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Supplementary Information

CO_2 Reduction on Single-Atom Ir Catalysts with Chemical Functionalization

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1. Thermodynamics data

Table S1 Standard formation free energies and saturated vapor pressure at standard conditions

	CO_2(g)	H_2(g)	H_2O(l)	CO(g)	HCOOH(l)	HCHO(g)	CH_3OH(g)	CH_4(g)
$\Delta_f G_m^{\ominus}$(kJ/mol)	-394.359	0	-237.129	-137.168	-361.35	-102.53	-161.96	-50.72
P (Pa)	–	–	3534	–	6050	–	–	–

Table S2 Standard Gibbs free energy change

Reaction	$\Delta G_m^{\ominus}$(kJ/mol)
$CO_2(g) + H_2(g) \rightarrow CO(g) + H_2O(l)$	20.07
$CO_2(g) + H_2(g) \rightarrow HCOOH(l)$	32.99
$CO_2(g) + 2H_2(g) \rightarrow HCHO(g) + H_2O(l)$	54.70
$CO_2(g) + 3H_2(g) \rightarrow CH_3OH(g) + H_2O(l)$	-4.73
$CO_2(g) + 4H_2(g) \rightarrow CH_4(g) + 2H_2O(l)$	-130.72

2. The diffusion of Au and $AuCl_3$

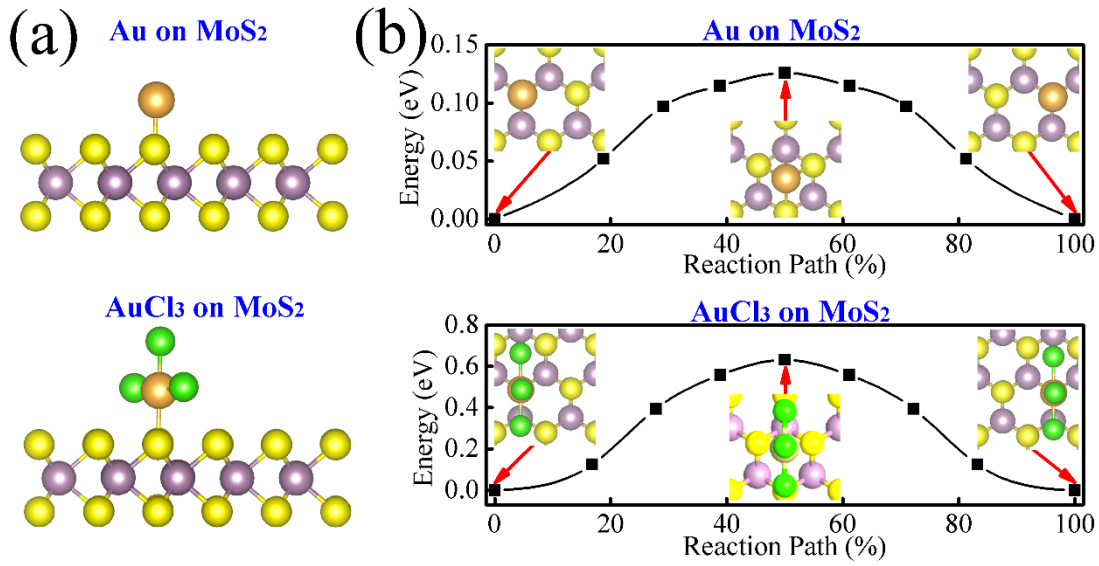

Fig. S1 The structure and migration barrier of (a) Au and (b) $AuCl_3$ on MoS_2.

3. Molecular dynamics and the diffusion barriers of IrX_3 on MoS_2

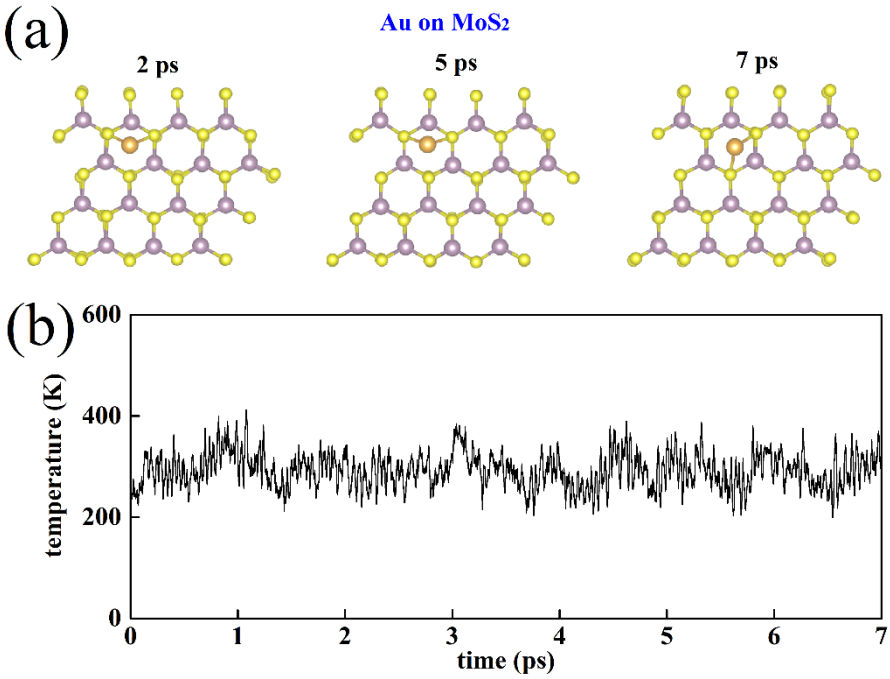

Fig. S2 Molecular dynamics of Au on MoS_2 at 300 K.

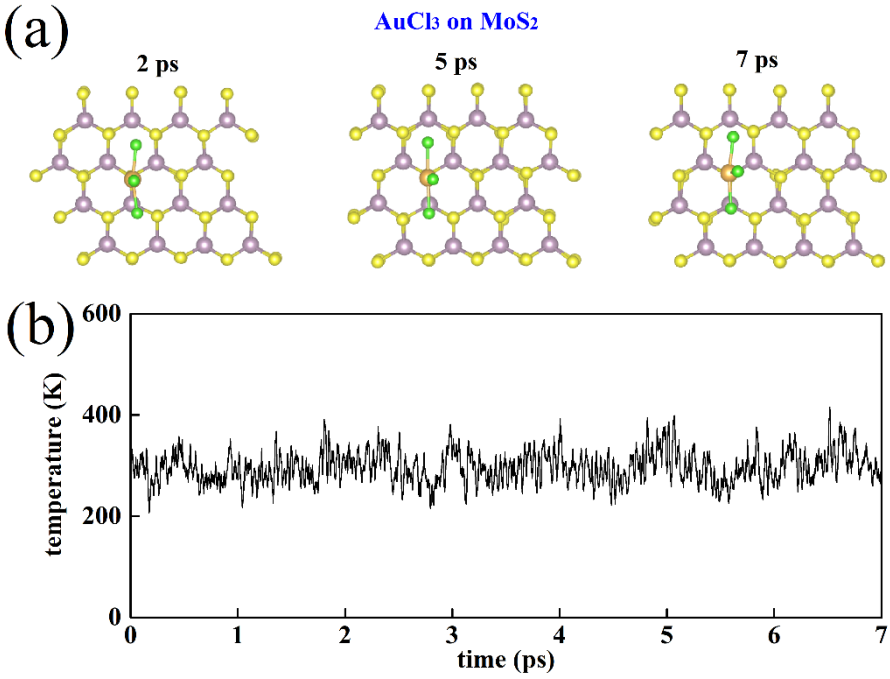

Fig. S3 Molecular dynamics of $AuCl_3$ on MoS_2 at 300 K.

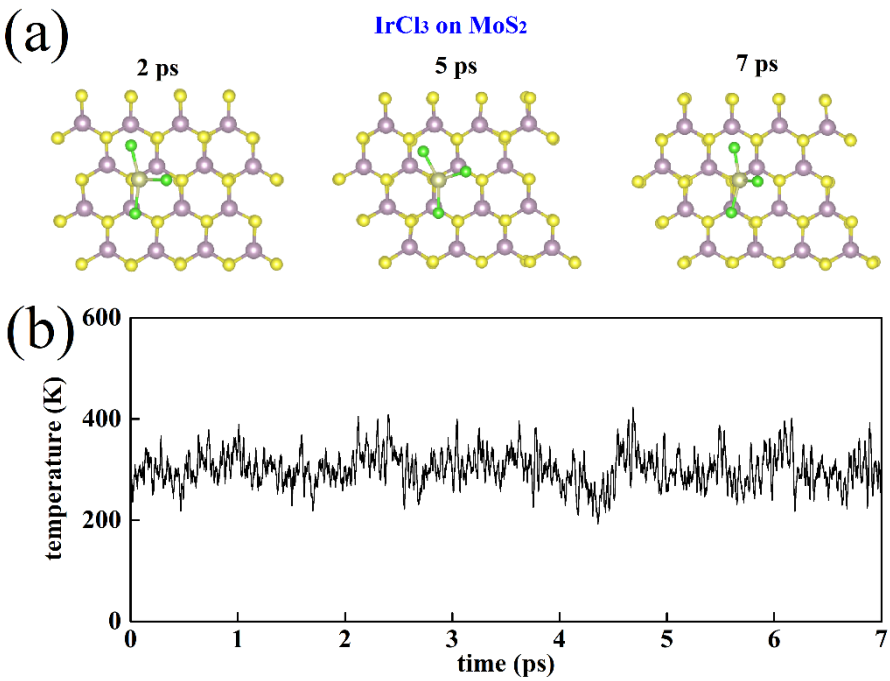

Fig. S4 Molecular dynamics of $IrCl_3$ on MoS_2 at 300 K.

Table S3 The diffusion barriers of IrX_3 on MoS_2

functional	Au	AuCl3	IrF3	IrCl3	IrBr3
r^2SCAN	0.13	0.63	1.42	0.53	0.25
PBE-D3	0.03	0.62	1.32	0.83	0.72

4. Hydrogen evolution reaction

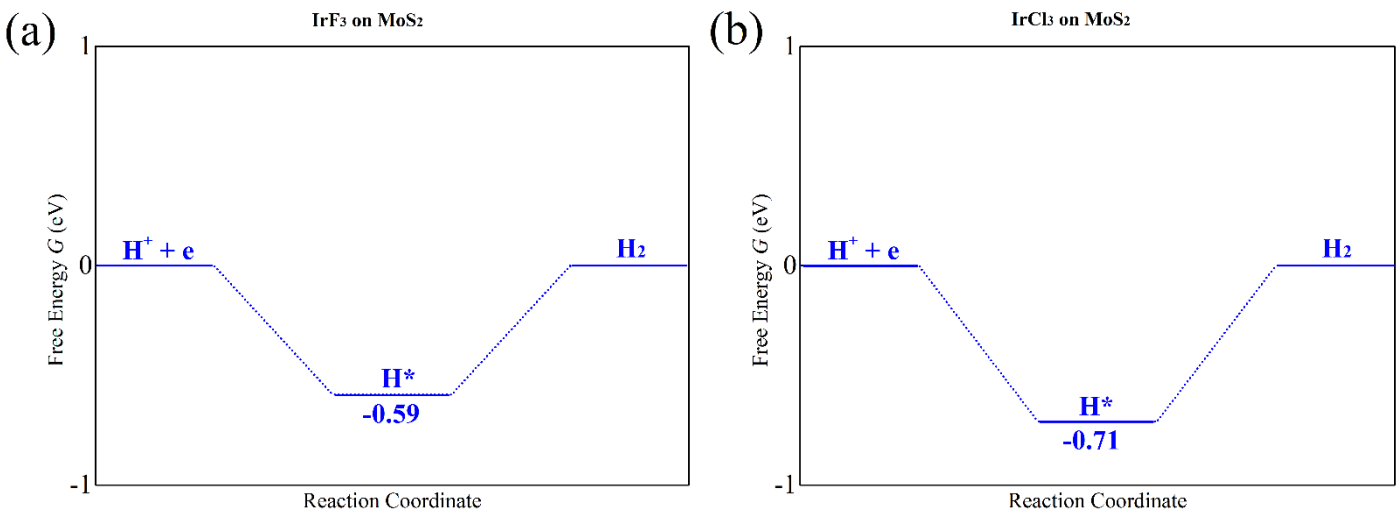

Fig. S5 The reaction free energy of hydrogen evolution reaction on (a) MoS_2-IrF_3 and (b) MoS_2-$IrCl_3$.

5. Energy bands and carrier concentration

With certain empty 5*d* orbitals above the Fermi level, IrX_3 induces p-type doping in MoS_2. According to the Fermi-Dirac distribution, the occupation of an electronic state with energy E is $\frac{1}{e^{(E-E_F)/kT}+1}$, i.e. the average number of holes in this state is $1-\frac{1}{e^{(E-E_F)/kT}+1}$. In the energy bands (**Figs. S6(a)** and **(b)**), we can see impurity levels near and above the Fermi energy, which accept excited electrons from the valence bands. So, the hole concentration is

$$p=\int_{E<VBM} D(E)(1-\frac{1}{e^{(E-E_F)/kT}+1})dE \tag{S1}$$

where $D(E)=\sum_i \delta(E-E_i)$ is the density of states per area. In the calculation, we take a discrete summation

$$p=\frac{\sum_{E_i<VBM}\left(1-\frac{1}{e^{(E_i-E_F)/kT}+1}\right)}{N_{kx}N_{ky}N_{kz}S} \tag{S2}$$

over the Brillouin zone. Here, N_{kx}, N_{ky}, N_{kz} are the number of *k*-points in KPOINTS, and S is the area of supercell in POSCAR. With enough sampled *k* points, the evaluation of this equation is accurate. In the following text, we provide a FORTRAN code and explain how it works.

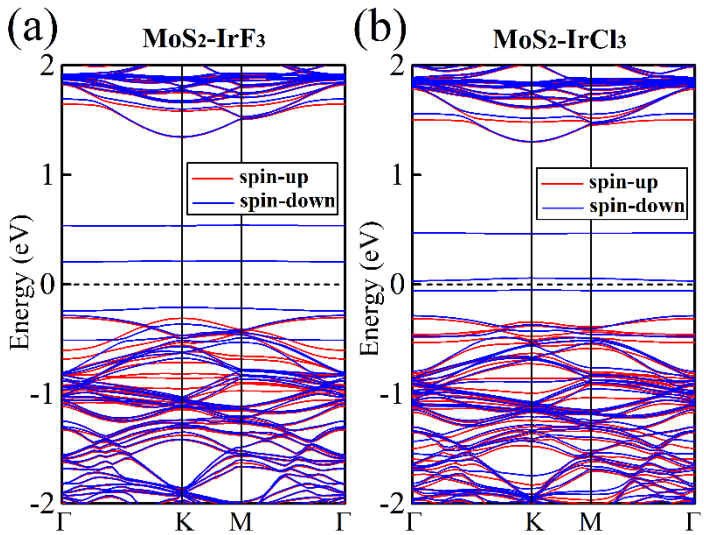

Fig. S6 The energy bands of (a) MoS_2-IrF_3 and (b) MoS_2-$IrCl_3$. The Brillouin zone is sampled in a 4 × 4 MoS_2 supercell.

The FORTRAN code **carrier.90** and the VASP calculation datafiles (INCAR, KPOINTS, POSCAR, POTCAR, EIGENVAL, IBZKPT, OUTCAR) are provided in **Supplementary III**. The program input files are EIGENVAL, IBZKPT and OUTCAR. To precisely calculate the hole number, the Fermi energy need to be refined because the value from VASP is not accurate enough. The code automatically recognizes that it is a normal of spin-orbit calculation, and read the total electron number N from OUTCAR. Then, all the energy levels E_i are read from EIGENVAL. The Fermi energy E_F is adjusted to let

$$N = \sum_i \frac{1}{e^{(E_i - E_F)/kT} + 1} \tag{S3}$$

strictly hold. By the accurate Fermi energy, the hole number is calculated by Eq. (S2).

The FORTRAN code can be compiled as "**gfortran carrier.f90 –o carrier.x**". The temperature T can be inputted as a parameter (like **carrier.x 300** for T = 300 K). If no parameters are inputted, the code takes T = 300 K as default. In this paper, we use T = 300 K to calculate the hole number at room temperature. The output is as follows.

```
detected: spin-polarized
   220 bands found
 NELECT =       318.00000
  25 k-points found
 Total:    7950.00000 electrons

 original:
      E-fermi:    -2.0632000000000001
      calculated electron number:      7953.2885507265946

 E-fermi adjusted:
      temperat    300.00 K
      E-fermi:    -2.0959148633983857
      calculated electron number:      7950.0000002015759

 carrier number:
 holes:          4.3841583608663526E-002      4.6169694869035438E-002
```

The output displays the read NELECT, and the total electron number is N = NELECT × N_{kx} × N_{ky} × N_{kz}. Then, it displays the E_F from the VASP calculation and the total

electron number calculated by Eq. (S3). Then, the program adjusts E_F to let the N calculated from Eq. (S3) accurately equals to NELECT × N_{kx} × N_{ky} × N_{kz}. By the adjusted E_F, it calculates the hole number of spin-up and spin-down (if it is a non-collinear-spin calculation, only one value is displayed). The total hole number

$$N_p = \sum_{E_i<VBM} \left(1 - \frac{1}{e^{(E_i - E_F)/kT} + 1}\right) \tag{S4}$$

is the sum of spin-up and spin-down hole numbers. Once the total hole number is obtained, the carrier concentration can be calculated by Eq. (S2), i.e. $p = N_p / N_{kx}N_{ky}N_{kz}S$.

6. Constant-potential grand canonical ensemble calculation

At a certain electrode potential U, the system is in grand canonical ensemble and the electron number will change (charge or discharge with the other electrode) to reach the lowest free energy. Single-point energy calculation in VASP is fixed-charge, i.e. with a constant electron number NELECT. A Legendre transformation

$$G(n, U) = F(n) - n\mu_{SHE} + neU \tag{S5}$$

is used to convert from fixed-charge free energy $F(n)$ of electrons (i.e. DFT total energy) to grand canonical $G(n, U)$. Here, n (i.e. NELECT) is the number of electrons. The vacuum level is obtained by LVHAR = T and getting the Hartree potential in the vacuum layer. μ_{SHE} (-4.44 eV below the vacuum level) is the chemical potential of electron in the standard hydrogen electrode (SHE).

We change NELECT with a step of ±0.5 and find the minimum of DFT total energy $F(n)$ by polynomial fitting. For example, we simulation MoS_2-IrF_3 with 4×4 MoS_2 supercell. The electron configurations are Mo ($4d^5 5s$), S ($3s^2 3p^4$), Ir ($5d^7 6s^2$) and F ($2s^2 2p^5$). The total electron number is NELECT = 318. The single-point energy calculations are performed with NELECT = 318.0, 318.5, 319.0, 319.5, 320.0. For the case of $U = 0$ vs SHE, $G(n, U)$ are calculated and the data fitting is shown in **Fig. S7**.

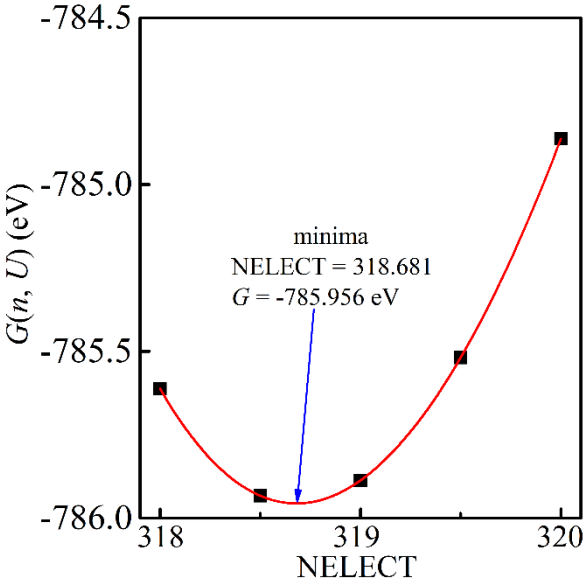

Fig. S7 The grand-canonical free energy *G*(*n*, *U*) of MoS_2-IrF_3 at *U* = 0. The *G*(*n*, *U*) data are calculated by Eq. S5 and fitted by a quartic polynomial (shown by the red curve).