Supplementary Information

Transition Metal Modification and Carbon Vacancies Promoted Cr_2CO_2 (MXenes): A New Opportunity for Highly Active Catalyst for Hydrogen Evolution Reaction

Yu-Wen Cheng[1], Jian-Hong Dai[2], Yu-Min Zhang[1] , Yan Song[2,]

1 Science and Technology on Advanced Composites in Special Environments Laboratory, Harbin Institute of Technology, Harbin 150001, PR China

2 School of Materials Science and Engineering, Harbin Institute of Technology at Weihai, 2 West Wenhua Road, Weihai, 264209, PR China

Corresponding author:

E-mail: sy@hitwh.edu.cn; zhym@hit.edu.cn

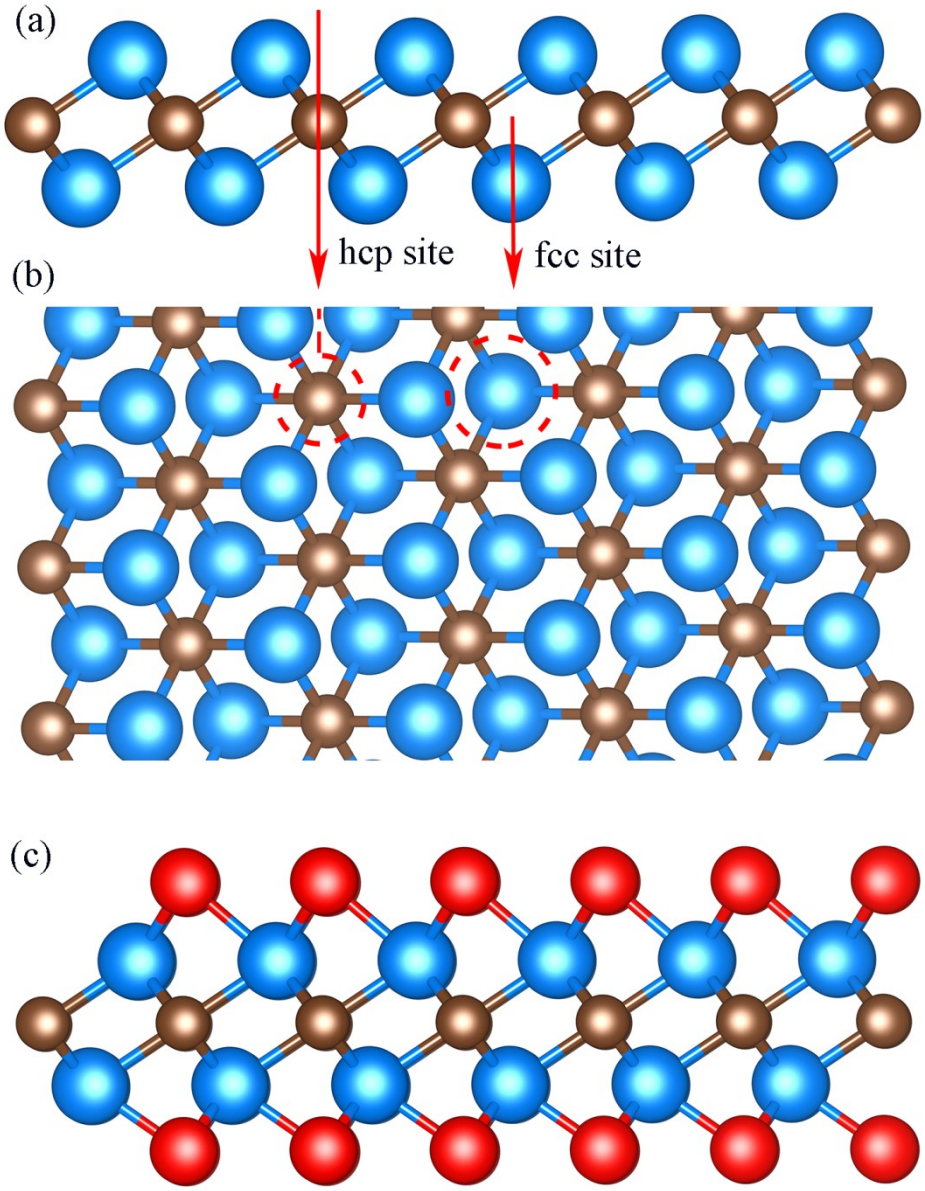


Figure S1. Lattice structures of Cr_2C and Cr_2CO_2. (a) side view of Cr_2C, (b) top view of Cr_2C, and (c) side view of Cr_2CO_2

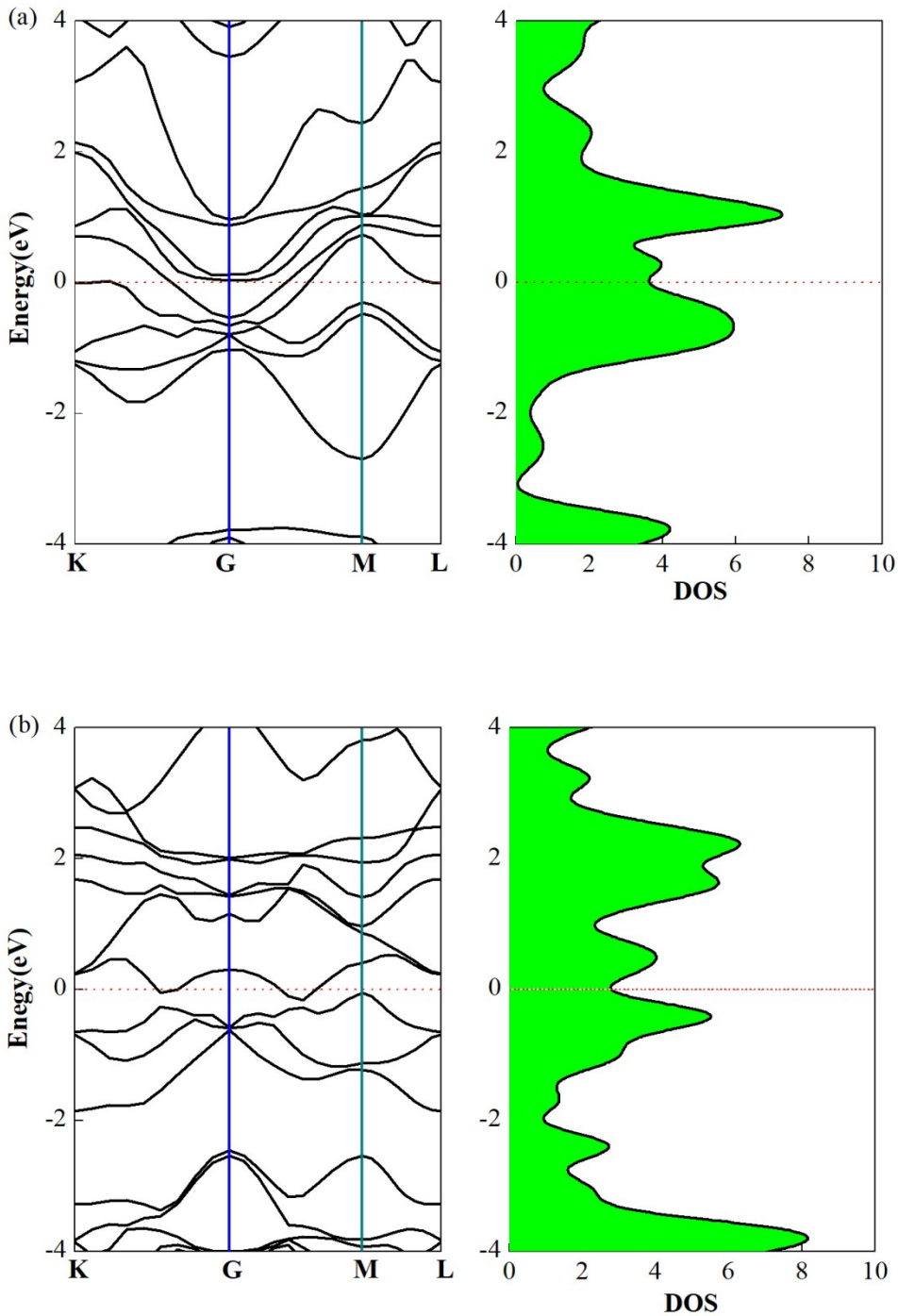


Figure S2. Band structure (left) and density of states (right) of (a) Cr_2C and (b) Cr_2CO_2.

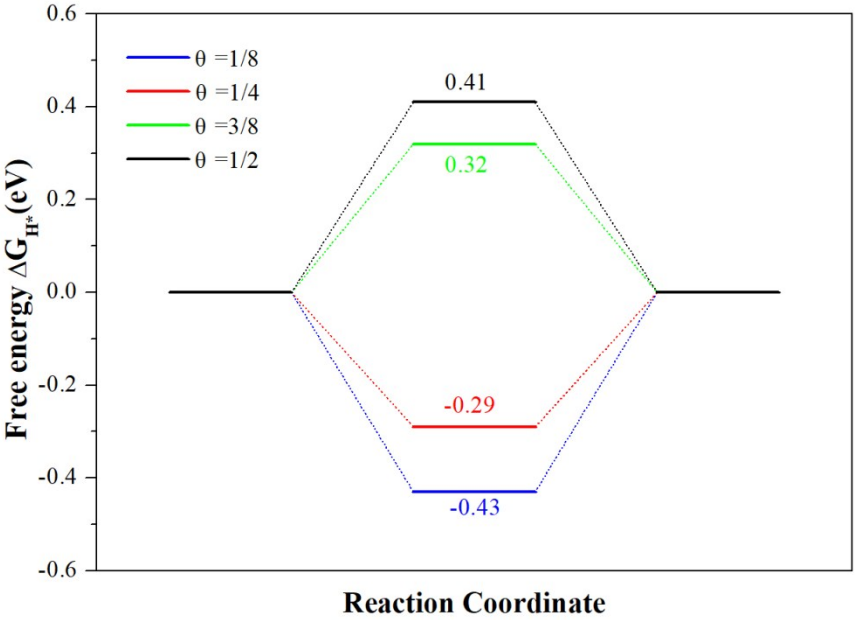
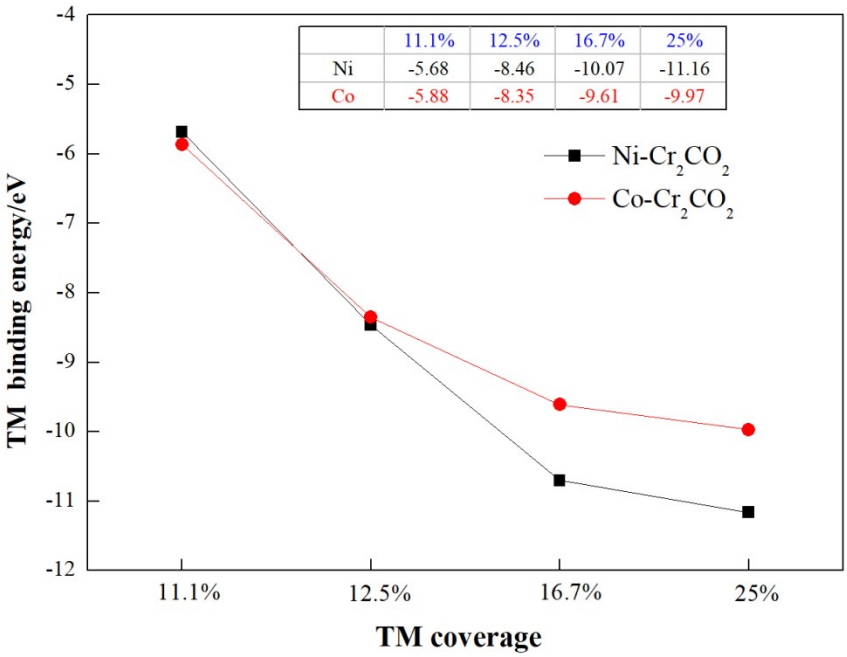


Figure S3. Free energy diagram of HER processing of Cr_2CO_2 under different H coverage □.



	11.1%	12.5%	16.7%	25%
Ni	-5.68	-8.46	-10.07	-11.16
Co	-5.88	-8.35	-9.61	-9.97

Figure S4.The binding energy of transition metal with Cr_2CO_2 surface.

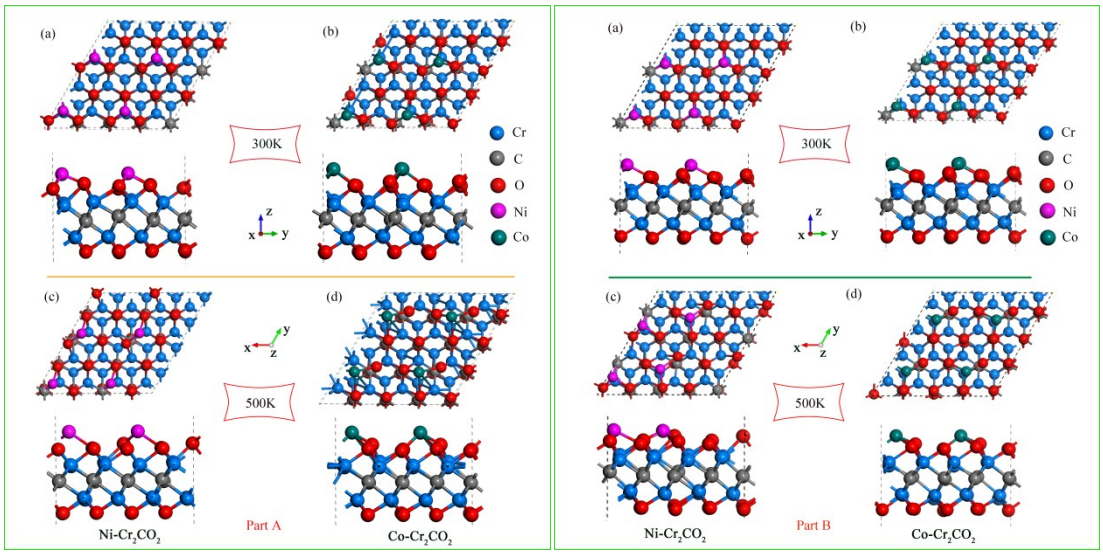
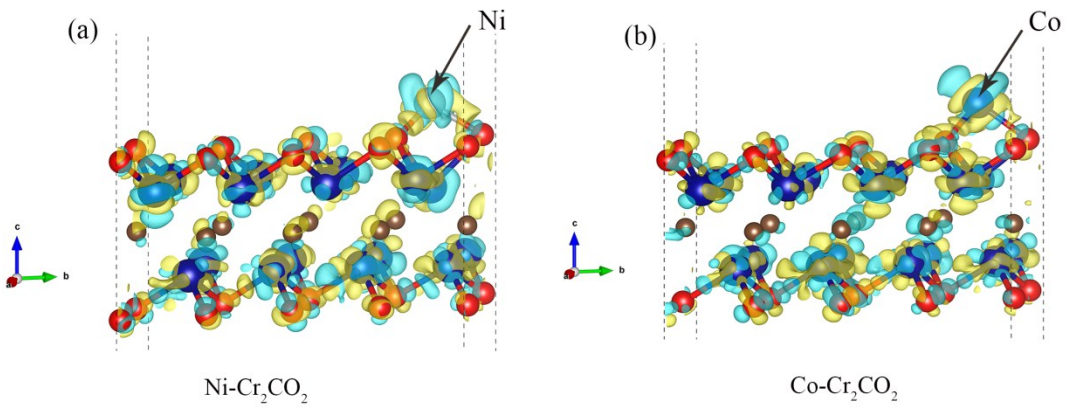


Figure S5. Atomic configurations of TM-Cr_2CO_2 after AIMD simulations under 300K and 500K. The AIMD calculations were typically run for 8ps (Part A) and 4ps (Part B), with a time step of 2 fs.



Figures S6. Charge density difference of (a) Ni-$Cr_2CO_2$and (b) Co-Cr_2CO_2 under 12.5% TM coverage. The light blue and yellow colors denote the negative and positive areas, respectively.

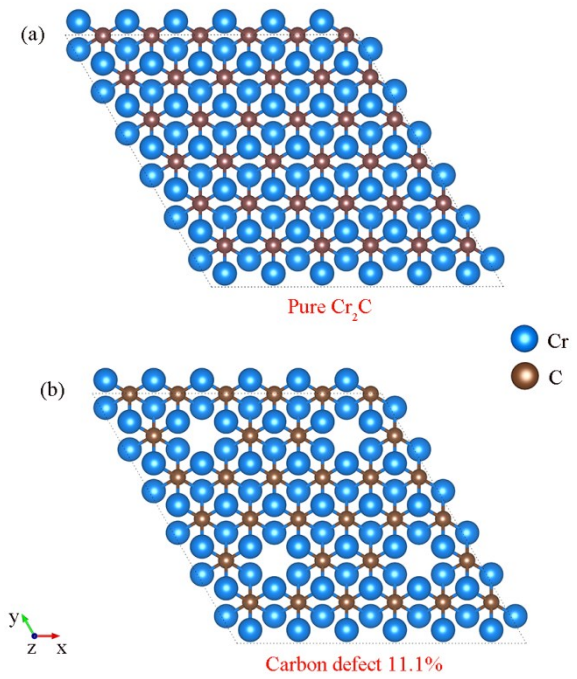


Figure S7. The schematics of (a) perfect Cr_2CO_2 and (b)V_C-Cr_2CO_2. The concentration of carbon vacancies is 11.11%.In this figure we use Cr_2C rather than Cr_2CO_2 to identify the carbon vacancies.

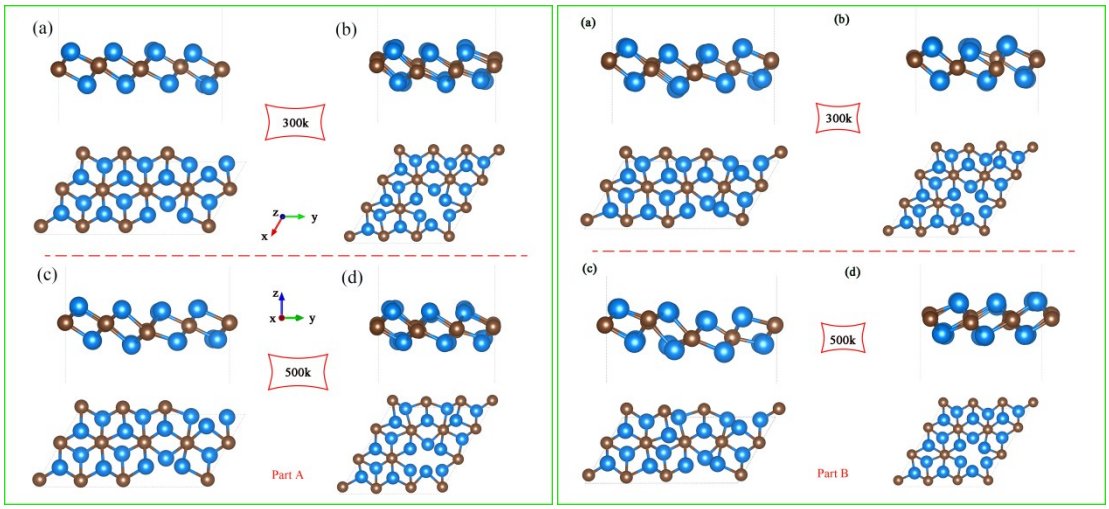


Figure S8. Atomic configurations of V_C-Cr_2C after *ab initio* molecular dynamics (AIMD) simulations under the temperature of 300K and 500K. The AIMD calculations were typically run for 8ps (Part A) and 4ps (Part B), with a time step of 2 fs. (a) 12.5%V_C-Cr_2C at 300K, (b) 11.11%V_C-Cr_2C at 300K, (c) 12.5%V_C-Cr_2C at 500K, and (d) 11.11%V_C-Cr_2C at 500K.

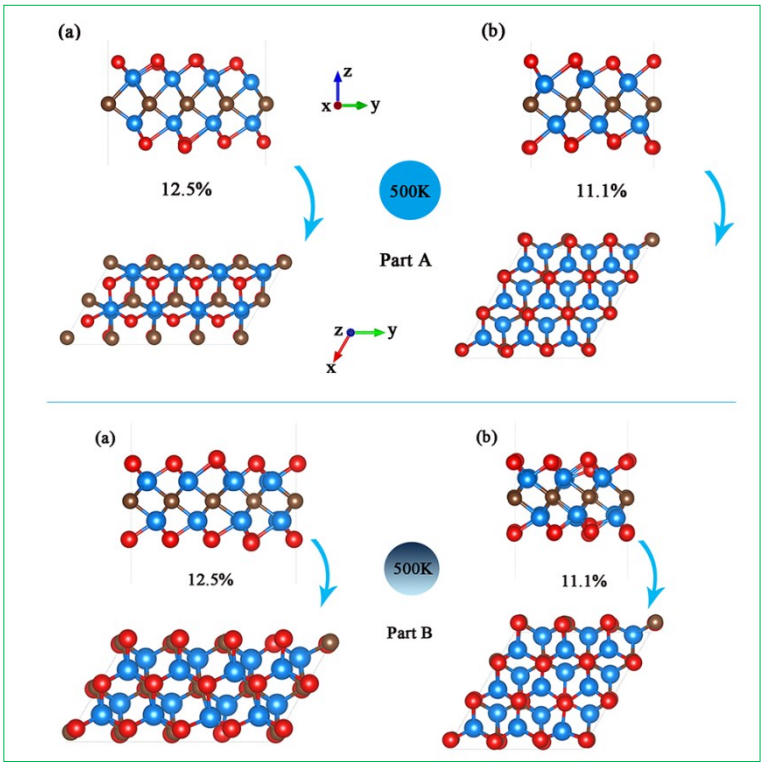


Figure S9. Atomic configurations of V_C-Cr_2CO_2 at end of a*b initio* molecular dynamics (AIMD) simulations under the temperature of 500K. The AIMD calculations were typically run for 8ps (Part A) and 4ps (Part B), with a time step of 2fs.(a) 12.5%V_C-Cr_2CO_2 at 500K and (b) 11.11%V_C-Cr_2CO_2 at 500K.