Supporting Information

Where photogenerated holes at the g-C$_3$N$_4$/water interface go for water splitting: H$_2$O or OH$^-$?

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Figure S1. Electronic levels (relative to vacuum) of the highest occupied molecular orbitals localized on OH\(^-\) and g-C\(_3\)N\(_4\) at \(\Gamma\) point in DFT-PBE for 11 snapshots taken between 3 ps and 4 ps in the room-temperature (RT) relaxation for (a) g-C\(_3\)N\(_4\)/OH\(^-\)\(_\text{inter}\) and (b) g-C\(_3\)N\(_4\)/OH\(^-\)\(_\text{bulk}\). Two sets of results are compared. Square and circle: for structures derived from RT relaxation by DFT-PBE directly. Up and down triangles: for structures that are further optimized by van der Waals interaction corrected PBE.
Figure S2. Convergence tests of parameters in $GW$ using a $g$-$C_3N_4^{OH_{bulk}}$ structure as the example. (a) and (b): evolution of CBM, the highest valence band localized on O atom in OH$^-$ [VBM(O)], the highest valence band localized on N atoms in $g$-$C_3N_4$ [VBM(N)], the band gap between CBM and VBM(O) [$E_g$(O)] and the band gap between CBM and VBM(N) [$E_g$(N)] at Γ point with the cutoff energy applied in the band summation over unoccupied orbitals ($E_{\text{cut}}$) for the evaluation of self-energy. In this test, $E_{\text{cut}}$ for the evaluation of electronic screening is set to 13 eV. (c) and (d): evolution of CBM, VBM(O), VBM(N), $E_g$(O) and $E_g$(N) at Γ point with $E_{\text{cut}}$ for the evaluation of electronic screening. In this test, $E_{\text{cut}}$ for the evaluation of self-energy is set to 13 eV. In (a)-(d), $E_{\text{cut}}$=0 corresponds to CBM, and the length of supercell along the normal of $g$-$C_3N_4$ is set to 30 Å. (e) and (f): evolution of CBM, VBM(O), VBM(N), $E_g$(O) and $E_g$(N) at Γ point with the length of supercell along the normal of $g$-$C_3N_4$. In this test, $E_{\text{cut}}$ for both self-energy and electronic screening are set to 9.5 eV to save the computational cost.
Figure S3. Configurations and DFT-LDA band structures for the g-C$_3$N$_4$/H$_2$O interfaces with planar [(a) and (c)] and distorted [(b) and (d)] g-C$_3$N$_4$.

Figure S4. Total and partial DOS for g-C$_3$N$_4$/H$_2$O, g-C$_3$N$_4$/OH$_{\text{inter}}$ and g-C$_3$N$_4$/OH$_{\text{bulk}}$ computed within DFT-PBE. Interface configurations are derived from the snapshot at 5 ps in the room-temperature relaxation.
Figure S5. Top (a) and side (b) views of $\text{g-C}_3\text{N}_4^{OH_{\text{inter}}}$ with an $\text{OH}^-$ at the interface in a rectangular $2 \times 2\sqrt{3}$ supercell. This structure corresponds to the 5 ps snapshot in the room-temperature relaxation of this supercell. $\text{OH}^-$ and its $\text{H}_2\text{O}^+$ counterpart are marked by a black circle and a cyan circle respectively in (b).
Figure S6. (a): Total and partial DOS computed within DFT-LDA for the structure in Figure S5. (b) and (c): Molecular orbital distributions at Γ point for the two energy levels which are marked by α and β in (a) respectively.

Figure S7. Structures of g-C$_3$N$_4$$^{\text{OH\_inter}}$ with one (a), two (b) and three (c) layers of g-C$_3$N$_4$. 
Figure S8. Energy level difference at \( \Gamma \) point between the highest occupied molecular orbital localized on \( \text{OH}^- \) and that on \( \text{g-C}_3\text{N}_4 \) calculated by DFT-LDA for \( \text{g-C}_3\text{N}_4'/\text{OH}^- \) with monolayer, bilayer and trilayer \( \text{g-C}_3\text{N}_4 \) (see Figure S7 for the structures).

Structures for monolayer \( \text{g-C}_3\text{N}_4 \) are taken from 11 snapshots between 3 ps and 4 ps in the room-temperature relaxation of \( \text{g-C}_3\text{N}_4'/\text{OH}^- \) as described in the main context. To get structures for bilayer and trilayer ones, one or two additional \( \text{g-C}_3\text{N}_4 \) layers are placed beneath the monolayer \( \text{g-C}_3\text{N}_4 \) with initial interlayer distance set to 3.3 Å, and then the full system is optimized by DFT-PBE with the van der Waals interaction taken into account.
Figure S9. Corresponding molecular orbitals for the electronic levels related to OH\(^{-}\) and H\(_2\)O shown in Figure 3.

Figure S10. Spatial distributions of the photogenerated hole (a) and electron (b) for the lowest charge-transfer excited state \(S_1(\text{OH}^-)\) at 3.3 eV in g-C\(_3\)N\(_4\)/OH\(_{\text{bulk}}^-\).