACS Catalysis, **2014**, 4, 2866-2873.*
$MoSe_2$/rGO	Hydrothermal	-20	~200	101	-	*J. Mater. Chem. A, **2014**, 2, 360-364.*
		-40	~275			
$MoSe_2$/Carbon paper	CVD	-10	~250	59.8	1.3	*Nano letters, **2013**, 13, 3426-3433.*
$MoSe_2$/G	CVD	-10	159	61	-	*Small, **2015**, 11, 414-419.*
$MoSe_2$/Carbon Cloth	Electrophoresis Deposition	-10	220	76	15.3	*Scientific reports, **2016**, 6, 22516-22524*
$MoSe_2$	Exfoliation	-10	360	~65	-	*ACS nano, **2014**, 8, 12185-12198.*
$MoSe_2$/C	Hydrothermal	-10	179	62	-	*ACS applied*

arbon fiber						*materials & interfaces,* ***2016****, 8, 7077-7085.*
CNT@ MoSe$_2$	Solvothermal	-10	178	58	-	*Nanoscale,* ***2015****, 7, 18595-18602.*
MoSe$_{2\text{-}x}$ (x~0.47)	Reflux	-10	~100	98	-	*Nanoscale,* ***2014****, 6, 11046–11051.*
MoSe$_2$/rGO	Hydrothermal	-10	150	69	-	*J. Mater. Chem. A,* ***2014****, 2, 360–364.*
S-doped MoSe$_{2-x}$	Hydrothermal	-20	235	68	-	*Inorg. Chem. Front,* ***2015****, 2, 931-937.*

Supporting Figures

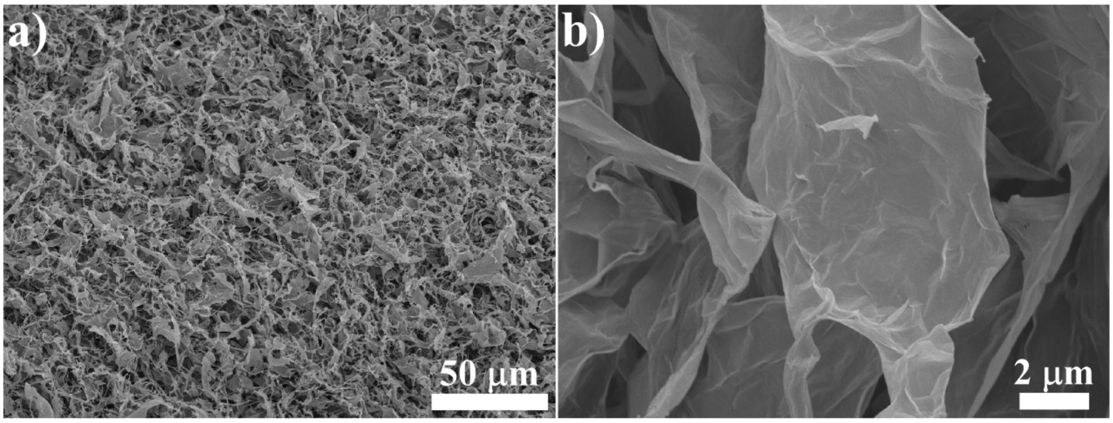


Figure S1. SEM images of polyacrylamide modified graphene oxide (GO-PAM). **a)** Low-magnification SEM image of GO-PAM. **b)** High-magnification SEM image of GO-PAM.

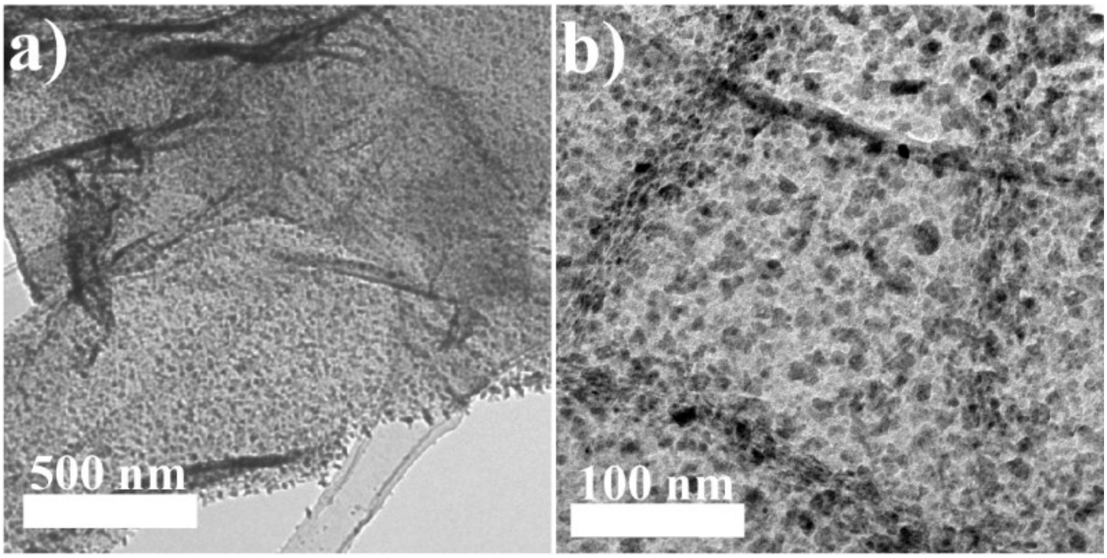


Figure S2. Morphology Characterization of MoO$_3$/NG. a) TEM image of surface of MoO$_3$/NG, MoO$_3$ nanopaticles are well-distributed on N-doped graphene sheet. b) High-resolution TEM image of MoO$_3$/NG.

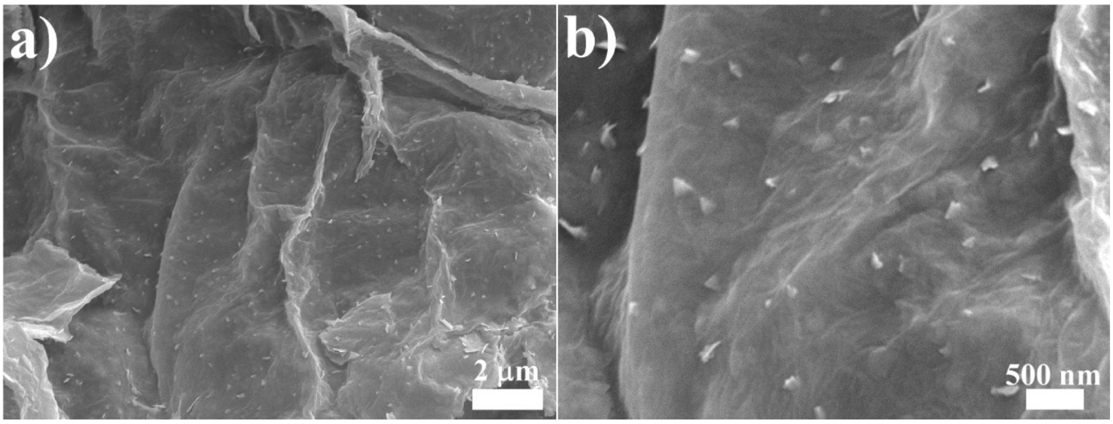


Figure S3. Morphology Characterization of High density $MoSe_2$ on N-doped graphene (HD-$MoSe_2$/NG). a) SEM image of surface of HD-$MoSe_2$/NG, triangular $MoSe_2$ nanocrystals are well-distributed on the graphene layer. **b)** High resolution SEM image of HD-$MoSe_2$/NG, the side length of $MoSe_2$ nanocrystals is ~150 nm.

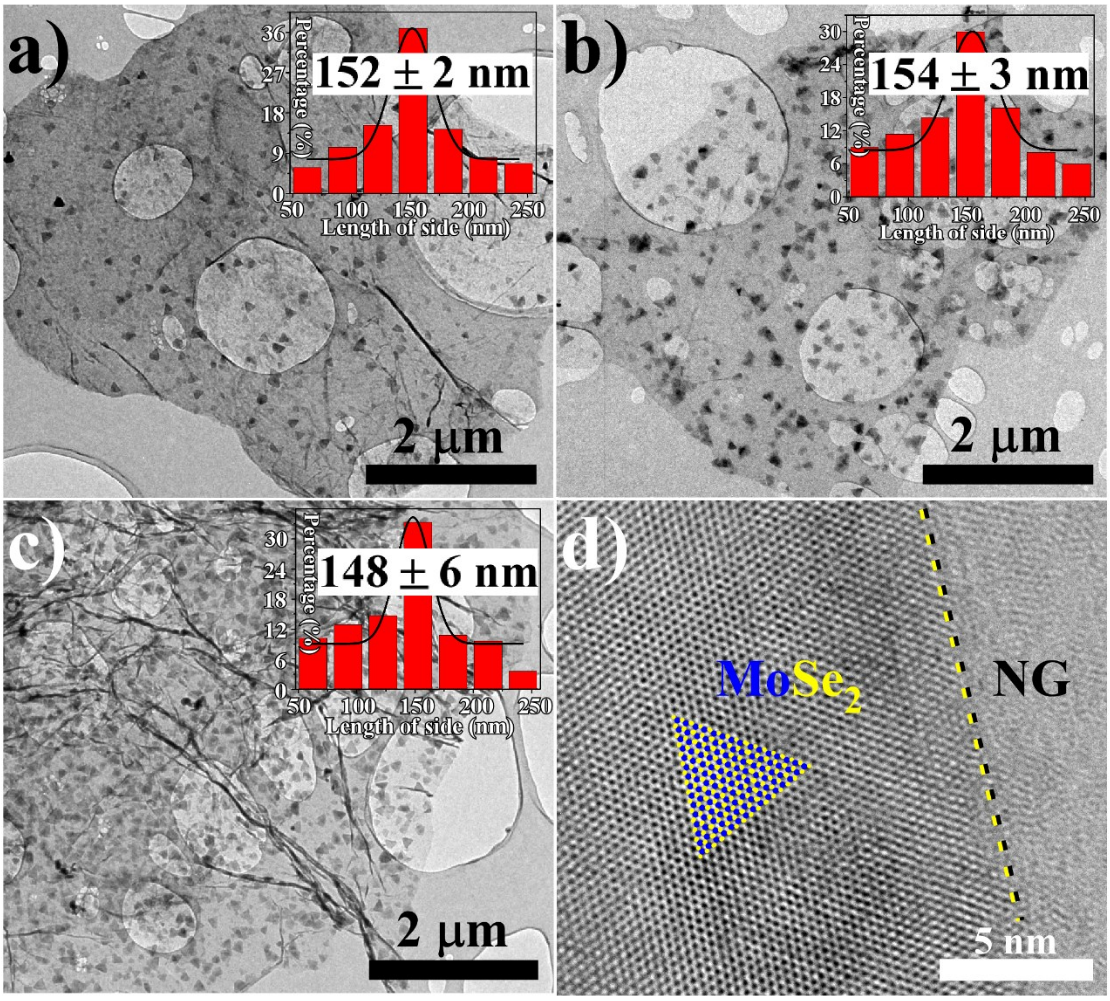


Figure S4. Transmission Electron Microscope (TEM) Characterization on $MoSe_2$/NG with Various Growth Density. a) Low, **b)** Medium and **c)** High density of pristine $MoSe_2$ on N-doped graphene sheet. Inset is the histograms of $MoSe_2$ edge length distribution for each TEM images: **a)** 152 ± 2 nm, **b)** 154 ± 3 nm, **c)** 148 ± 6 nm. **d)** A close-up view of boundary between $MoSe_2$ and N-doped graphene. The inset shows the hexagonal arrangement of Mo and Se atoms.

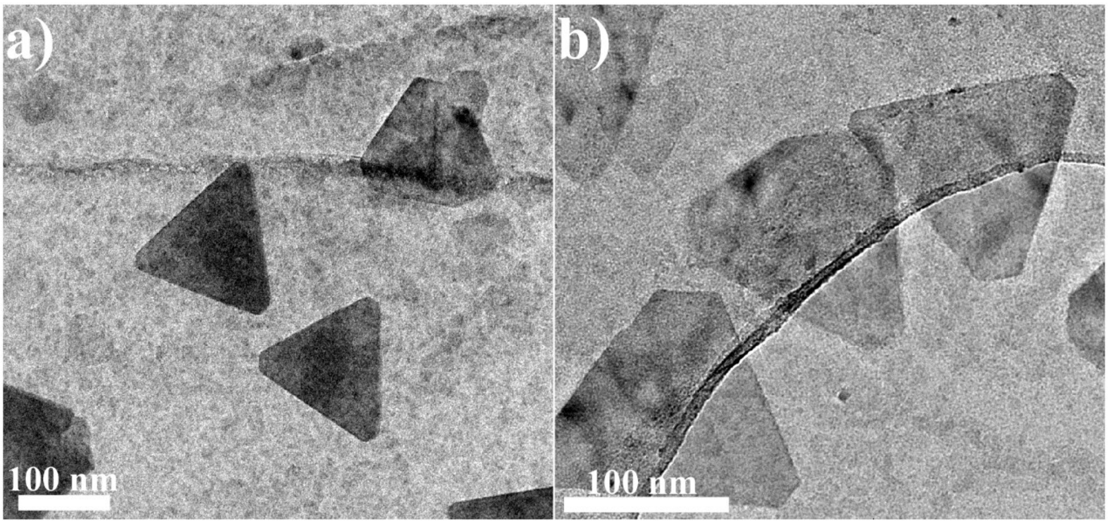


Figure S5. Additional High-resolution TEM images of Pristine MoSe$_2$/NG at different position a) and b).

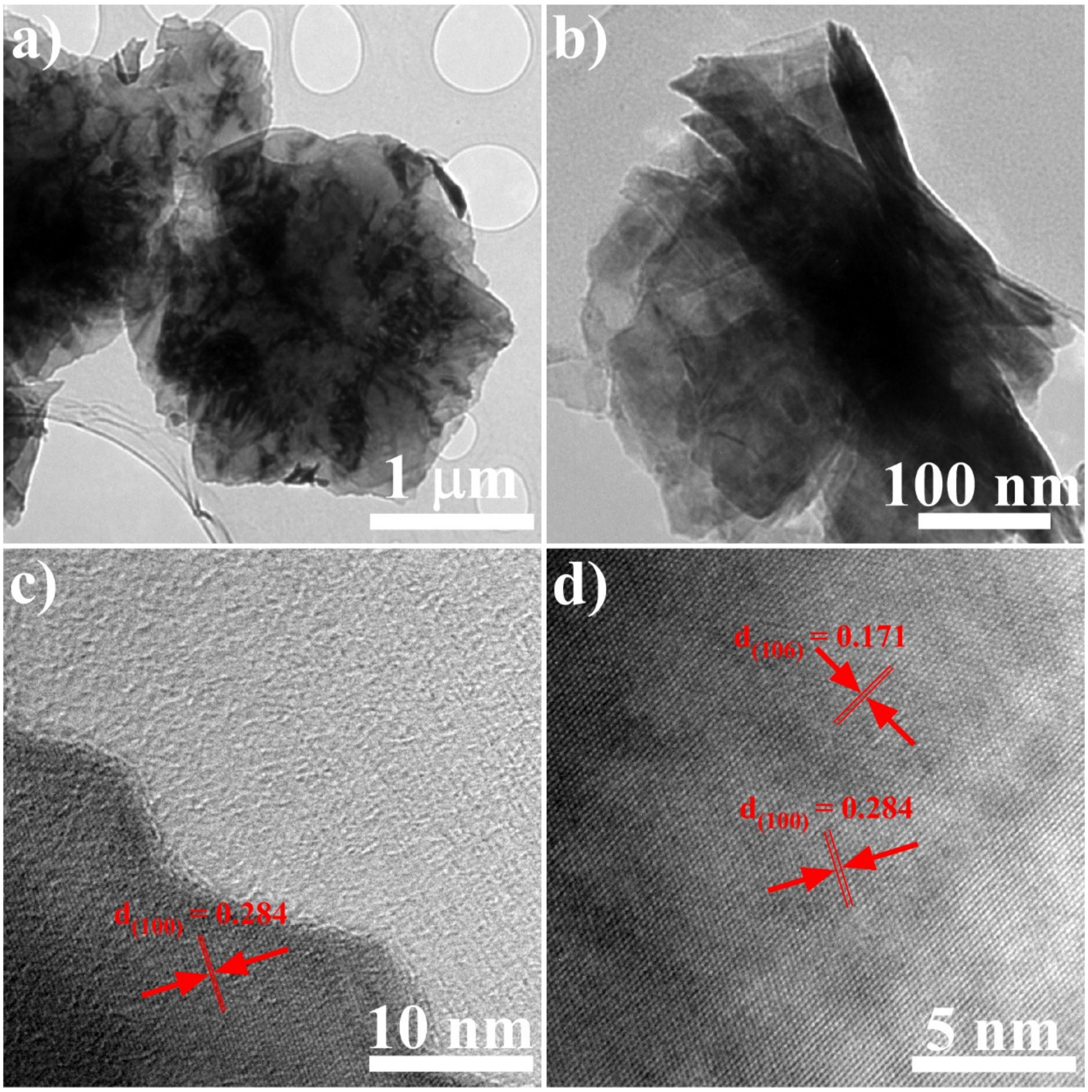


Figure S6. TEM images of flower-like bulk $MoSe_2$ particles. a) Top-down view and **b)** side view of bulk $MoSe_2$ flower. **c, d)** High-magnification TEM images of bulk $MoSe_2$ flower at different positions, indicating the uniform crystalline structure.

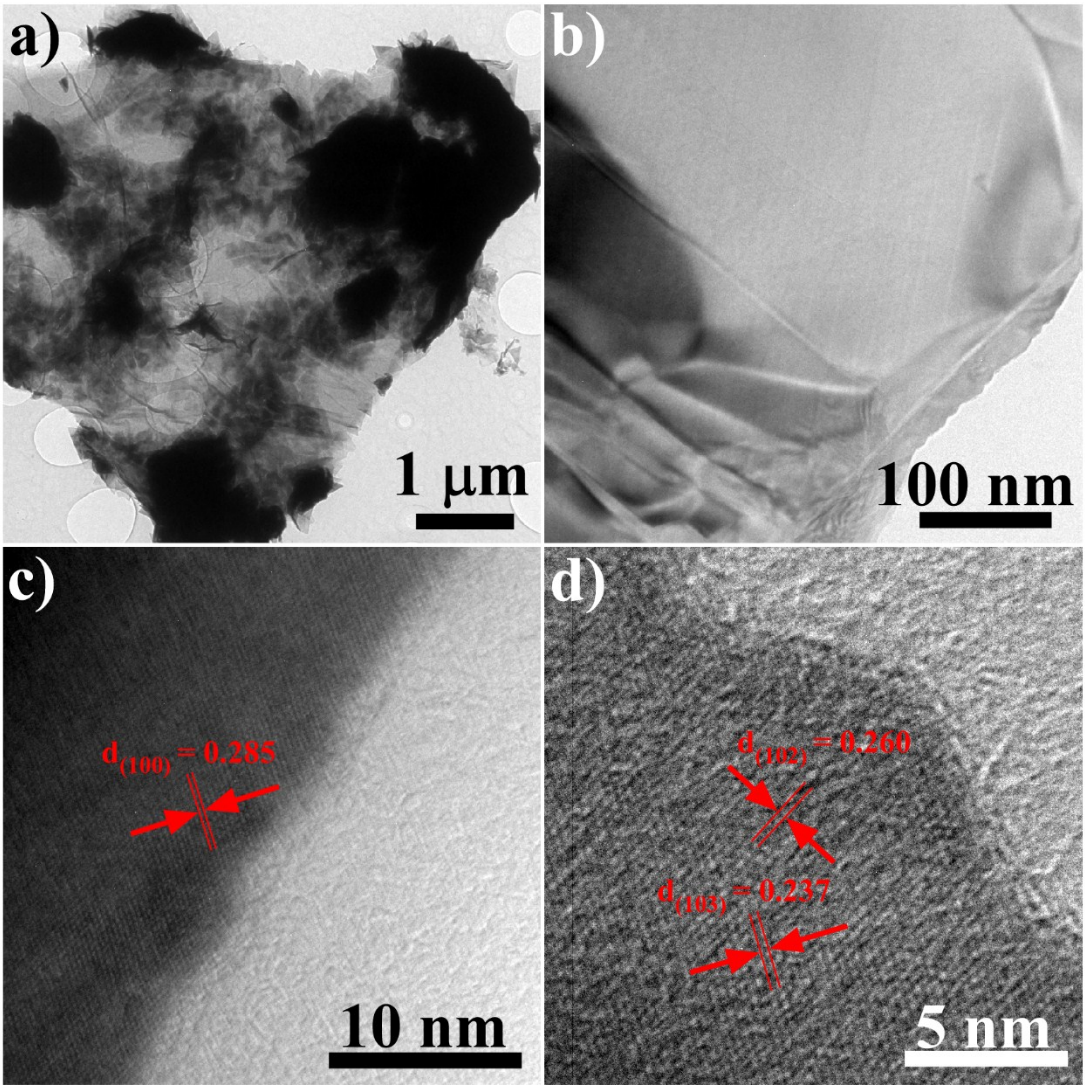


Figure S7. TEM images of control sample of $MoSe_2$/Graphene. a) Typical picture of $MoSe_2$/Graphene, the black particles are bulk $MoSe_2$. **b)** The close-up of bulk $MoSe_2$ sheet. **c, d)** High-magnification TEM images at different positions of bulk $MoSe_2$ sheet on graphene sheets.

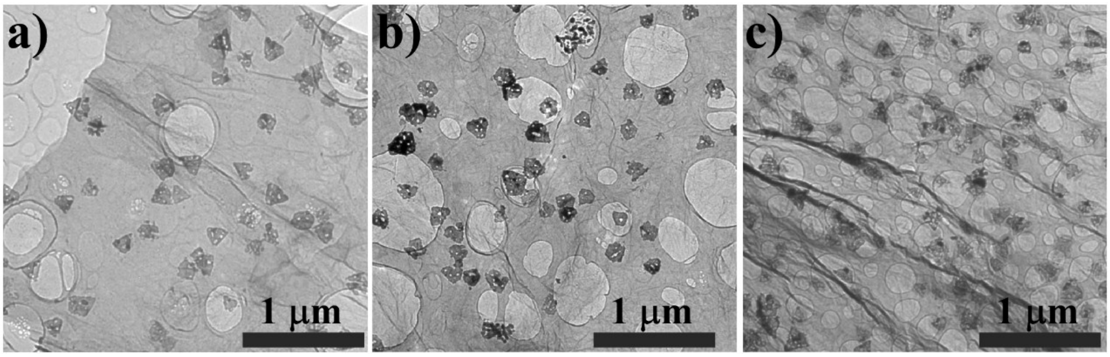
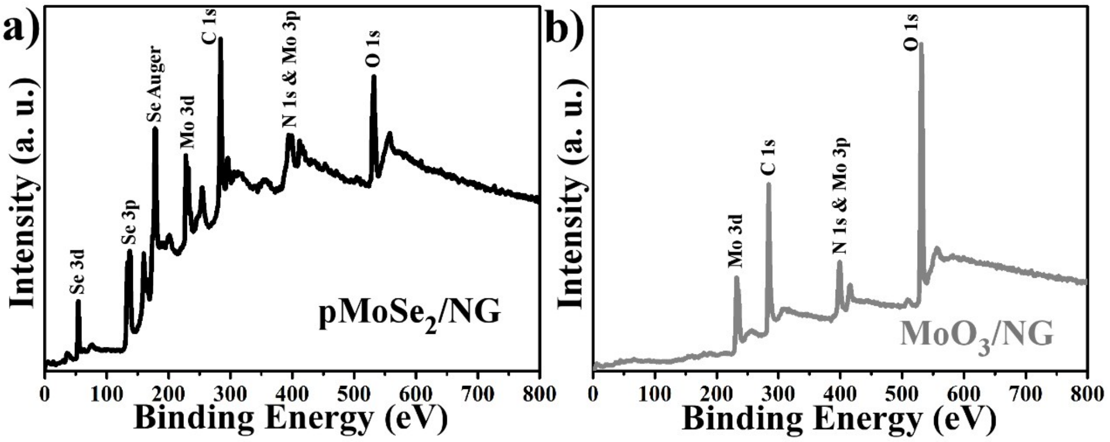


Figure S8. TEM Characterization on Perforated $MoSe_2$/NG with Various Growth Density. **a)** Low, **b)** Medium and **c)** High density of perforated $MoSe_2$ on N-doped graphene sheet after H_2 etching.



c)

Sample	Mo (wt%)	Se (wt%)	O (wt%)	C (wt%)	N (wt%)
pMoSe$_2$@NG	22.97	36.33	4.80	32.45	3.45
MoO$_3$@NG	24.87	0.00	31.45	37.94	5.74

Figure S9. XPS curves of High density perforated MoSe$_2$ on N-doped graphene (HD-pMoSe$_2$/NG) and MoO$_3$/NG. XPS spectrum of a) HD-pMoSe$_2$/NG and b) MoO$_3$/NG. c) Summary of the elemental mass loading in the composites derived from a) and b).

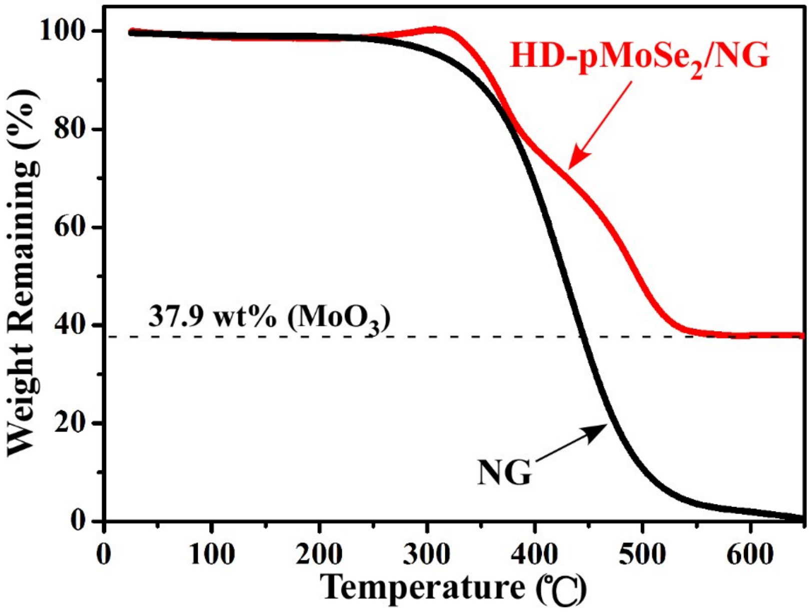


Figure S10. TGA curves of N-doped graphene (NG) and High density perforated $MoSe_2$ on N-doped graphene (HD-p$MoSe_2$/NG). The black and red curves represent NG and HD-p$MoSe_2$/NG, respectively. After 600 °C, N-doped graphene has been totally burned out. For the HD-p$MoSe_2$/NG sample, at low temperature (200-300 °C), the reaction "$2MoSe_2 + 7O_2 = 2MoO_3 + 4SeO_2$" happens, resulting in solid-state SeO_2 with a total weight increment. As the temperature reaches the sublimation temperature of SeO_2, i.e., 315 °C, SeO_2 starts to volatilize with the total weight decreasing, meanwhile, the N-doped graphene also starts to be oxidized into NO_x and CO_2, and after 600 °C, finally obtained 37.9 wt% of MoO_3 solid residue, so the $MoSe_2$ mass loading in HD-p$MoSe_2$/NG can be approximately calculated as 66.9 wt%.

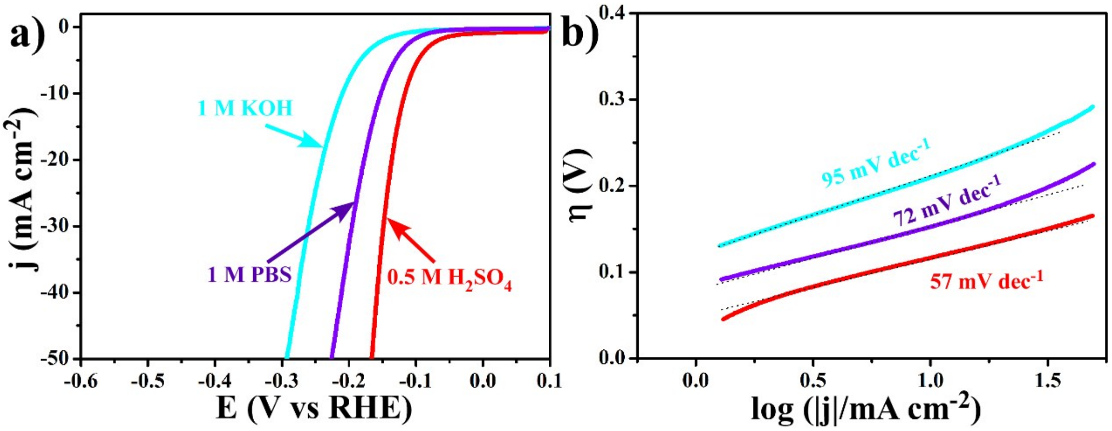


Figure S11. Characterization of the HER electrocatalytic activities of HD-pMoSe$_2$/NG in the electrolytes with different pH. a) The polarization curves of HD-pMoSe$_2$/NG modified cathodes in 0.5 M H_2SO_4, 1 M PBS and 1 M KOH media, respectively and **b)** corresponding Tafel plots of the data from a.

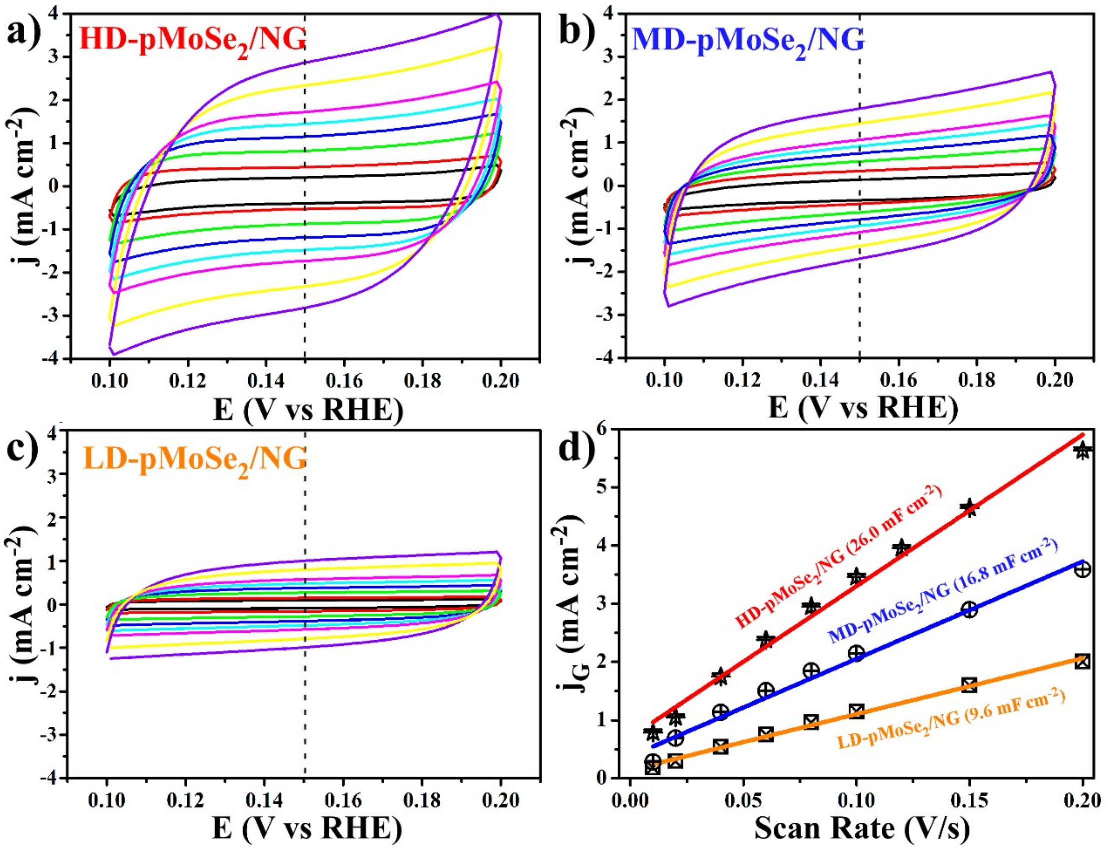


Figure S12. Electrochemical double-layer capacitances of perforated MoSe$_2$/NG with low, medium and high density. Cyclic voltammograms within the range of no faradiac reaction of **a)** HD-pMoSe$_2$/NG, **b)** MD-pMoSe$_2$/NG and **c)** LD-pMoSe$_2$/NG, scan voltage ranges from +0.1 V to +0.2 V (vs RHE), and scan rate from 0.01 to 0.2 V/s. **d)** Variation of double-layer charging currents at +0.15 V (vs RHE) as a function of scan rate. Symbols and solid lines are the experimental data from a-c) and the linear fit, respectively.

Reference

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