Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

A Caveat of the Charge-Extrapolation Scheme for Modeling Electrochemical Reactions on Semiconductor Surfaces: An Issue Induced by a Discontinuous Fermi Level Change

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S1. Atomic structures of the Pt and GaP large-surface supercells

We show the atomic structures of the 2×2 Pt and the 3×3 GaP large-surface supercells (defined in the Methods section of the main text) in Figure S3 and S4. We highlight the reaction unit for producing one H_2 molecule by pink dashed boxes. We can see that there are 4 and 9 reaction units in the large supercells of Pt and GaP surfaces respectively. We note that only one reaction unit is involved in the reaction of one H_2 molecule formation modeled by the large-surface supercells.

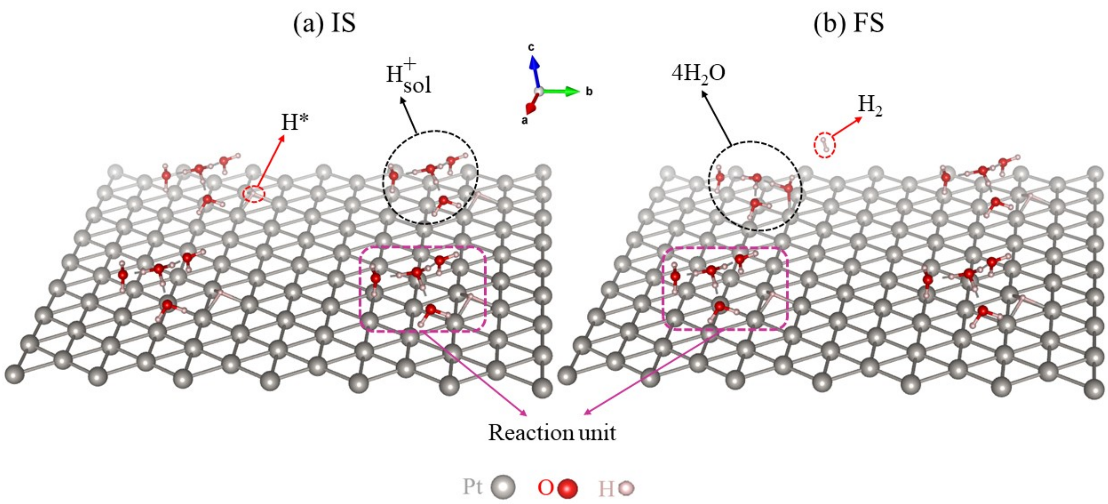

Figure S1. Schematic atomic structures of the 2×2 Pt (111) surface supercells. (a) The IS with one H* atom and one [H_3O^+-$3H_2O$+e^-_{slab}] cluster per reaction unit (denoted as H^+_{sol}) on the Pt slab. (b) The FS with the products of one H_2 molecule and $4H_2O$ in one of the reaction units on the Pt slab. There are 4 reaction units in the supercell, one of which is marked by the pink dashed box. Only the top layer of the Pt slab is displayed here for simplicity.

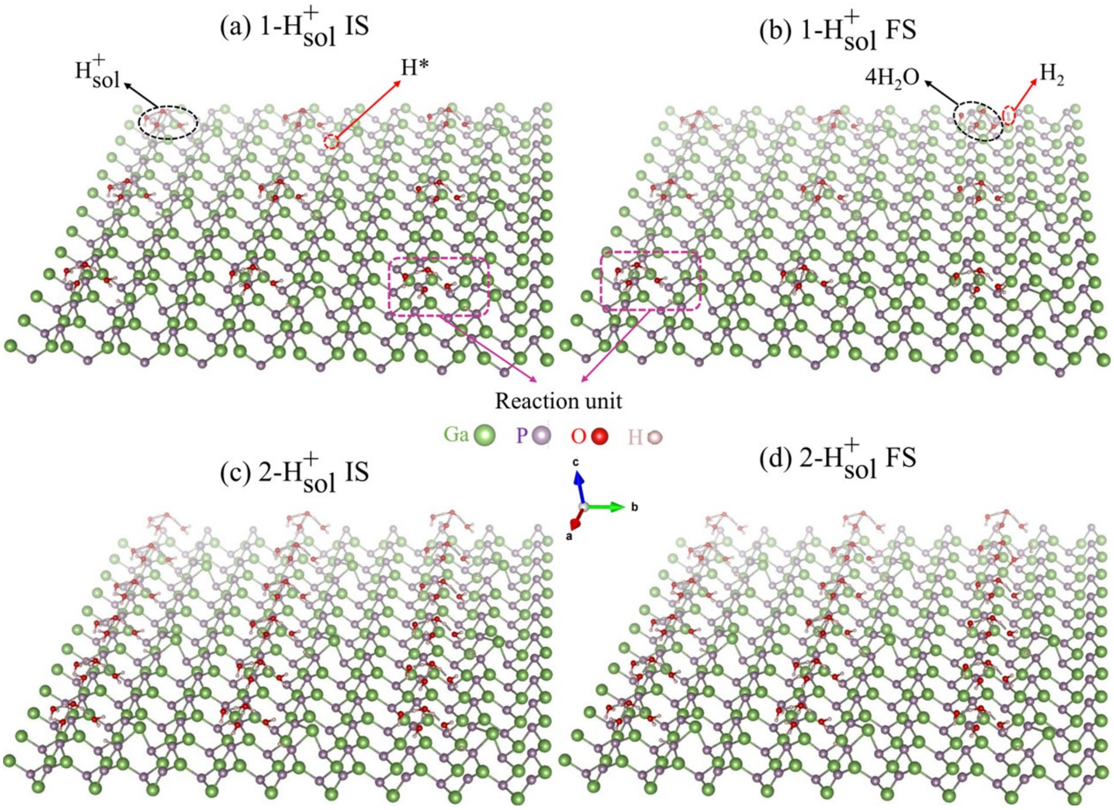

Figure S2. Schematic atomic structures of the 3×3 GaP (110) surface supercells. (a) The IS with one H* atom and one H^+_{sol} cluster per reaction unit on the GaP slab, denoted as 1-H^+_{sol}. (b) The FS with the products of one H_2 molecule and $4H_2O$ in one of the reaction units on the GaP slab for the 1-H^+_{sol} case. (c)(d) The IS and FS of the H_2 formation reaction on the GaP (110) surface with two H^+_{sol} clusters per reaction unit, denoted as 2-H^+_{sol}. There are 9 reaction units in the supercell, one of which is marked by the pink dashed box. Only the top and the subsurface layers of the GaP slab are displayed here for simplicity.

S2. Hydrogen evolution reaction step H^+_{sol} + H* + e^- → H_2 on the semiconductor AlAs surface

Considering the computational costs and the surface area of the slab in order to ensure that two electron-donating species can be accommodated in the cell, we simulate the hydrogen evolution reaction step $H^{+}_{sol} + H^{*} + e^{-} \rightarrow H_2$ on the semiconductor AlAs surface. Specifically, we construct an AlAs slab with the (110) facet exposed. The supercell consists of five atomic layers (12 Al and 12 As atoms per layer) with the dimensions of 16.228×17.213×30.388 $Å^3$. Each layer consists of 12 (3×4) primitive surface units, and the atoms of the third layer are fixed at the bulk positions of the zinc-blende-structure AlAs. Similarly, the issue of applying the charge-extrapolation scheme for semiconductor surface reactions with cross-bandgap Fermi level changes also exists in the additional semiconductor surface reaction simulation, which can be avoided by our solutions of adding an extra electron-donating species on the semiconductor surface.

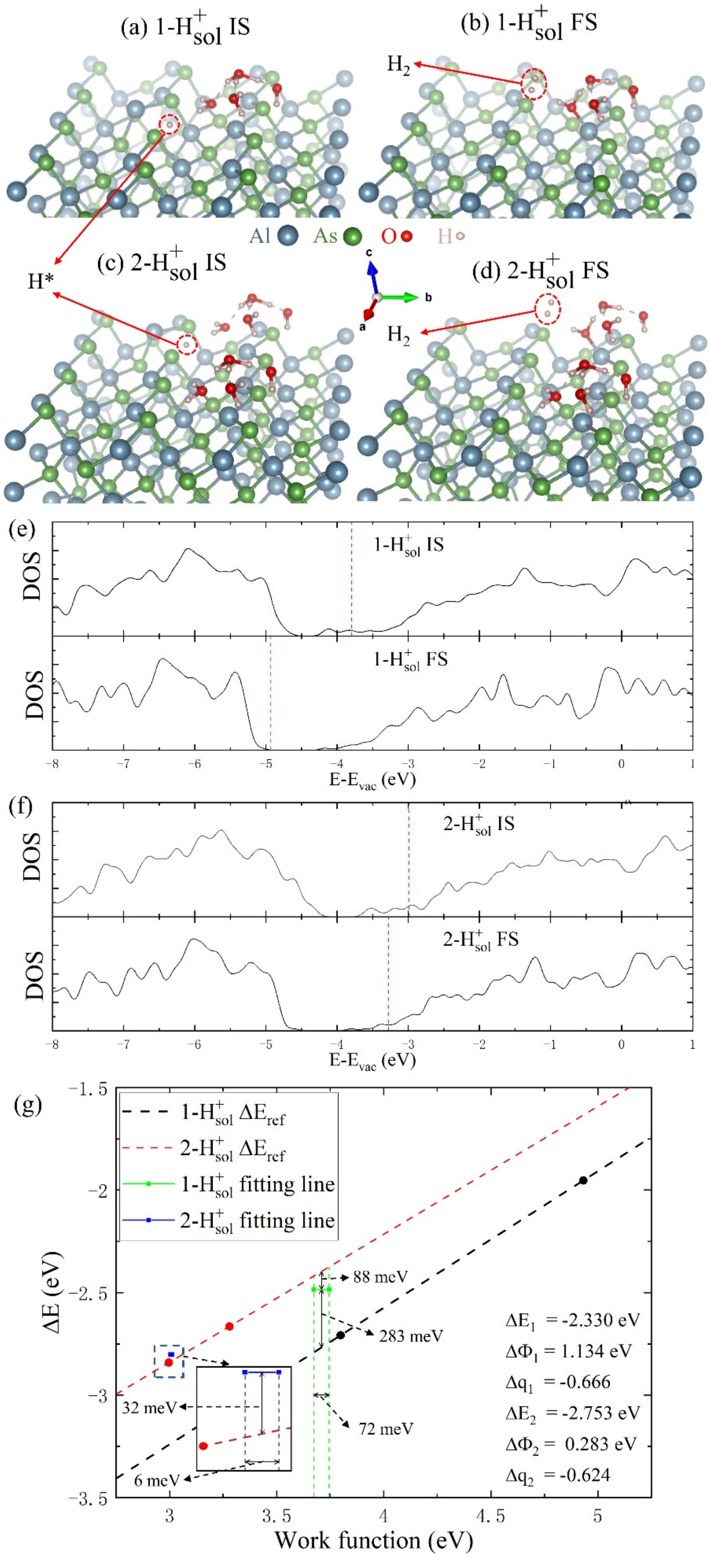

Figure S3. Schematic atomic structures of (a) the IS with one H* atom and one H^+_{sol} cluster, and (b) the FS with the products of H_2 and $4H_2O$ in the AlAs (110) 1×1 small surface cell, denoted as 1-H^+_{sol}. (c)(d) The IS and FS of the reduction reaction on the AlAs (110) surface analogous to (a)(b), except for two H^+_{sol} clusters placed on the AlAs surface, denoted as 2-H^+_{sol}. (e)(f) The IS and FS DOS with 1-H^+_{sol} cluster and 2-H^+_{sol} clusters on the surface computed by the 1×1 small supercells. (g) ΔE_{ref} (the green/blue solid bar) and $\Delta E_{chg\text{-}ex}$ (the black/red dashed line) of the surface reduction reactions with 1-H^+_{sol}/2-H^+_{sol} clusters per reaction unit on the surface. Subscript i of ΔE, ΔΦ, and Δq stands for the i-H^+_{sol} system.