Supplementary Information

Atomic adsorption on monolayer Cu_2Se: a first-principles study

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Available content:

Computational Details

Formation energy calculation:

The formation energy (ΔH) of Cu_2Se per formula unit (f.u.) is defined as:

$$\Delta H = [E_{tot}(Cu_2Se) - n_{Cu}E_{tot}(Cu) - n_{Se}E_{tot}(Se)]/n_{Cu2Se}$$

where $E_{tot}(Cu_2Se)$ is the total energy of ζ-Cu_2Se or λ-Cu_2Se, $E_{tot}(Cu)$ and $E_{tot}(Se)$; $n_{Cu,}$ n_{Se} and n_{Cu2Se} represent the number of Cu, Se, Cu_2Se units, respectively; $E_{tot}(Cu)$ and $E_{tot}(Se)$ are the total energy of Cu and Se atom in its bulk form, which is face-centered cubic Cu and $P3_121$ Se, respectively.

Gibbs free energy calculation:

The Gibbs free energy (ΔG) is calculated by:

$$\Delta G = \Delta E + \Delta ZPE - T\Delta S$$

where ΔE, ΔZPE and ΔS represent the hydrogen adsorption energy, zero-point energy and entropy, respectively. Particularly, the value of $T\Delta S$ for a hydrogen atom is 0.20 eV at 298 K.[1]

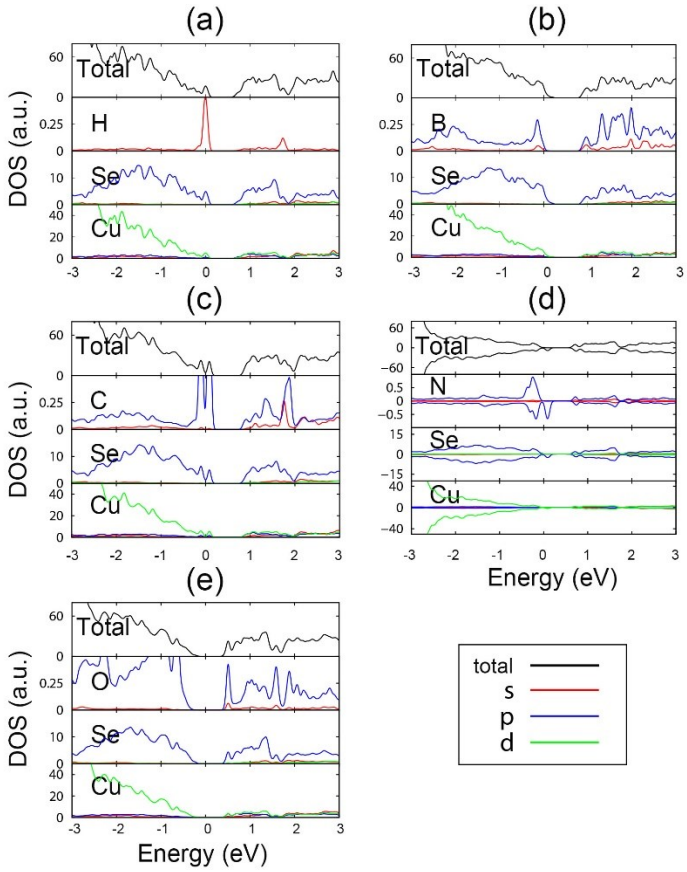

Figure S1. The fully orbital-decomposed DOS of ζ-Cu_2Se decorated with adatoms within the PBE-D3+U scheme: (a) H, (b) B, (c) C, (d) N, and (e) O.

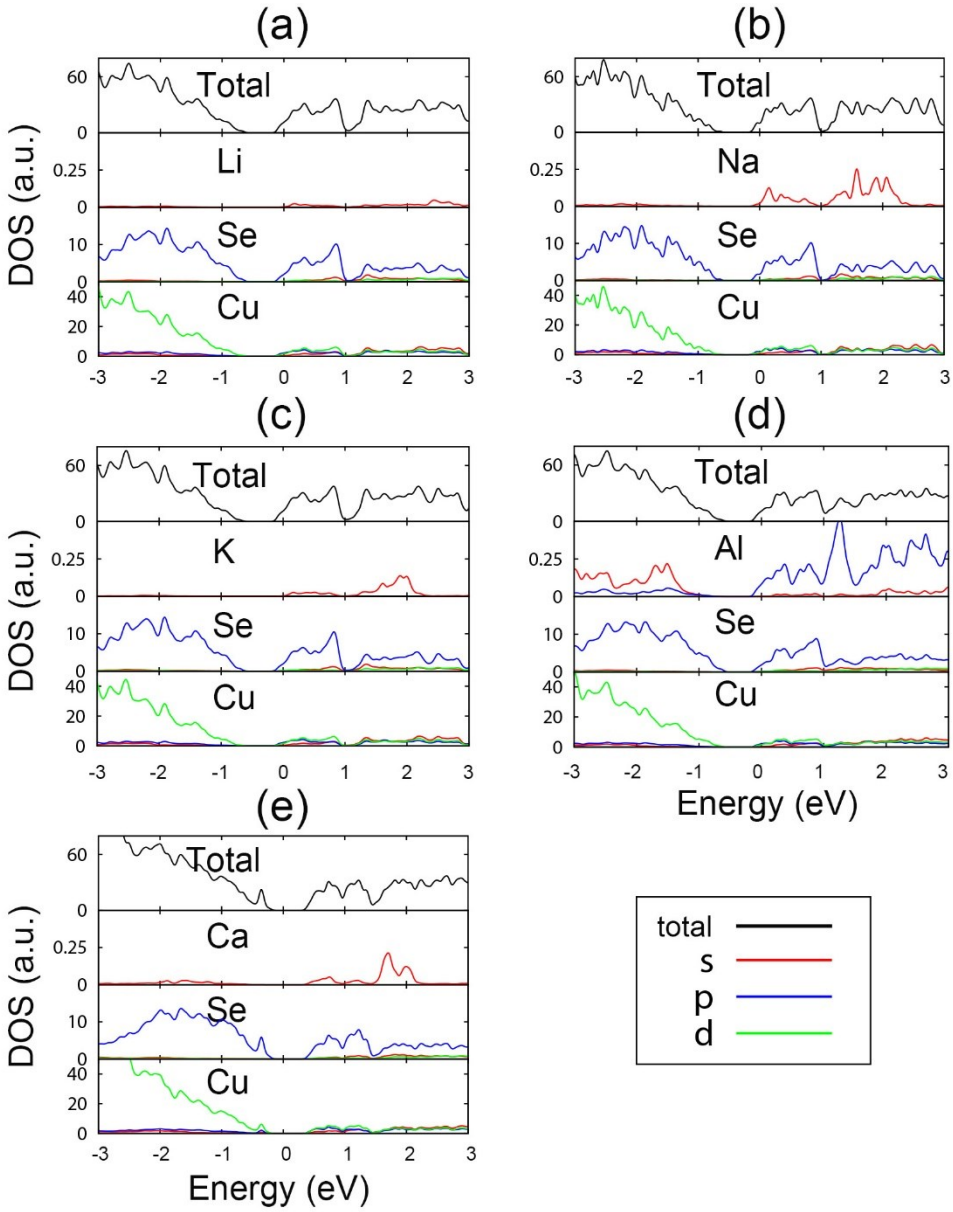

Figure S2. The fully orbital-decomposed DOS of ζ-Cu_2Se decorated with adatoms within the PBE-D3+U scheme: (a) Li, (b) Na, (c) K, (d) Al, and (e) Ca.

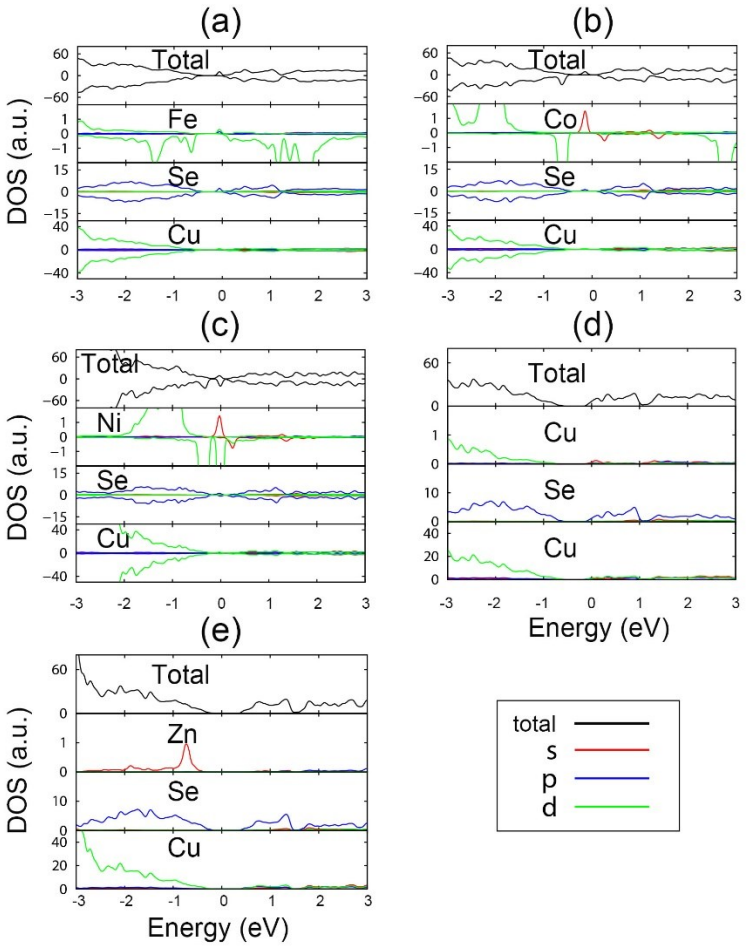

Figure S3. The fully orbital-decomposed DOS of ζ-Cu_2Se decorated with adatoms within the PBE-D3+U scheme: (a) Fe, (b) Co, (c) Ni, (d) Cu, and (e) Zn.

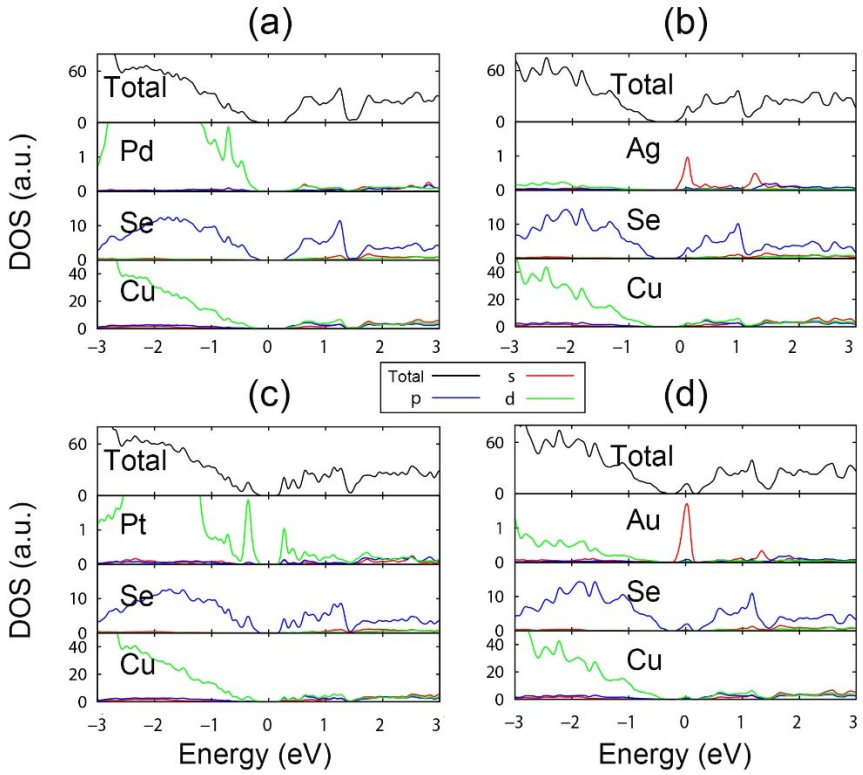

Figure S4. The fully orbital-decomposed DOS of ζ-Cu_2Se decorated with adatoms within the PBE-D3+U scheme: (a) Pd, (b) Ag, (c) Pt, and (d) Au.

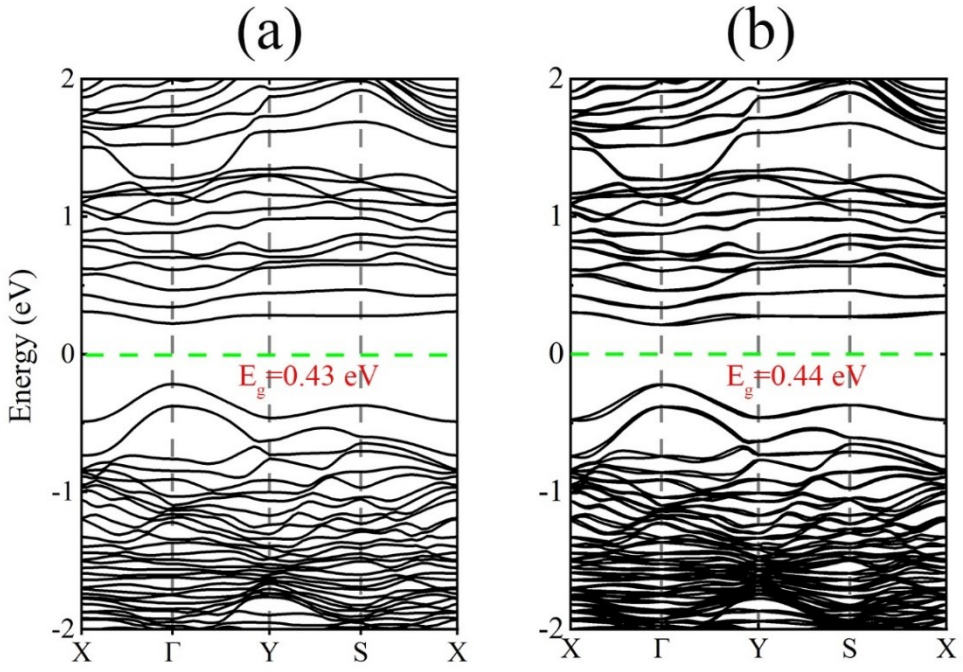

Figure S5. Band structures of Pt/Cu_2Se using PBE-D3+U method (a) without and (b) with spin-orbit coupling effect.

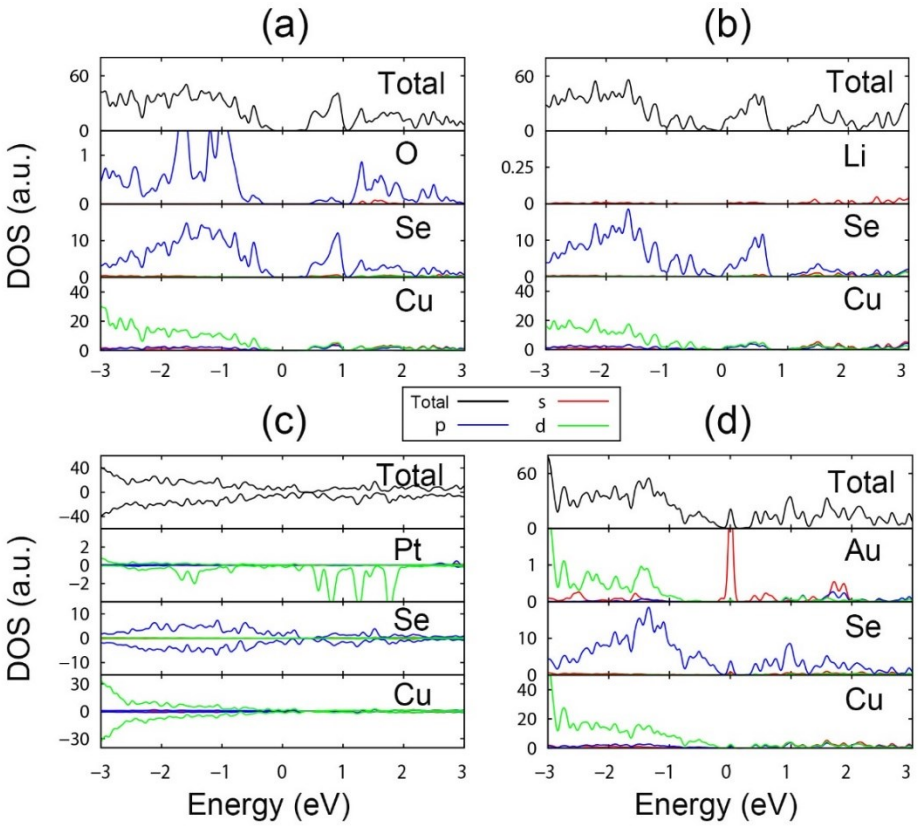

Figure S6. The fully orbital-decomposed DOS of λ-Cu_2Se decorated with adatoms within the PBE-D3+U scheme: (a) O, (b) Li, (c) Fe, and (d) Au.

Reference

1 Y. Ouyang, C. Ling, Q. Chen, Z. Wang, L. Shi and J. Wang, Activating Inert Basal Planes of MoS_2 for Hydrogen Evolution Reaction through the Formation of Different Intrinsic Defects, *Chem. Mater.*, 2016, **28**, 4390–4396.