Electronic Supplementary Information for

A Novel Energy Dependent Heterojunction of *p*-Semiconductor—Metal—*n*-Semiconductor for Selectively Steering Charge Flow in Z-scheme Photocatalyst

Xiyu Li,[a†] Mesfin Eshete,[a†] Xin Li,[a†] Tian Xie,[b] Guozhen Zhang,[a] Liyan Xie,[a] Chuanyi Jia,[c] Yi Luo[a] and Jun Jiang*[a]

[a]Hefei National Laboratory for Physical Sciences at the Microscale, CAS Center for Excellence in Nanoscience, CAS Key Laboratory of Mechanical Behavior and Design of Materials, School of Chemistry and Materials Science, University of Science and Technology of China (USTC), Hefei, Anhui 230026, China

[b]State Key Laboratory of Efficient Utilization for Low Grade Phosphate Rock and Its Associated Resources, Wengfu Group, Guiyang 550014, China

[c]Guizhou Provincial Key Laboratory of Computational Nano-material Science, Institute of Applied Physics, Guizhou Education University, Guiyang, 550018, China

E-mail: jiangj1@ustc.edu.cn

Xiyu Li, Mesfin Eshete and Xin Li contributed equally to this work.

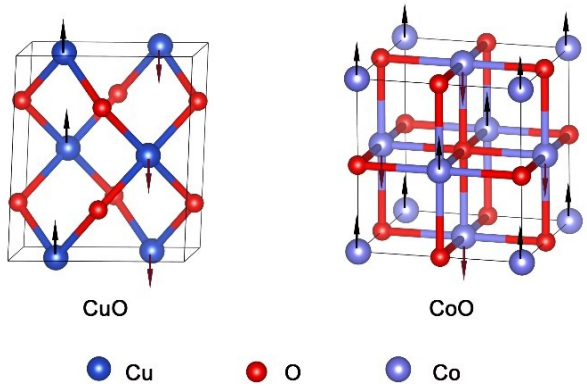

Fig. S1 Structural illustration of CuO and CoO unit cells and their anti-ferromagnetic spin ordering, respectively. Arrows on the metal ions indicate the orientation of local magnetic moments.

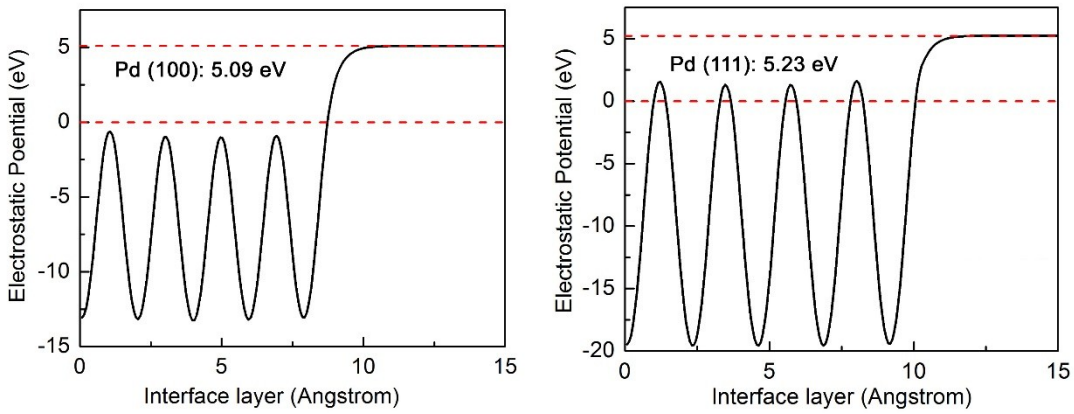

Fig. S2 Calculated work functions of Pd (100) and Pd (111), consecutively.

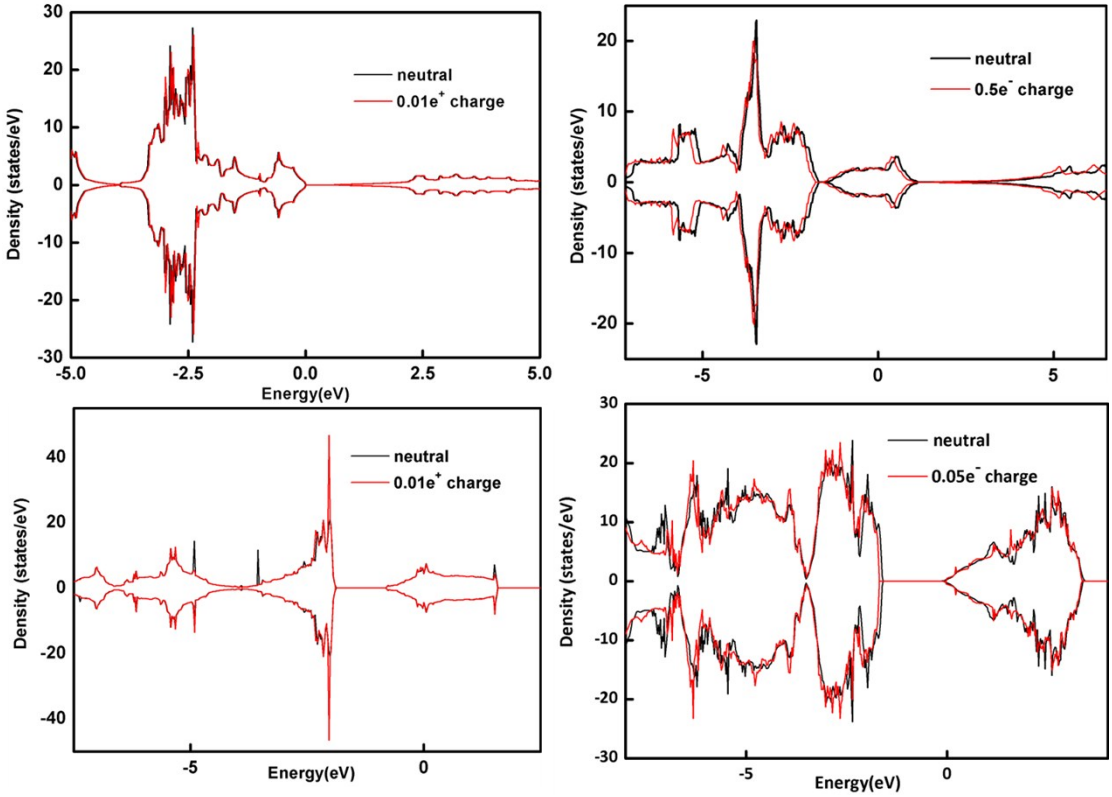

Fig. S3 (a) neutral and $0.01e^+$ charge of Cu_2O (b) neutral and $0.5e^-$ charge of CuO (c) neutral and $0.01e^+$ charge of CoO and (d) neutral and $0.05e^-$ charge of WO_3.

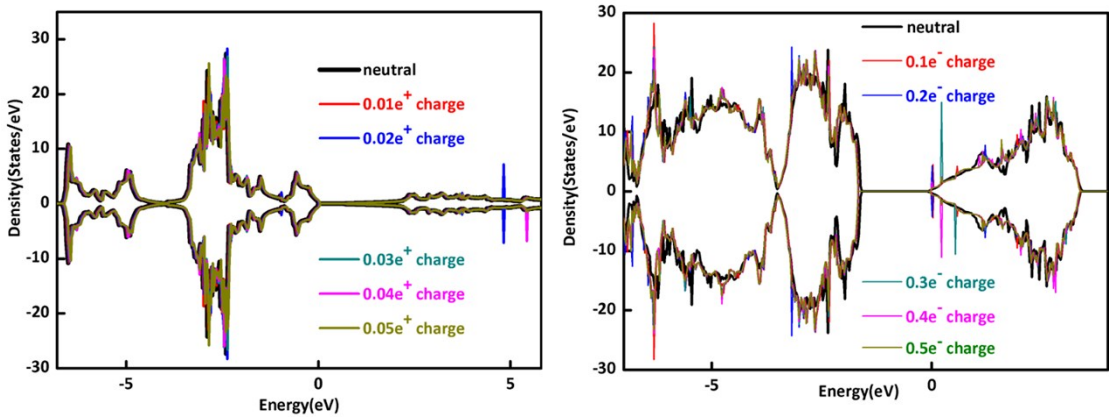

Fig. S4 (a) neutral, $0.01e^+$, $0.02\ e^+$, $0.03\ e^+$, $0.04\ e^+$ and $0.05e^+$ charge of Cu_2O (b) neutral,$0.01e^-$, $0.02\ e^-$, $0.03\ e^-$, $0.04\ e^-$and $0.05\ e^-$ charge of WO_3.

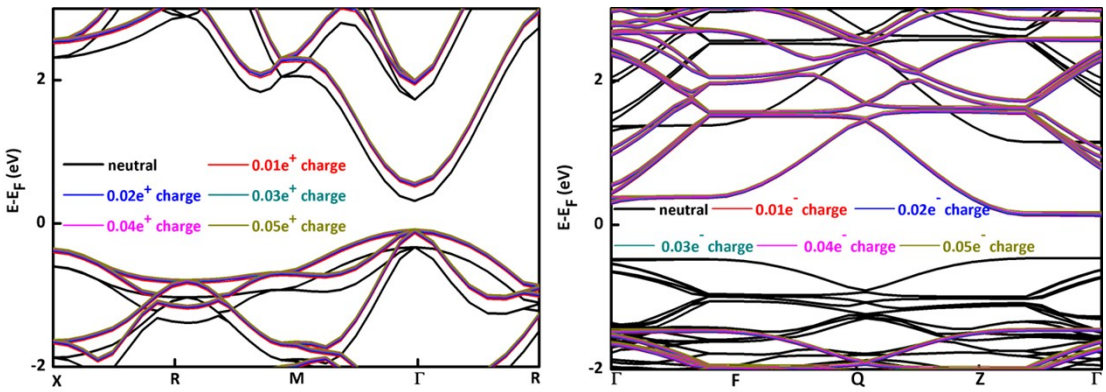

Fig. S5 (a) neutral,0.01 e^+,0.02 e^+, 0.03 e^+, 0.04 e^+ and 0.05 e^+ charge of Cu_2O (b) neutral,0.01 e^-, 0.02 e^-, 0.03 e^-, 0.04 $e^-$and 0.05 e^- charge of WO_3.

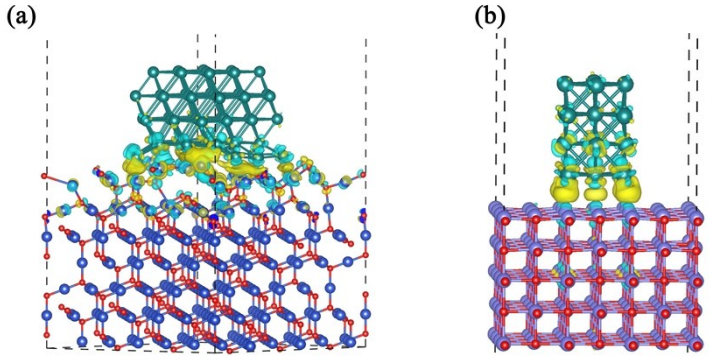

Fig. S6 (a) and (b) are differential charge densities at *p-m* junctions of $Cu_2O(100)$-Pd(cluster) and CoO(100)-Pd(cluster), respectively, with an iso-value of 0.004 $eÅ^{-3}$. Yellow and blue bubbles represent electron accumulation and donation/depletion in space, respectively. Based on Bader charge analysis, the charge transfer from p-type semiconductors of $Cu_2O(111)$ and CoO(100) to Pd cluster is 0.29 and 0.22 e^-, respectively.

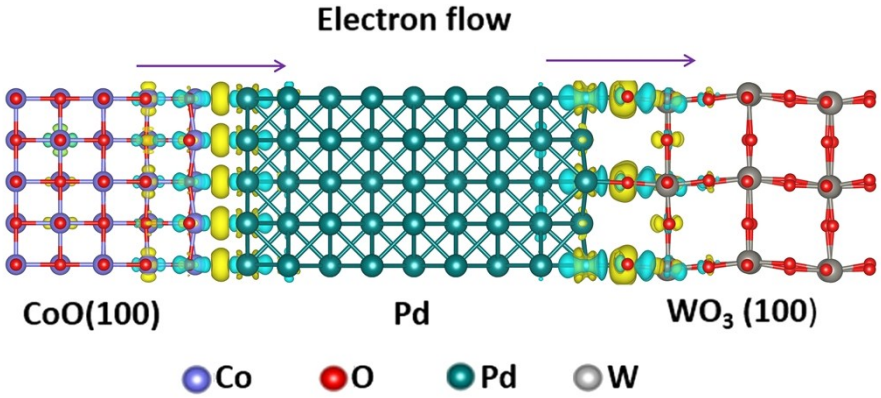

Fig. S7 Differential charge densities at *p-m-n* junctions of ternary CoO(100)-Pd(100)-WO_3(100) with an iso-value of 0.004 eÅ^{-3}. Yellow and blue bubbles represent electron accumulation and donation/depletion in space, respectively.

Table S1. Calculated lattice parameters of unit cells and band gap (E_g) compared to experimental data.

	Parameter (Å)	Cal. E_g (eV)	Exp. E_g (eV)
Cu_2O	a=b=c=4.28	0.7	2.2
CuO	a=4.69, b=3.47, c=5.14	1.4	2.6
CoO	a=b=c=4.21	0.6	1.7
WO_3	a=7.53, b=7.69, c=7.83	1.4	2.7
Pd	a=b=c=3.94	--	--

Table S2. The position of Fermi level (E_F) *versus* vacuum energy level (E_v=0), parameters of slab models for semiconductors surface and Pd for building interface junctions.

	Parameter (Å)	E_F (eV)	Supercell	Matched with Pd	Mis-matching
Cu_2O(111)	μ=6.09,υ=6.09	-4.74	2×2	4×4	8.3%, 8.3%
CuO(010)	μ=5.18,υ=3.80	-6.53	3×2	4×2	2.0%, 2.5%
CoO(100)	μ=4.21,υ=4.21	-4.20	2×2	2×2	6.3%, 6.3%
WO_3(100)	μ=7.69,υ=7.83	-6.71	1×1	2×2	2.3%, 0.5%