Supporting information for:

Density Functional Theory Calculation of the

Band Alignment of $(10\bar{1}0)$ In$_x$Ga$_{1-x}$N/Water

Interfaces

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The DFTMD calculation of the valence band edge (VBE) and conduction band edge (CBE) of the fully solvated model systems listed in Table 1 of the main text follows the procedure outlined in detail in previous technical papers. The method was developed for the DFTMD computation of the equilibrium constants of homogeneous acid-base and redox reactions[S1–S3] and was subsequently extended to heterogeneous systems.[S4] The relevant equations are given in the method section. The practical implementation of these equations will be illustrated here for the example of the HSE06 bandedges for GaN and InN. For a detailed explanation we refer to the original publications. The necessary data are summarized in Table S1. This includes the vertical gaps not given in the main text.

Table S1: MD averaged vertical energy gaps $\langle \Delta E \rangle_\eta$ and corresponding thermodynamic integrals $\int_0^1 d\eta \langle \Delta E \rangle_\eta$ used to compute the HSE06 results for the fully solvated GaN and InN systems given in Table 1 of the main text. The thermodynamic integrals have been obtained from the vertical energies using Eq. 3 (see text). Units are eV. The pbc qualifier added in brackets indicates that the energies have been computed from total energy differences of model systems under full periodic boundary conditions. X stands for the solvated neutral slab. $q = 0$ in the calculation of the VBE and CBE as carried out here.

		$\langle \Delta E(\mathrm{pbc}) \rangle_\eta$			$\int_0^1 d\eta \langle \Delta E(\mathrm{pbc}) \rangle_\eta$
	η	0.0	0.5	1.0	
GaN	$X^q \rightarrow X^{q+1} + e^-$	0.42	0.33	-0.01	$\mathrm{AIP}_q(\mathrm{pbc}) = 0.27$
	$H_3O^+ \rightarrow H_2O + H^+$	20.97	18.76	13.90	$W_{H^+}(\mathrm{pbc}) = 18.10$
	$X_{q-1} + H_3O^+ \rightarrow X_q + H_2O + e^- + H^+$	18.45	14.96	10.78	$\mathrm{AEA}_q + W_{H^+} = 14.79$
InN	$X^q \rightarrow X^{q+1} + e^-$	0.10	-0.31	-1.00	$\mathrm{AIP}_q(\mathrm{pbc}) = -0.38$
	$H_3O^+ \rightarrow H_2O + H^+$	20.60	18.96	14.84	$W_{H^+}(\mathrm{pbc}) = 18.34$
	$X_{q-1} + H_3O^+ \rightarrow X_q + H_2O + e^- + H^+$	19.37	16.74	13.53	$\mathrm{AEA}_q + W_{H^+} = 16.60$

Following the generalized notation of the technical summary of the MDHE method, the neutral solid is indicated by X^q with $q = 0$. The ionization reaction $X^q \rightarrow X^{q+1} + e^-$ and hydronium deprotonation $H_3O^+ \rightarrow H_2O + H^+$ are half reactions. The corresponding vertical energies are directly obtained from total energy differences under periodic boundary conditions (pbc). For the ionization reaction the energy gap ΔE is the vertical ionization

potential IP and is computed as

$$\Delta E_q = E_{q+1} - E_q \tag{1}$$

where E_{q+1} and E_q are the total energy of the ionized and neutral system respectively (recall $q = 0$). ΔE_q is specific to the composition of the model system.

The computation of the vertical energy gap for deprotonation of an hydronium, $H_3O^+ \rightarrow H_2O + H^+$ is again based on total energy differences for fixed ionic configurations, one configuration having one proton more than the other. The proton is however not completely removed. Instead its charge is set to zero turning it into a "ghost" proton H^* invisible to all charge in the system but still attached to the reactant hydronium by a harmonic potential. We can therefore write

$$\Delta E_{H_3O^+} = E_{H_3O^+} - E_{H_2OH^*} \tag{2}$$

where $E_{H_3O^+}$ is the total energy of the system containing a certain number of water molecules plus the solid slab and one single hydronium ion H_3O^+ placed in the middle of the water zone away from the surface. $E_{H_2OH^*}$ is the total energy of the system with one of the three hydronium protons exchanged for a charge neutral ghost proton. Technical details of this procedure can be found in Refs. S1 and S2. The method has been validated by comparing the computed pKa of a number of small acids to experiment.[S2,S3] The experimental values could be reproduced within 2 pK units corresponding to an uncertainty of 0.10 - 0.15 eV.

The instantaneous vertical gap ΔE is averaged over MD trajectories generated by the mapping Hamiltonian Eq. 2 for a set of values of the coupling parameter η. The resulting time average is indicated by $\langle \Delta E \rangle_\eta$ in Table S1. Because of the computational costs of HSE06 calculations the number of η values is limited to three ($\eta = 0.0, 0.5, 1$). This leads to a three point numerical estimate of the thermodynamic integral $\int_0^1 d\eta \langle \Delta E \rangle_\eta$. The three point approximation used here is the trapezium rule

$$\int_0^1 d\eta \langle \Delta E \rangle_\eta = \frac{h}{2} \left(\langle \Delta E \rangle_{\eta=0} + \langle \Delta E \rangle_{\eta=0.5} \right) + \frac{h}{2} \left(\langle \Delta E \rangle_{\eta=0.5} + \langle \Delta E \rangle_{\eta=1.0} \right) \tag{3}$$

with interval width $h = 0.5$. Note that the three point approximation used in our previous publications is the Simpson rule

$$\int_0^1 d\eta \langle \Delta E \rangle_\eta = \frac{1}{6} \left(\langle \Delta E \rangle_{\eta=0} + \langle \Delta E \rangle_{\eta=1} \right) + \frac{2}{3} \langle \Delta E \rangle_{\eta=0.5} \qquad (4)$$

which gives an end point ($\eta = 0.0, 1.0$) a slightly smaller weight (1/6 instead of the 1/4 of Eq. 3). The differences in the estimate of the thermodynamic integrals are however small.

The thermodynamic integral $W_{\mathrm{H}^+}(\mathrm{pbc}) = 18.10$ eV in Table S1 is the proton workfunction of Eq. 7 for the GaN model system. Combining with the constants $\mu_{\mathrm{H}^+}^{g,\circ} = 15.81$ eV and $\Delta E_{\mathrm{zp}} = 0.35$ and substituting in Eq. 6 we obtain the MDHE potential $U_{\mathrm{H}^+/\mathrm{H}_2}^\circ(\mathrm{pbc}) = -1.94$ V. We repeat the warning that this is not an universal parameter, but specific to the chosen GaN model system. $\mathrm{AIP}_q(\mathrm{pbc}) = 0.27$ eV of Table S1 is the adiabatic ionization potential of Eq. 3 of the main text. Substituting in Eq. 12 we recover the adiabatic GaN VBE at 1.21 V vs SHE listed for HSE in Table 1 of the main text.

To obtain the corresponding CBE the electron and proton have been inserted simultaneously applying what we called the full reaction scheme. Separate calculation of the adiabatic electron affinity $\mathrm{AEA}_q(\mathrm{pbc})$ and $W_{\mathrm{H}^+}(\mathrm{pbc})$ is avoided. We directly obtain the sum $\mathrm{AEA}_q + W_{\mathrm{H}^+}$ which is not affected by the uncertainty in the electrostatic reference potential (hence we have omitted the (pbc) argument) but still, of course, sensitive to finite system system size errors. All what is needed is to subtract the constant offset $\mu_{\mathrm{H}^+}^{g,\circ} + \Delta E_{\mathrm{zp}} = 16.16$ eV from the $\mathrm{AEA}_q + W_{\mathrm{H}^+} = 14.79$ eV estimate of Table S1 and we obtain the -1.37 V SHE alignment of the GaN CBE in Table 1 of the main text.

The full reaction scheme has certain advantages over the half reaction scheme because systems with net total charge are avoided. The full reaction scheme for calculation of the VBE is however more involved. Removing an electron and proton from the neutral system leaves it with a hole in the solid and an OH^- ion. To transform to the SHE potential a separate calculation of the dissociation constant (pKw) of water is needed. This calculation

has been carried out for pure water.[S3] While this result should in principle be transferable to "bulk" water in heterogeneous systems, finite system size errors are in practice a complication, which is why we have used the half reaction scheme to determine the VBE.

References

(S1) Cheng, J.; Sulpizi, M.; Sprik, M. Redox Potentials and pKa for Benzoquinone from Density Functional Theory Based Molecular Dynamics. *J. Chem. Phys.* **2009**, *131*, 154504.

(S2) Costanzo, F.; Della Valle, R. G.; Sulpizi, M.; Sprik, M. The Oxidation of Tyrosine and Tryptophan Studied by a Molecular Dynamics Normal Hydrogen Electrode. *J. Chem. Phys.* **2011**, *134*, 244508.

(S3) Cheng, J.; Liu, X.; VandeVondele, J.; Sulpizi, M.; Sprik, M. Redox Potentials and Acidity Constants from Density Functional Theory Based Molecular Dynamics. *Acc. Chem. Res.* **2014**, *47*, 3522–3529.

(S4) Cheng, J.; Sprik, M. Alignment of Electronic Energy Levels at Electrochemical Interfaces. *Phys. Chem. Chem. Phys* **2012**, *14*, 11245–11267.