Supporting Information

Energy Level Modulation of MoS_2 Monolayers by Halide Doping for Enhanced Hydrogen Evolution Reaction

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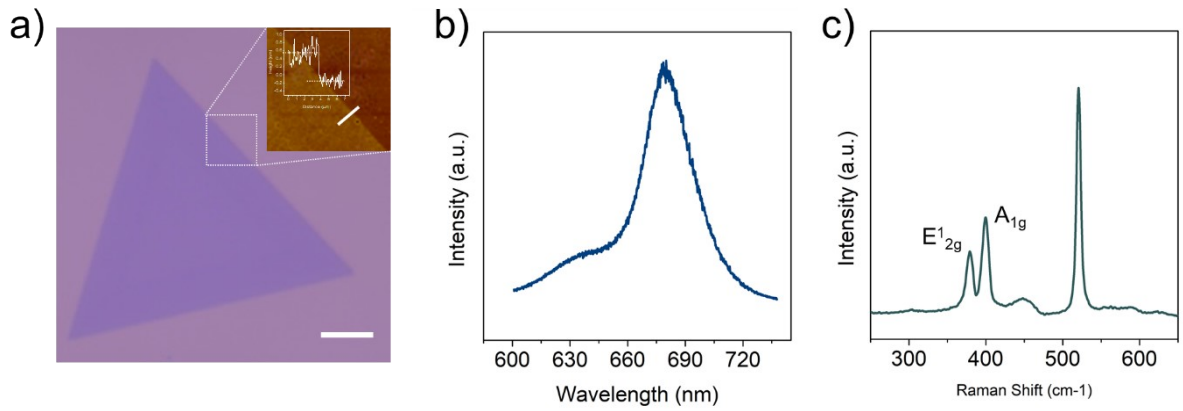

Figure S1. (a) Optical microscope image of CVD grown MoS_2. Inset, atomic force microscope mapping image and height profile. (b) Photoluminescence (PL) spectra and (c) Raman spectra of MoS_2 crystals. Scale bar: 20μm

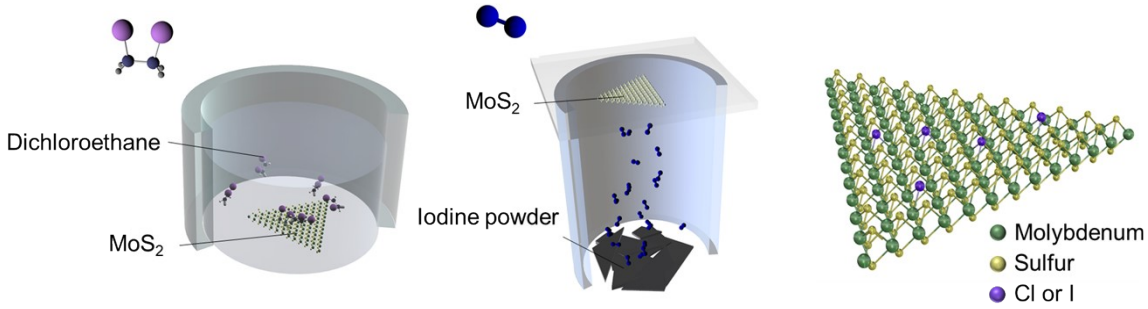

Figure S2. Schematics illustration of halide doping technique. Dichloroethane solution was used for chlorine doping and iodine powder were used for iodine doping, respectively.

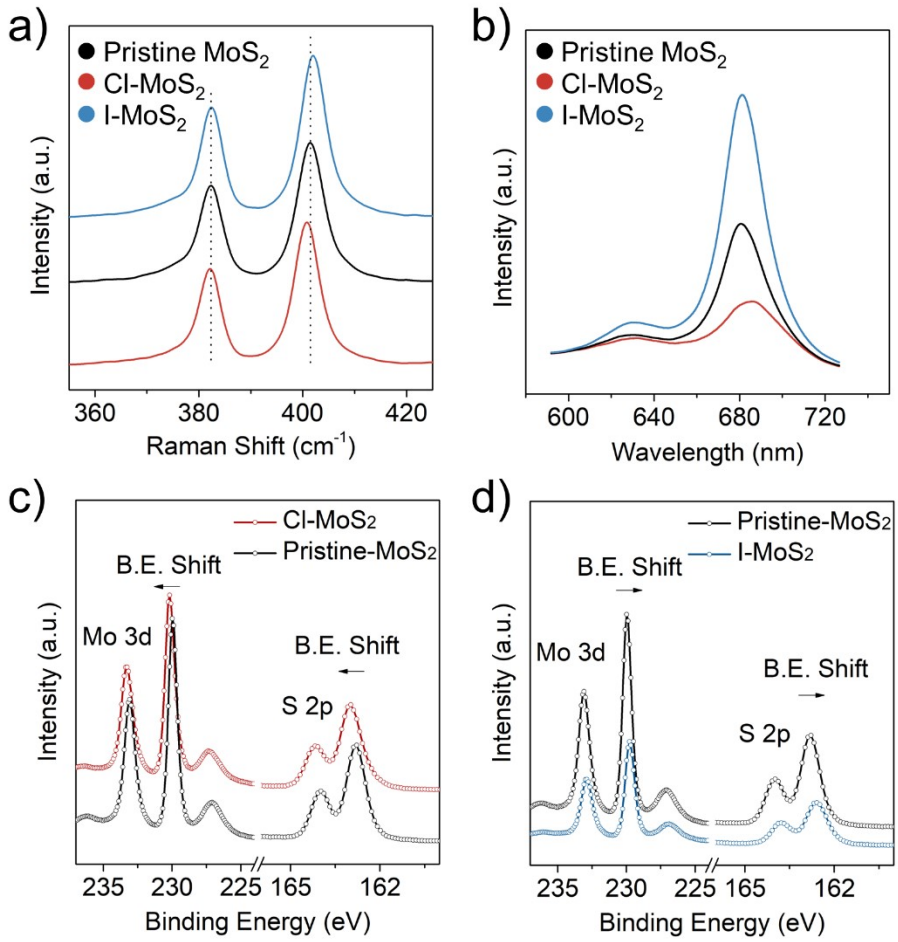

Figure S3. Raman, photoluminescence (PL) and X-ray photoelectron spectroscopy (XPS) measurements of MoS_2 monolayer halide doped with Cl and I. (a) Raman and (b) PL spectra of Cl and I-MoS_2 compared with pristine MoS_2 monolayers. (c) XPS spectra of Cl-MoS_2 and (e) I-MoS_2 compared with pristine MoS_2.

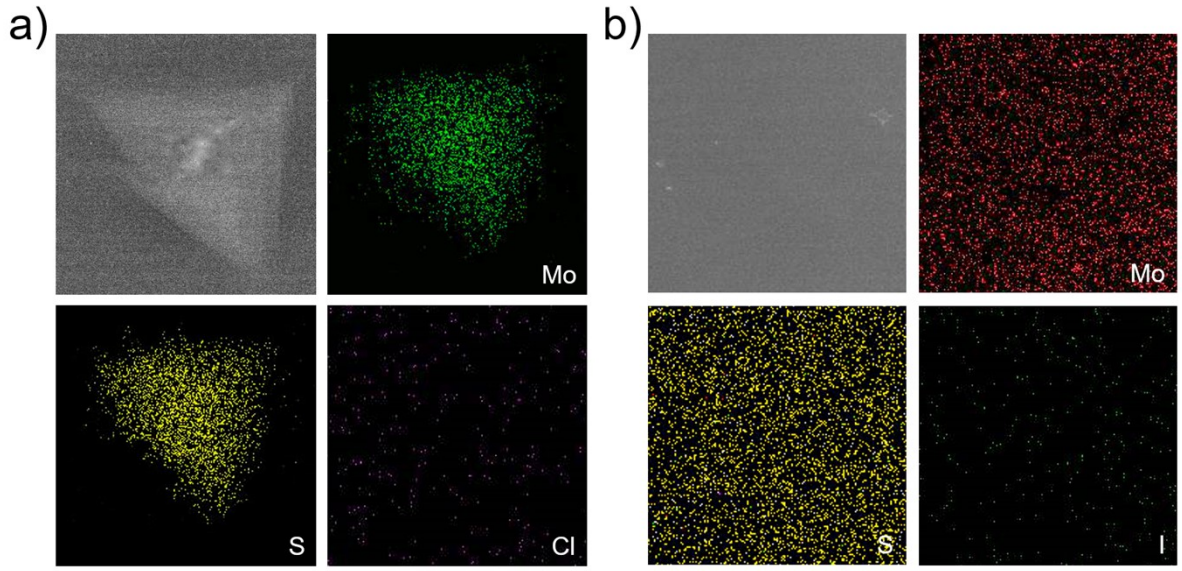

Figure S4. EDS mapping image of halide doped MoS_2. (a) Cl-MoS_2 and (b) I-MoS_2 EDS mapping images.

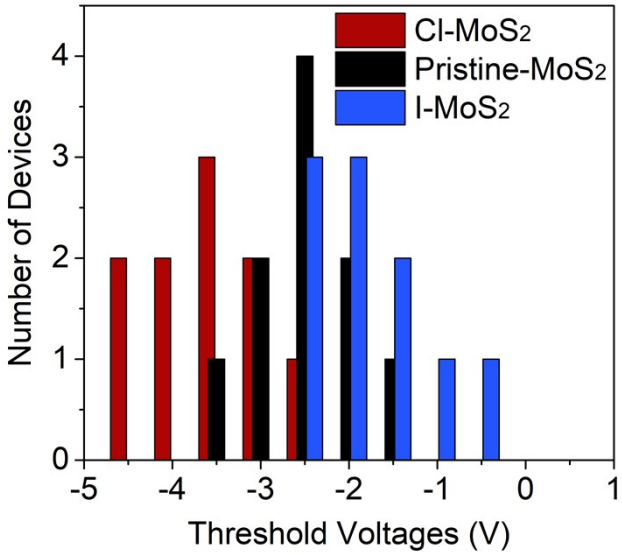

Figure S5. Statistical chart showing the threshold voltage of MoS_2 transistor before and after halide doping.

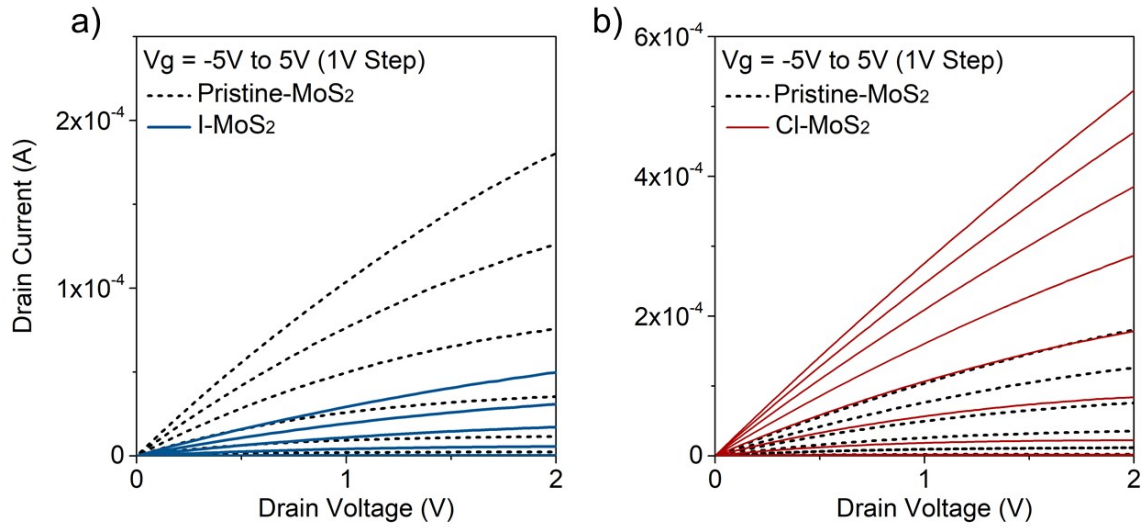

Figure S6. Output curves at difference gate bias (V_g) acquired from Cl-MoS_2 and I-MoS_2 FET devices.

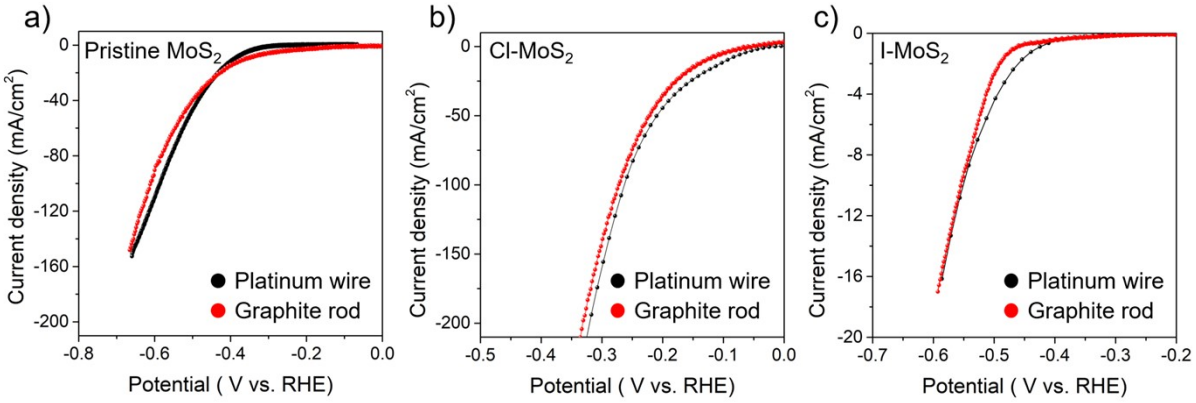

Figure S7. Electrochemical hydrogen evolution performance measurements with graphite rod counter electrode. The polarization curve of (a) pristine, (b) Cl-MoS_2, and I-MoS_2 catalysts.

Carrier density dependent current flow at the interface.

To illustrate the increased current with doping, we use the quantum tunneling model and diffusion model to describe the charge transfer characteristics between semiconductor and electrolyte with doping. The classical drift current is described by the equation

$$J_{n=}\left(\frac{q^2 D_n N_c}{k_B T}\right)\sqrt{\frac{2q(V_D - V_a)N_D}{\varepsilon_0 \varepsilon_s}} exp\left(-\frac{q\phi_{Bn}}{k_B T}\right)\left[\exp\left(\frac{qV_a}{k_B T}\right) - 1\right], \quad V_D = \phi_{Bn} + \frac{k_B T}{q}\ln\left(\frac{N_D}{N_C}\right) \tag{1}$$

where V_D is built-in potential $D_n = (k_B T/q)\mu_n$is the electron diffusion coefficient, k_B is Boltzmann constant, T is absolute temperature, $N_c = 2\left(\frac{2\pi m_n k_B T}{h^2}\right)^{\frac{3}{2}}$ is effective density of state, N_D is dopant density, V_a is applied bias and ϕ_{Bn} is barrier height of junction. From equation (E1), it is seen that built-in potential will increase with nature logarithm of dopant density and also drift current density J_n will increase with square root of dopant density and built-in potential. Finally, when semiconductor is doped with n-type doping, drift current will increase. In semiconductor-electrolyte junction, depletion width will decrease with increasing dopant density. The tunneling current density is given by

$$J_t \approx \left(-q\phi_{Bn}/E_{00}\right) \tag{2}$$

where $E_{00} = (q\hbar/2)\sqrt{N_D/m^* \varepsilon_0 \varepsilon_s}$ is tunneling transmission coefficient and m^* is effective mass of electron. From equation (2), it is verified that the tunneling current density will increase exponentially with square root of dopant density and decrease exponentially with increasing barrier height. Then we can find that when semiconductor is doped with n-type doping, tunneling current will also increase. Charge transport between the junction also can be described by the thermionic emission model. Thermionic emission current is given by

$$J_0 = A^* T^2 \exp\left(-\frac{q\phi_{Bn}}{k_B T}\right)\left[\exp\left(\frac{qV_a}{k_B T} - 1\right)\right] \quad (3)$$

where $A^* = 4\pi m_n^* q k_B^2 / h^3$ is effective Richardson constant. But, in equation (3), there is no dependence of dopant density. Therefore, we can confirm that current density between the semiconductor and electrolyte will increase with equation (1) and (2).[1-3]

Reference

1. V. Balzani and I. Wiley, *Electron transfer in chemistry*, Wiley-VCH, Weinheim ; New York, 2001.
2. S. S. Li, S. S. Li and SpringerLink, *Semiconductor Physical Electronics*, Springer New York, New York, NY, 2006.
3. K. D. Karlin and I. Wiley, *Progress in inorganic chemistry*, Wiley

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