Supporting Information Catalytic Activity and Stability of Two-Dimensional Materials for the Hydrogen Evolution Reaction

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S-I. Computational Details

The calculations are performed using the plane-waves DFT code Quantum Espresso.¹ The vdW-DF2-C09 van der Waals (vdW) density functional²⁻⁴ is employed to incorporate the electron exchange interactions and the library of SSSP efficiency pseudopotentials^{5,6} is used to treat the electron ion interactions. Wavefunction and charge density cutoffs of 45 and 360 Ry respectively are chosen. The Brillouin Zone is sampled using a Γ -centered Monkhorst-Pack grid, with a maximum k-point distance along the periodic distance less than 0.1 Å⁻¹. The relaxations and the binding energies of the 3D structures have been calculated using a Marzari-Vanderbilt cold smearing of 0.02 Ry.⁷ A vacuum space of 20 Å is added along the non-periodic direction for the 2D materials, in order to remove fictitious interactions between the periodic images. Moreover, periodic boundary conditions along the direction perpendicular to the slab are corrected using a parabolic correction scheme, as derived by Andreussi and Marzari⁸ for simulations in vacuum or in continuum dielectric media and extended in Ref.⁹ for continuum electrolyte media.

The electrochemical interface has been defined by an implicit solvation model, where the

2D material surfaces and the adsorbed H⁺ ions are treated quantum mechanically using a symmetric slab approach and the aqueous medium is represented by a polarizable continuum (PC) with dielectric permittivity of 78.3. The geometry of the dielectric cavity is determined from the electronic density of the quantum mechanical system following the self-consistent continuum solvation (SCCS) model^{8,10,11} implemented in the ENVIRON-1.1 module¹² and coupled with the Quantum Espresso code.¹³ The electrostatic potential within the bulk of the dielectric continuum represents the absolute reference for electrostatic potentials. The potential of the electrode is changed by varying the total number of the electrons in the system. These net charges are compensated by the counter charges of the electrolyte ions in the electrochemical double layer within the solution. Charge neutrality insures that the reference potential in the bulk of the solution is flat. The applied electrode potential is computed from the Fermi energy of the system, as obtained in the absolute electrostatic potential scale. While the solution of the full non-linear Poisson-Boltzmann equation for the diffuse layer is available in Environ 1.1,^{9,14} due to the regular planar nature of all of the studied systems, a more robust and computational inexpensive approach is used to model the diffuse layer. Namely, the screening of the electrolyte double layer is described by the Gouy-Chapman-Stern model, such that one-dimensional Poisson-Boltzmann equation is solved analytically considering planar-averaged counter charges of the electrolyte on both sides of the surfaces at a distance of 6.5 Å along the non-periodic z-axis.⁹ The electrolyte concentration is considered to be 1 M. The surface energy values and the H⁺ electrosorption energies are calculated using Grand-Potential Simulation scheme as discussed in the next section. 15

In a recent study, it has been found that a hybrid continuum-explicit solvent model provides a better description of the electrochemical interfaces.^{16,17} Considering the large number of the 2D materials studied, we avoided the inclusion of the explicit solvation effects at this stage of the screening process. However, we study the effect of explicit water molecules on the H^+ adsorption free energies for the two compounds as CoO₂ and FeS, without any external potential. The section S-VII provides the details of the hybrid (continuum-explicit) simulations for these two materials.

S-II. Grand-Potential Simulation Scheme

The Grand Potential of the 2D materials interfaced with the dielectric medium is determined by the minimization of interfacial free energy $J_{IP}(\alpha, N_s, N_i, N_e)$, defined as the Legendre transformation of the DFT calculated Gibbs free energies $G_{DFT}^{2D}(\alpha, N_s, N_H, N_e)$ with respect to the configuration space (α, N_s, N_H, N_e) as shown in eq. S1. The configuration space denotes the local basin in the phase space represented by the number of the atoms present in the 2D-materials N_s , the adsorbed H⁺ ions N_H , the electronic charge N_e and equilibrium structure α of the 2D-materials.

$$J_{IP}(\alpha, N_s, N_e, N_H) = G_{DFT}^{2D}(\alpha, N_s, N_e, N_H) - \mu_s N_s - \mu_e N_e - \mu_H N_H + T\Delta S_{conf}$$
$$= G_{DFT}^{2D}(\alpha, N_s, N_e, N_H) - G_{DFT}^{3D} - \mu_e N_e - \mu_H N_H + T\Delta S_{conf} \qquad (S1)$$
$$= \Delta G_{DFT} - \mu_e N_e - \mu_H N_H + T\Delta S_{conf}$$

The possible 3D structures as reported by Mounet et. al.,¹⁸ from which the 2D material could be exfoliated serves as the reservoir for the atoms (N_s) and hence $\mu_s N_s$ corresponds to the G_{DFT}^{3D} . Thus, ΔG_{DFT} corresponds to the binding energy or exfoliation energy of the 2D materials with respect to most stable 3D structure. However, for some of the 2D materials, the reported bulk structures have intercalated heterostructural units. For these compounds, the atomic reservoirs are considered as the alternative stable 3D bulk materials with similar composition as the 2D materials. The absolute surface charge N_e is the number of electrons exchanged with the external circuit, measured with respect to corresponding the chargeneutral state. This is denoted in eq. S2 as the sum of the charges needed to compensate the charges of the adsorbed H⁺ ions and the net surface charges N_e^{net} , which induces counter

charges of the electrolyte in the diffuse layer.

$$N_e = N_H + N_e^{net} \tag{S2}$$

The μ_e corresponds to the workfunction or the absolute electrode-potential (Φ , eq. S3) and μ_H represents the electrochemical potential of the H⁺ ions at the corresponding pH. The μ_H is obtained using the Nearst equation (eq. S4) considering the standard potential equivalent to the experimental absolute Standard Hydrogen Electrode potential (SHE) of 4.44 V.

$$\mu_e = WF = -e\Phi \tag{S3}$$

$$\mu_H = \frac{1}{2}\mu_{\mathrm{H}_2(g)} - k_B T ln(10) \cdot pH + 4.44 eV \tag{S4}$$

In eq. S4, $\mu_{H_2(g)}$ is the DFT calculated total energy of the molecular H₂ at 0 K. The $T\Delta S_{conf}$ term in eq. S1 denotes the configurational entropy term defined by eq. S5. Here, θ is the surface coverage, calculated as the ratio of the adsorbed H⁺ ions to the total number of accessible sites on the surface of the 2D materials.

$$T\Delta S_{conf} = N_H k_B T [\theta l n \theta + (1 - \theta) l n (1 - \theta)]$$
(S5)

The equilibrium Grand potential free energy $J(\Phi)$ of the clean 2D-material surface is obtained by interpolation of interfacial free energy $(J_{IP}(\alpha, N_s, N_e), \text{ eq. S1})$ on Φ without the adsorbed ions, followed by the minimization with respect to the extensive variable N_e (eq. S6). In the presence of the adsorbed H⁺ ions, the equilibrium Grand potential free energy $J(\Phi, \mu_H)$ is calculated in the similar way, however in this case the interpolation and the minimization of the interfacial free energy is done also accounting the surface coverage of the H⁺ ions and pH of the medium. At first the potential dependence of the interface energy $J_{IP}(\alpha, N_H, N_s, N_e)$ is interpolated on Φ for each H⁺ coverage. The interface energy obtained at each Φ is subjected to interpolate with respect to the different surface coverage with a polynomial upto order 2. In these calculations, we limit the surface coverage upto 50%, since with higher coverage, some of the 2D materials show considerable surface reconstruction. The expression obtained after addition of the analytic terms, involving the contribution from the pH ($k_B Tln(10) \cdot pH$), configuration entropy correction ($T\Delta S_{conf}$) and electrochemical potential of H⁺ ions in solution ($\mu_H N_H$) to the interface energy is then minimized with respect to coverage at the target pH to obtain the equilibrium Grand potential of the H⁺ covered surface (eq. S7). The surface energies for the clean 2D-materials surface (γ) and H⁺ ions covered surface (γ_H) is determined by normalizing the equilibrium Grand Potential free energies respectively with respect to the interfacial area A (eq. S6 and eq. S7).

$$\gamma = \frac{1}{2A} J(\phi) = \frac{1}{2A} \min_{(N_e)} \{ J_{IP}(\alpha, N_s, N_e) \}$$
(S6)

$$\gamma_H = \frac{1}{2A} J(\Phi, \mu_H) = \frac{1}{2A} \min_{(N_e, N_H)} \{ J_{IP}(\alpha, N_s, N_e, N_H) \}$$
(S7)

$$\Delta G_{ads}^{sol}(\Phi, pH) = J(\Phi, \mu_H) - J(\phi) + \Delta E_{ZPE} - T\Delta S_{ads}$$
(S8)

The binding energy of H^+ on the surface at certain applied potential and pH is the corresponding energy differences between the grand potentials of H^+ ions covered surface and the clean surface (eq. S8). In order to account for the Zero Point Energy (ZPE) and the entropy of the H^+ ions, we have added an energy correction term. The ΔE_{ZPE} represents the Zero Point Energy difference between the free and adsorbed H^+ ions. Since the vibrational entropy for the adsorbed state is small, the entropy term ΔS_{ads} is considered almost equivalent to experimental entropy of gaseous H_2 at standard state, i.e. $\Delta S_{ads} \approx -\frac{1}{2}S_{H_2}^o$. The ΔE_{ZPE} is calculated from the vibrational frequencies of the adsorbed H atoms using normal mode analysis.

S-III. Choice of SCCS parameters

A simplified version of the SCCS model is used, where the total energy of the system includes the DFT computed energy and the electrostatic interactions comprising of the dielectric and the counter electrolyte charges. Other non-electrostatic contributions to the solvation free energy are not incorporated, as their formulation in terms of the quantum-surface of the $system^{10,19}$ makes them less important for the studied two-dimensional systems and would add marginal shifts in the total energy values. With this simplification, the onset and the width of the dielectric continuum depends upon two parameters denoted as ρ_{max} and ρ_{min} values.¹⁰ The effect of these parameters is determined by studying their dependence on the surface energy values (eq. S6) of graphene monolayer with and without the aqueous solvation and validated with respect to the corresponding experimental value. The ρ_{max} value is varied within the range of the 0.001 to 0.020, whereas the ρ_{min} is varied from 0.0001 to 0.002. The variation in the surface energy values for graphene in water, i.e. with an embedding dielectric permittivity corresponding to 78.3, is shown in Figure S1. The surface energy of the graphene in vacuum has been determined in several theoretical studies. The latest theoretical study is by Bjorkman et. al.,²⁰ where the surface energy of graphene is calculated to be around 9.16 and 9.31 meV/Å 2 using the random phase approximation and vDW-Density Functional theory respectively. Compared to these theoretical values, in a recent experimental study, 21 the vacuum surface energy value is found to be around 7.18 meV/Å^2 , whereas in presence of aqueous medium, the value is reduced to 5.61 meV/Å². In our calculations, the surface energy of the Graphene without any implicit solvation is obtained to around 10.15 $\mathrm{meV/\AA^2},$ shifted by around 2.97 meV/Å 2 with respect to the experimental magnitude. Considering the similar shift for the calculated surface energy values in implicit aqueous solvation with respect to the experiment, the region enclosed within black dotted lines in the Figure S1 corresponds to the ρ_{max} and ρ_{min} values. In this region, the surface energy values vary from 8 to 8.77 meV/Å². The black circle denotes the final choice of the parameters for this study corresponding to $\rho_{max} = 0.01025$ and $\rho_{min} = 0.0013$, for which the surface energy is found to be 8.55 meV/Å², shifted by around 2.94 meV/Å² with respect to the experimental value. The solvation energy ΔE_{solv} , obtained as the difference between the vacuum and the aqueous surface energy values, is found to be around 1.60 meV/Å². This energy difference is in very good agreement with the experimentally determined energy difference between the vacuum and solvated surface energies (1.57 meV/Å²) as shown in Table T1.



Figure S1: The dependence of the surface energy values of graphene in implicit SCCS solvation with respect to different ρ_{min} and ρ_{max} values. The colormap denotes the surface energy values in meV/Å². The preferred values for the ρ_{min} and ρ_{max} used for this study is shown with the black circle.

Table T1: The experimental and the calculated surface energy values for graphene monolayer. The energy values are in meV/Å². The ΔE_{solv} denotes the solvation energy calculated as the difference between the vacuum and the aqueous surface energy values.

	γ_{exp}^{21}	γ_{calc}	$\gamma_{exp} - \gamma_{calc}$
vac	7.18	10.15	2.97
$\epsilon = 78.3$	5.61	8.55	2.94
ΔE_{solv}	1.57	1.60	

S-IV. Aqueous Stability of the 2D materials



Figure S2: The aqueous decomposition free energy, $\Delta G_{pbx}(\Phi, pH)$ in eV/atom for the reference compounds reported by singh et. al,²² benchmarked with respect to the experimental aqueous stability.

The aqueous stability of the 2D materials are calculated as the Gibbs free energy differences with respect to the different Pourbaix stable domains as reported in Materials Project (MP) database²³ at the corresponding pH and applied potentials following the formalism proposed by Singh et. al.²² The reference energies of the solid elements, solid oxides, water, oxygen, hydrogen and other gaseous molecular compounds is calculated using the methodology reported by Persson et. al.^{24,25} The aqueous energies of the ions and the neutral species are also calculated using the similar formulations from ref. 23, with the reference energies taken from ref. 24. For the 2D-materials solvated in aqueous medium, the reference energies are obtained from the Grand-potential calculations. The concentration of the aqueous species is considered to be 10^{-6} M. The enthalpy difference $(\Delta G_{pbx}(\Phi, pH))$ with respect to the decomposition products equivalent to 0 is regarded as stable, however the compounds with decomposition energy up to 0.5 eV normalized with respect to the non-H and O atoms is found to be stable by Singh et. al.²² We recalculated the decomposition energies for the reference compounds benchmarked in ref. 21 and compared with the corresponding decomposition energies obtained from the MP database,²³ re-normalized with respect to the total number of atoms as shown in Figure S2. The threshold for aqueous stability, $\Delta G_{pbx}(\Phi, pH)$ is obtained to around 0.3 eV/atom.

S-V. Band Structures

The band-structure calculations are done using the GGA-PBE functional with the Hubbard correction term U.^{26,27} We have used the U values, already optimized for different elements following the pseudo-hybrid Hubbard density functional ACBN0.²⁸ The Figure S3, S4 and S5 shows the Band-structure diagrams for the 22 monolayers which show lower over-potentials for HER and found to have zero band-gap at GGA-PBE functional. All the monolayers remain metallic with GGA+U functional except for TiSe₂. An in-direct band-opening of around 0.18 eV is observed for TiSe₂, along with the direct band-gap of around 0.57 eV at Γ . The red-dotted line denotes the Fermi-level.



Figure S3: Band-Structure plots for monolayers. All these monolayers have an orthorhombic unit cells except for Graphene and Zr_2PTe_2 .



Figure S4: Band-Structure plots for monolayers belonging to MoS₂ prototype



Figure S5: Band-Structure plots of the monolayers belonging to ${\rm CdI}_2$ prototype.

S-VI. The potential vs pH plot



Figure S6: The Φ vs pH plot for the six monolayers for which the electrocatalytically active region (the unshaded area) do not coincide with the aqueous stability region. These compounds would decompose to stable aqueous species at reducing potentials and acidic pH. The colormap of the plots refers to the aqueous decomposition free energies $\Delta G_{pbx}(\Phi, pH)$ with respect to the most stable compound-specific ionic, molecular, elemental and solid decomposition products.

S-VII. Hybrid continuum-explicit simulations

The Hybrid continuum/explicit simulations are performed with neutral simulation cells in the presence of an embedding SCCS solvent for CoO_2 and FeS, having one proton adsorbed on the surface. The explicit water arrangement are obtained following four different simplified hybrid models: 1) a single water molecule coordinating the adsorbed proton; 2) two water molecules coordinating the adsorbed proton; 3) seven uncorrelated realizations of a random water bilayer, generated with the packmol package²⁹ at the experimental water density; 4) one ice-like structure of a water bilayer. The Figure S7 and S8 show the arrangement of the water molecules after relaxation with the difference in the adsorption free energies obtained for the full implicit and hybrid models.



Figure S7: The relaxed arrangement of the water molecules on the FeS surface. The yellow spheres represent the surface S atoms and the Fe atoms are represented by the brown spheres. The energy values correspond to the difference in the adsorption energies computed with the full implicit and the hybrid models $(E_{implicit} - E_{hybrid})$.

The adsorption free energies of the proton on the material surfaces are stabilized for both the monolayers. The stabilization is small for the FeS monolayer, however CoO_2 shows effectively larger stabilization except for the random arrangement of the water molecules. This is due to the presence of relatively greater hydrogen bond interactions between the water molecules and the surface O atoms, compared to FeS. The effect of increased stabilization would result into shifting the catalytically active region (denoted as the unshaded area in



Figure S8: The relaxed arrangement of the water molecules on the CoO_2 surface. The red spheres represent the surface O atoms and the Co atoms are represented by the blue spheres. The energy values correspond to the difference in the adsorption energies computed with the full implicit and the hybrid models $(E_{implicit} - E_{hybrid})$.

Figure 3, main text) towards slightly higher pH values for both FeS and CoO_2 . FeS would show a rather small shift, since the interaction between the surface and adsorbates are weak. On the other hand, the average stabilization obtained from the considered models for CoO_2 would shift the catalytic active region of this material to around neutral pH values. Figure S9 shows a comparative plot for the relative shift of the catalytic active region in CoO_2 obtained with the full continuum solvation model and the hybrid model with the water overlayers having hexagonal ice like arrangement.

In general, extensive molecular dynamics simulations are required to determine the accurate shift of the catalytic active region due to the stabilization obtained when explicit layer of water molecules are added in the hybrid solvation models.^{30,31} In our models, the thermodynamic effects linked to the mobile statistical nature of water molecules are mostly omitted, owing to the fact that all configurations are optimized in a zero temperature limit. While cluster calculations and ice-like structures appear to significantly stabilize hydrogen adsorption, inclusion of thermal effects may favor more disordered configurations, for which the stabilization is shown to be negligible. Therefore the relative positioning of the catalytic active region might deviate slightly within the plots shown in Figure S9.



Figure S9: The Φ vs pH plot for CoO₂ surface. (a) The catalytic active region (unshaded area) is determined with the full continuum solvation model. (b) The catalytic active region shown for the hybrid explicit/continuum solvation model with the water overlayers forming hexagonal ice like arrangment. The extra stabilization of -0.26 eV (Figure S8 panel 4) shift the catalytic active region to around neutral pH in (b) compared to the full continuum solvation model in (a). The colormap of the plots correspond to the aqueous decomposition free energies $\Delta G_{pbx}(\Phi, pH)$ as shown in Figure S6.

Overall, as the aqueous stability enhances at the higher pH values in presence of reducing

applied potentials, the catalytic performance for HER is expected to increase for both FeS and CoO_2 .

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