

Deciphering the Role of Hydrogen Bonding and Water Dynamics in Hole Transfer on Anatase TiO₂(101): An ab Initio Quantum Dynamics Study

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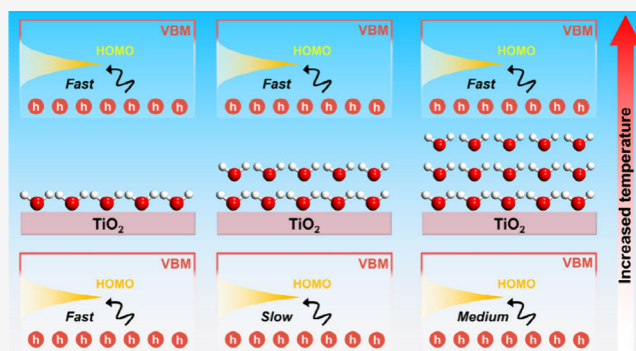


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Supporting Information

ABSTRACT: Using time-dependent density functional theory (TD-DFT) and nonadiabatic molecular dynamics (NAMD) simulations, we elucidate how hydrogen bonding and water dynamics regulate hole transfer at the anatase TiO₂(101)/water interface. Compared to low-density water (LW), moderate-density water (MW) enhances hydrogen bonding between surface- and nonsurface-adsorbed water, restricting interfacial water mobility. This suppresses nonadiabatic coupling and slows the hole transfer. Conversely, higher-density water (HW) near the vacuum destabilizes hydrogen bonding networks, freeing interfacial water and amplifying thermal motion. Enhanced disorder strengthens nonadiabatic coupling, accelerating the hole transfer. Temperature-dependent simulations show that thermal energy overcomes hydrogen bonding constraints: elevated temperatures intensify water dynamics and nonadiabatic coupling, accelerating hole transfer. These results establish hydrogen bonding and thermal fluctuations as key regulators of charge dynamics at the semiconductor/liquid interfaces.



Photocatalytic overall water splitting has emerged as a promising strategy for hydrogen production.¹ Following the seminal study of photocatalytic water splitting by Fujishima and Honda,² considerable efforts have been devoted to designing advanced photocatalytic materials, including two-dimensional layered material,³ metal–organic framework,⁴ and metal oxides.^{5–7} Among various photocatalytic materials, TiO₂ is widely applied due to its advantages such as abundant raw materials, nontoxicity, and high chemical stability.^{8,9} Despite these advancements, current overall water splitting efficiencies remain orders of magnitude below the thresholds required for viable solar fuel production.^{10,11}

Overall water splitting comprises two thermodynamically distinct half-reactions: hydrogen evolution reaction (HER, 2H⁺ + 2e[−] → H₂) and oxygen evolution reaction (OER, 2H₂O → O₂ + 4H⁺ + 4e[−]). The HER proceeds through a facile two-electron transfer pathway, while the OER mechanism involves a complex four-electron oxidation process with multistep proton-coupled electron transfer, rendering it thermodynamically demanding and kinetically sluggish. This inherent disparity in reaction pathways establishes OER as the principal kinetic bottleneck limiting the overall efficiency of photocatalytic water splitting systems.^{12,13}

Generally, the capture of photogenerated holes by water molecules is a crucial step in enhancing the overall OER process. Numerous researchers have conducted systematic

studies on the hole transfer mechanism at water/metal-oxide interfaces.^{14–16} For example, extensive research has proposed that hydrogen bonding formed at the solid–liquid interface is the primary factor responsible for facilitating hole transfer.^{17–19} Hydrogen bonding can provide a channel for hole transfer, thereby accelerating the process of hole transfer. In contrast, other studies have shown that multilayered water can inhibit the process of hole trapping, even if more hydrogen bonding are introduced.^{15,16} The observed phenomenon originates from the weakened interface interaction between the primary hydration layer and catalytic surfaces induced by multilayered hydration structures.²⁰ These findings demonstrate that specific solid–liquid interfacial interactions, rather than hydrogen-bonding effects alone, govern hole capture by water molecules.

To date, the mechanism underlying photogenerated hole capture by water molecules has not been fully elucidated. This fundamental knowledge gap necessitates a systematic investigation to unravel the interfacial charge transfer dynamics.

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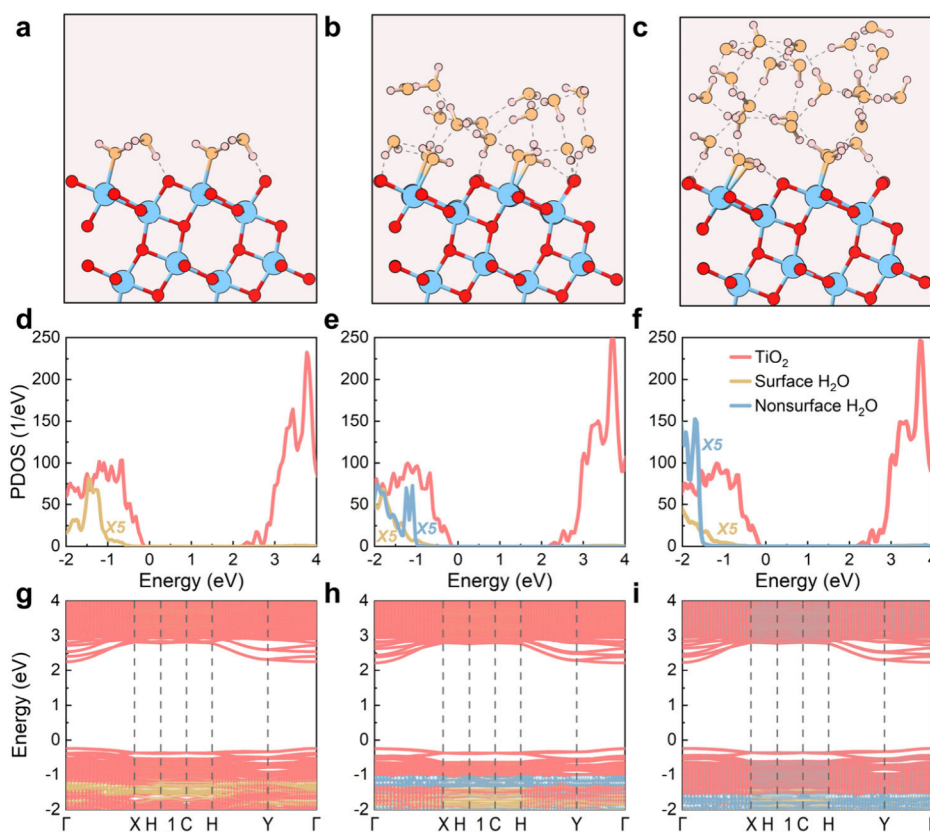


Figure 1. Optimized geometries, projected density of states (PDOS), and band structures of (a, d, g) TiO₂@LW, (b, e, h) TiO₂@MW, and (c, f, i) TiO₂@HW systems. The Ti, H, O in TiO₂ and H₂O are represented by blue, pink, red, and yellow spheres, respectively. The Fermi level is set to zero.

Nonadiabatic molecular dynamics (NAMD) is a universal atomic-scale simulated method that can investigate the processes of the photogenerated charge carrier dynamic. In this study, we employed the time-dependent density functional theory (TD-DFT)²¹ combined with NAMD^{22–24} methods to simulate the hole capture process by water molecules on TiO₂ surface, with a focus on the effects of hydrogen bonding and water dynamics on hole transfer process. Our simulations demonstrate that compared to low-density water (LW), moderate-density water (MW) enhances the hydrogen bonding between surface-adsorbed and nonsurface-adsorbed water molecules. This interaction suppresses the atomic mobility of surface-adsorbed water, leading to a reduced level of nonadiabatic coupling and sluggish hole transfer. Conversely, high-density water (HW) near the vacuum phase disrupts hydrogen bonding networks, thereby liberating surface water molecules and enhancing their thermal motion. These changes boost nonadiabatic coupling and accelerate the hole transfer. Temperature-dependent effects further amplify thermal agitation, overcoming hydrogen-bond-mediated constraints on the water mobility. At higher temperatures, the inhibitory role of hydrogen bonding diminishes, resulting in enhanced surface water dynamics, stronger nonadiabatic coupling, and faster hole transfer processes. These findings elucidate the fundamental physical mechanism by which water molecules modulate the charge carrier dynamics.

All DFT calculations, including geometry optimization, electronic structure, adiabatic molecular dynamics (MD), and nonadiabatic (NA) coupling, were performed using the Vienna ab initio simulation package (VASP).²⁵ The exchange–

correlation interaction was treated with the Perdew–Burke–Ernzerhof (PBE) functional,²⁶ and the electron–ion core interaction was described via the projector augmented wave (PAW) method.²⁷ The plane-wave energy cutoff was set to 400 eV. A $4 \times 2 \times 1$ Γ -centered Monkhorst–Pack k-point mesh was adopted for geometry optimization and electronic structure calculations. To overcome the shortcoming of the PBE functional that underestimates the band gap of metal oxides, we used the DFT+U method to describe the local properties of Ti 3d orbitals ($U = 4.2$ eV).²⁸ The energy convergence criterion of the electronic self-consistent field was 10^{-5} eV, and the structures were relaxed until the ionic force was less than 0.02 eV/Å. The weak van der Waals interactions were described using the Grimme DFT-D3 approach.²⁹ To identify the species of the weak interactions, we further analyzed the noncovalent interactions (NCI)³⁰ based on the reduced density gradient (RDG) method using the Visual Molecular Dynamics (VMD)³¹ and Multiwfn software.³²

The optimized geometries were heated to 100, 300, and 500 K via repeated velocity rescaling lasting for 1 ps. Subsequently, 6 ps MD trajectories were obtained in the microcanonical ensemble (NVE) with a 1 fs time step, and these adiabatic trajectories were used to compute the NA Hamiltonian. The 1000 trajectories were chosen as initial configurations from the MD trajectories for the NAMD simulations with the PYthon eXtension for Ab Initio Dynamics (PYXAID) code.^{22,23} The simulations of the hole transfer process were performed by the fewest switches surface hopping (FSSH) approach³³ implemented within TD-DFT²¹ in the Kohn–Sham representation.^{34,35} The lighter and faster electrons were treated quantum

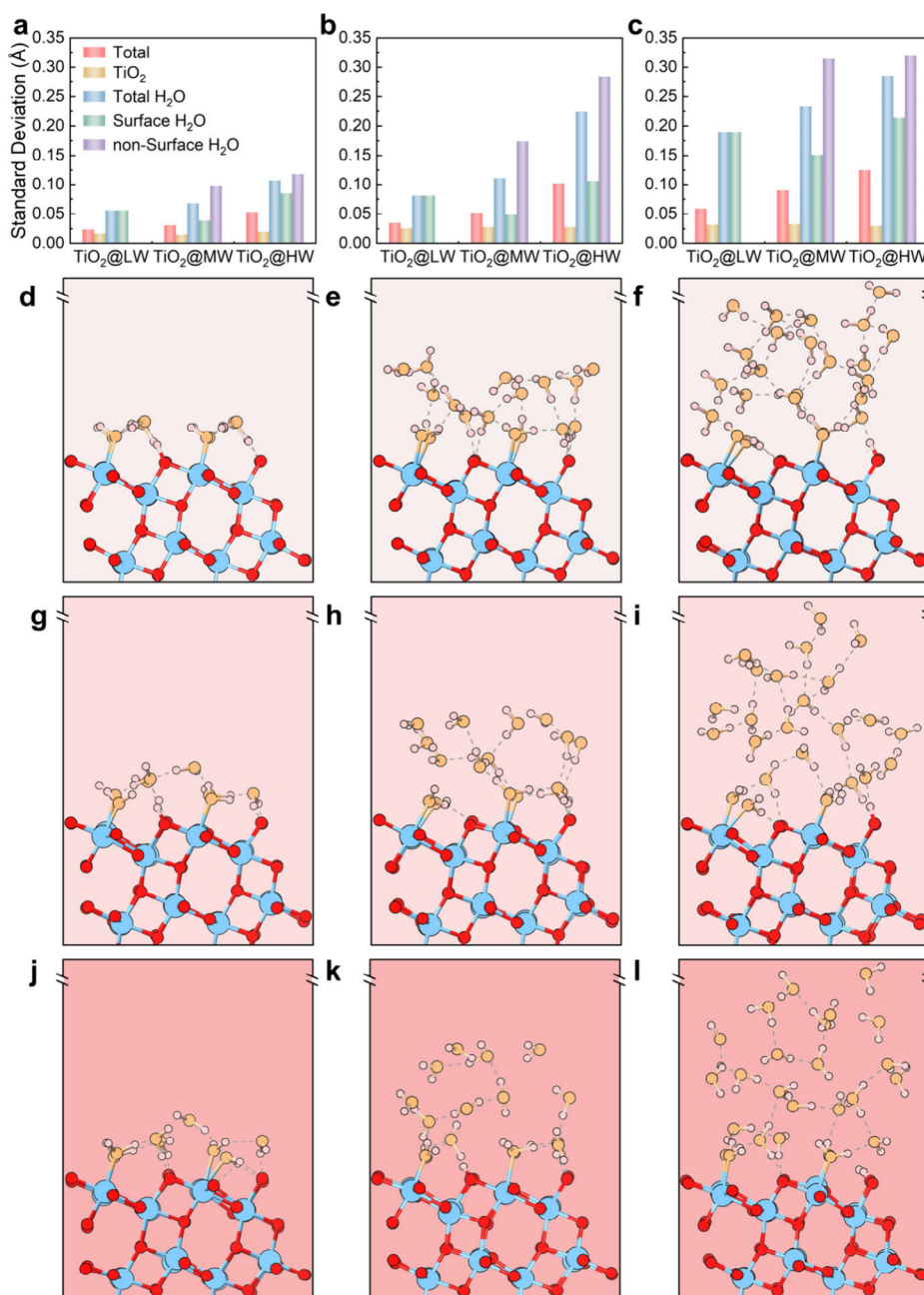


Figure 2. Averaged standard deviations in positions of all atoms in TiO₂@LW, TiO₂@MW, and TiO₂@HW systems at (a) 100 K, (b) 300 K, and (c) 500 K. Representative snapshots from (d–f) 100, (g–i) 300 K, and (j–l) 500 K MD trajectories in (d, g, j) TiO₂@LW, and (e, h, k) TiO₂@MW, and (f, i, l) TiO₂@HW systems. The Ti, H, O in TiO₂ and H₂O are represented by blue, pink, red, and yellow spheres, respectively.

mechanically, while the heavier and slower nuclei were described (semi)-classically. This approach has been used extensively and successfully to study excited-state dynamics in a broad range of materials,^{36–46} such as perovskites,^{36–40} silicon,⁴⁶ and transition metal dichalcogenides.⁴²

The optimized lattice constants of the unit cell of TiO₂ are $a = b = 3.771$ Å and $c = 9.430$ Å, which agree well with the experimental values of $a = b = 3.785$ Å and $c = 9.514$ Å.⁴⁷ A $2 \times 1 \times 1$ anatase TiO₂(101) surface is modeled as a periodic slab model, which has been employed in many theoretical studies.^{48–50} To explore the effect of hydrogen bonding and water dynamics on hole capture process on the anatase TiO₂(101) surface, we constructed three systems: TiO₂@LW, TiO₂@MW, and TiO₂@HW represent low-, moderate- and

high-density water on the surface of TiO₂. The “surface water” refers to water molecules that have strong interaction with the TiO₂ surface, and the “nonsurface water” refers to water molecules adsorbed above surface water via hydrogen-bonding interactions. To eliminate the interactions between adjacent layers, the vacuum region above the water layer was set to 15 Å.

First, we systematically investigate the geometric properties and electronic structures of TiO₂ across varying water density. Next, we analyze the temperature-dependent effects on the hydrogen bonding networks and water dynamics. Finally, we investigate the water-mediated hole capture process in three distinct systems to elucidate the interplay among hydrogen

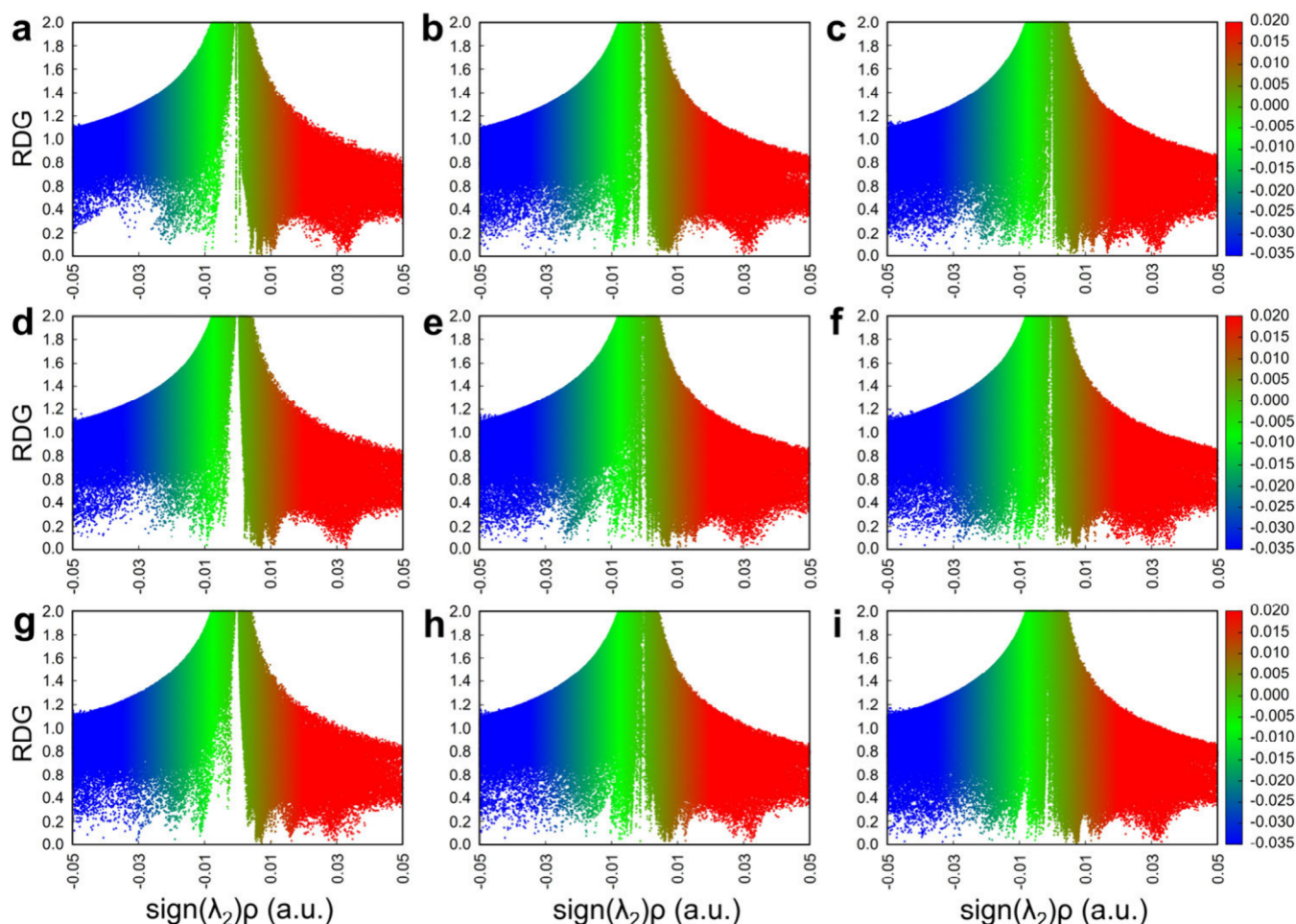


Figure 3. Reduced density gradient scatter graphs for (a, d, g) $\text{TiO}_2\text{@LW}$, (b, e, h) $\text{TiO}_2\text{@MW}$, and (c, f, i) $\text{TiO}_2\text{@HW}$ systems at (a–c) 100 K, (d–f) 300 K, and (g–i) 500 K.

bonding strength, water dynamics, and photogenerated hole capture efficiency.

Figure 1a–c displays the optimized geometries of $\text{TiO}_2\text{@LW}$, $\text{TiO}_2\text{@MW}$, and $\text{TiO}_2\text{@HW}$ systems. It can be seen that surface water molecules exhibit preferential adsorption at Ti_{5c} sites exposed on the TiO_2 surface in the three systems, while the remaining water molecules are stabilized through interconnected hydrogen-bond networks. The Ti–O frameworks exhibit perfect structural integrity with no observable distortion. Table S1 presents the average Ti–O bond lengths for these systems, revealing minimal variations among them (1.968 Å in $\text{TiO}_2\text{@LW}$, 1.970 Å in $\text{TiO}_2\text{@MW}$, and 1.972 Å in $\text{TiO}_2\text{@HW}$). These values align closely with experimental measurements.⁵¹

The projected density of states (PDOS) and band structures are divided into the contribution of TiO_2 , surface-adsorbed water, and nonsurface water molecules. As shown in Figure 1d–f, the conduction band minimum (CBM) and the valence band maximum (VBM) of the $\text{TiO}_2\text{@LW}$, $\text{TiO}_2\text{@MW}$, and $\text{TiO}_2\text{@HW}$ systems are separated by a band gap of 2.49, 2.46, and 2.47 eV, respectively. These values suggest minimal water adsorption effects on the intrinsic band gap of the TiO_2 semiconductor. Notably, the energy levels of surface water molecules within the valence band (VB) are positioned closer to the TiO_2 VBM compared to those of nonsurface water molecules. This spatial proximity indicates that photogenerated holes in the TiO_2 VB are preferentially trapped by surface-

adsorbed water molecules. Figure 1g–i further displays the calculated band structures, confirming that both VBM and CBM are localized at the Γ point. This direct band gap characteristic confirms that the anatase TiO_2 surface retains its direct band gap upon water adsorption.

To elucidate temperature effects on atomic dynamics in $\text{TiO}_2\text{@LW}$, $\text{TiO}_2\text{@MW}$, and $\text{TiO}_2\text{@HW}$ systems, we calculated canonically averaged atomic displacement standard deviations using the equation

$$\sigma_i = \sqrt{\langle (\vec{r}_i - \langle \vec{r}_i \rangle)^2 \rangle}$$

This analysis was performed for all atoms at 100, 300, and 500 K to quantify thermal fluctuations across the three systems. Here, r_i denotes the location of atom i , and the angular brackets represent ensemble averaging. Figure 2a–c and Tables S2–S4 present the computed standard deviations, where larger values indicate stronger atomic fluctuations. Corresponding representative snapshots are shown in Figure 2d–f and Figure S1. As the temperature increases, water molecules in all systems exhibit enhanced stochastic thermal motion and upward diffusion into the vacuum phase, while the Ti–O frameworks maintain structural integrity with negligible distortion.

At 100 K, increasing water density exhibits a minimal influence on the atomic fluctuations of TiO_2 , suggesting negligible effects on its structural stability. Relative to 0 K, the

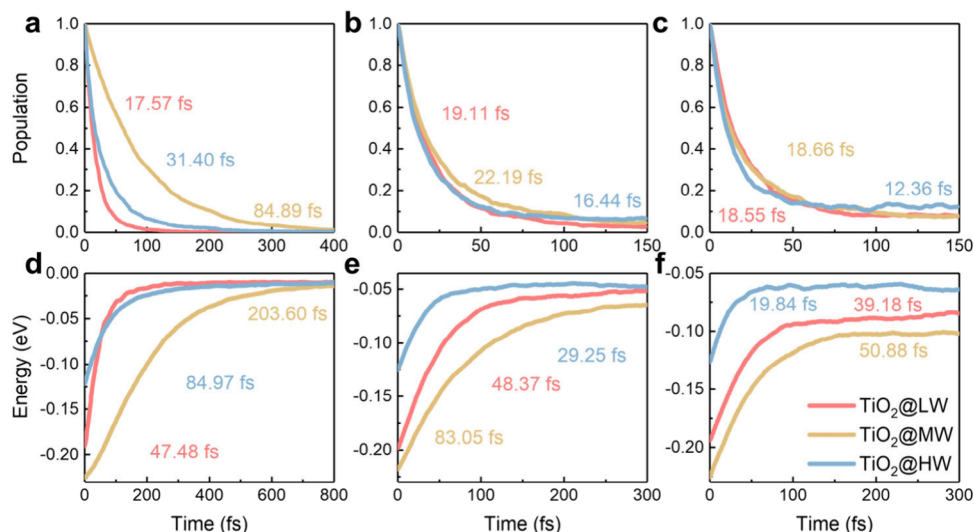


Figure 4. Time evolution of the population (a–c) and energy (d–f) decay of hole transfer in $\text{TiO}_2\text{@LW}$, $\text{TiO}_2\text{@MW}$, and $\text{TiO}_2\text{@HW}$ systems at (a, d) 100 K, (b, e) 300 K, and (c, f) 500 K.

averaged bond lengths of Ti–O at 100, 300, and 500 K show negligible increases (0.003–0.014 Å in $\text{TiO}_2\text{@LW}$, 0.000–0.014 Å in $\text{TiO}_2\text{@MW}$, and 0.002–0.010 Å in $\text{TiO}_2\text{@HW}$, Table S1). These small changes in averaged Ti–O bond lengths demonstrate preserved thermal stability across all systems. The standard deviations of atomic displacements for the three systems at 100 K follow the order $\text{TiO}_2\text{@LW} < \text{TiO}_2\text{@MW} < \text{TiO}_2\text{@HW}$, indicating enhanced atomic fluctuations with higher water density (Table S2). Notably, the surface water molecules in the $\text{TiO}_2\text{@MW}$ system demonstrate significantly reduced positional fluctuations compared to $\text{TiO}_2\text{@LW}$ and $\text{TiO}_2\text{@HW}$ systems (Tables S2–S4). This phenomenon arises because MW increases the interactions between surface water molecules and the TiO_2 surface via enhancing the hydrogen bonding between surface and nonsurface water molecules, restricting atomic motion of surface water molecules. Conversely, in the $\text{TiO}_2\text{@HW}$ system, an elevated water density increases the intermolecular collision frequency within confined spaces, promoting disorderly movements in the water layer. Although a hydrogen-bond network persists between surface and nonsurface water molecules, its structural constraint effect is counterbalanced by frequent molecular collisions. Moreover, the atomic fluctuations increase at higher temperatures compared to 100 K. The relative order of atomic displacement magnitudes remains consistent: $\text{TiO}_2\text{@LW} < \text{TiO}_2\text{@MW} < \text{TiO}_2\text{@HW}$.

To elucidate the temperature dependence of weak intermolecular interactions in the three systems, we performed noncovalent interaction (NCI) analyses, with results visualized in Figure 3. The blue, green, and red regions represent the hydrogen bonding, van der Waals interactions, and steric effects.⁵² Generally, the lower the RDG value, the stronger is the interaction. As shown in Figure 3, all systems exhibit pronounced hydrogen bonding. Both hydrogen bonding and van der Waals interactions intensify with increasing water density, as evidenced by the enhanced color saturation in $\text{TiO}_2\text{@HW}$ compared to $\text{TiO}_2\text{@LW}$ and $\text{TiO}_2\text{@MW}$. Temperature elevation induces a systematic shift of scatter points toward lower RDG regions in all three systems, suggesting enhanced dynamic strengthening of noncovalent interactions. This phenomenon arises from accelerated

molecular thermal motion at higher temperatures, which increases the frequency of transient interactions despite thermal disruption effects.

To simulate the process of photogenerated hole transfer from the VB of TiO_2 to surface-adsorbed water molecules, we selected an electronic state that is 0.7 eV below the VBM as the initial state, because the hot carrier energy of TiO_2 is approximately 0.7 eV.⁵³ As shown in Figure 1d–f, the electronic states of nonsurface water are more than 1.0 eV below the VBM of TiO_2 , and they cannot capture the photogenerated holes. In contrast, the HOMO of surface water is below the VBM of TiO_2 by less than 0.7 eV. Thus, we chose the HOMO of surface water as the final state. The corresponding time evolutions of Kohn–Sham eigenstates for three systems at 100, 300, and 500 K are present in Figure S2. Figure 4 shows the hole transfer and energy relaxation dynamics calculated using the FSSH method in three systems at 100, 300, and 500 K. The time scales presented in Figure 4 are obtained by fitting the curves with an exponential function: $P(t) = a + b \cdot \exp(-t/\tau)$. Here, τ is the hole transfer time scale. Parameter a represents the contribution of the direct hole transfer mechanism, and parameter b reflects the amplitudes of the nonadiabatic contribution to the hole transfer. Notably, the energy relaxation time scales (Figure 4d–f) consistently exceed the corresponding hole transfer time scales (Figure 4a–c) at all temperatures. Moreover, the observed hole transfer times (17.57–84.89 fs) are substantially shorter than the previously reported carrier cooling time in TiO_2 (1 ps),⁵⁴ indicating that photogenerated carriers remain available for capture prior to thermalization. The $\text{TiO}_2\text{@MW}$ system exhibits the longest hole transfer and energy relaxation times across the studied temperature range. At 100 K (Figure 4a,d), the time scales follow the order $\text{TiO}_2\text{@MW}$ (84.89 fs) > $\text{TiO}_2\text{@HW}$ (31.40 fs) > $\text{TiO}_2\text{@LW}$ (17.57 fs). However, at elevated temperatures (300 and 500 K), the sequence reverses for $\text{TiO}_2\text{@LW}$ and $\text{TiO}_2\text{@HW}$, yielding $\text{TiO}_2\text{@MW}$ (300 K, 22.19 fs; 500 K, 18.66 fs) > $\text{TiO}_2\text{@LW}$ (300 K, 19.11 fs; 500 K, 18.55 fs) > $\text{TiO}_2\text{@HW}$ (300 K, 16.44 fs; 500 K, 12.36 fs). This temperature-dependent inversion suggests competing kinetic effects between hydrogen bonding and thermal water dynamics in modulating the interfacial charge transfer.

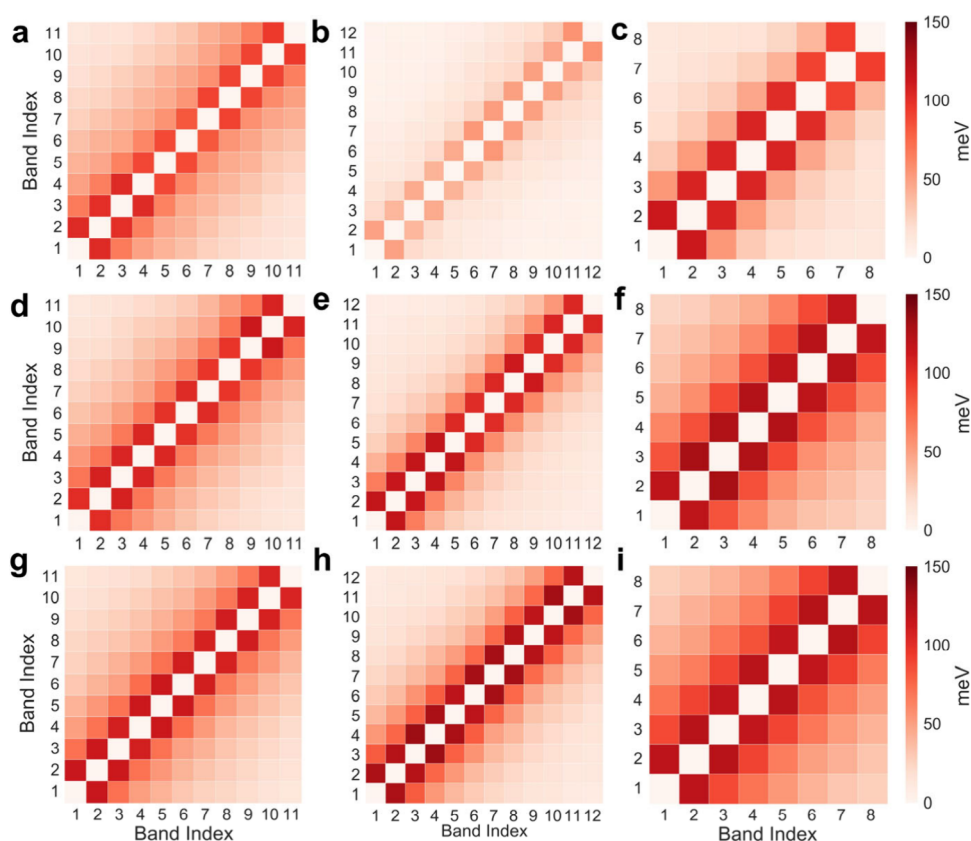


Figure 5. Visualization of the averaged NA coupling between states for hole transfer in (a, d, g) $\text{TiO}_2\text{@LW}$, (b, e, h) $\text{TiO}_2\text{@MW}$, and (c, f, i) $\text{TiO}_2\text{@HW}$ systems at (a–c) 100 K, (d–f) 300 K, and (g–i) 500 K.

Generally, the NA coupling is the main factor causing the hole transition. To investigate the regulatory mechanism of hydrogen bonding and thermal water dynamics on hole transfer from the VB of TiO_2 to surface-adsorbed water molecules in three systems, we further calculated the NA coupling between the adjacent and nonadjacent electronic states involved in hole transfer using the function

$$d_{ij} = -i\hbar \langle \phi_i | \nabla_R | \phi_j \rangle \cdot \dot{\mathbf{R}} = -i\hbar \left\langle \phi_i \left| \frac{\partial}{\partial t} \right| \phi_j \right\rangle$$

Figure 5 and Tables S5–S7 show the NA coupling between the electron states involved in hole transfer. The diagonal line is the NA coupling between adjacent electronic states, and the nondiagonal line represents the NA coupling between nonadjacent electronic states. As illustrated in Figure 5, the NA coupling along the diagonal line is strong, indicating that the nonradiative transition between adjacent electronic states is the major channel for hole transfer. The NA coupling along the nondiagonal line is weak because the strength of the nonadiabatic coupling is inversely proportional to the energy level difference,⁵⁵ which plays a minor role in hole transfer.

At 100 K (Figure 5a–c, Table S5), the $\text{TiO}_2\text{@MW}$ system (Figure 5b) exhibits weaker nonadiabatic coupling compared to the $\text{TiO}_2\text{@LW}$ system (Figure 5a). This phenomenon arises because MW enhances hydrogen bonding between surface-adsorbed and nonsurface-adsorbed water molecules. Consequently, the restricted atomic motion of surface-adsorbed water molecules leads to reduced nonadiabatic coupling (Figure 5b) and slower hole transfer rates (Figure 4a), consistent with experimental observations.^{15,16} In contrast, the $\text{TiO}_2\text{@HW}$ system demonstrates an intensified water molecule

mobility near the vacuum interface at elevated densities, which disrupts hydrogen bonding networks and accelerates surface water dynamics. This results in enhanced nonadiabatic coupling (Figure 5c) and faster hole transfer (Figure 4a). Elevated temperatures (300 and 500 K, Figure 5d–i) further amplify this effect: compared to the 100 K systems (Figure 5a–c), all configurations show significantly stronger nonadiabatic coupling. This temperature-dependent enhancement can be attributed to thermal agitation overcoming hydrogen-bond-mediated constraints on surface water motion. At higher temperatures, the previously inhibitory effect of hydrogen bonding on water mobility is progressively diminished, leading to enhanced surface water dynamics and consequently stronger nonadiabatic coupling (Figure 5d–i) as well as accelerated hole transfer processes (Figure 4b,c).

Using NAMD and TD-DFT simulations, we have elucidated the interplay between hydrogen bonding and water dynamics in modulating interfacial hole transfer on TiO_2 surfaces. The simulations reveal that compared to LW, MW strengthens hydrogen bonding between surface-adsorbed and nonsurface-adsorbed water molecules. This hydrogen-bond network suppresses the atomic mobility of surface-adsorbed water, resulting in a reduced nonadiabatic coupling and sluggish hole transfer. HW near the vacuum interface disrupts hydrogen bonding networks, liberating surface-adsorbed water molecules and enhancing their thermal motion. This boosts NA coupling and accelerates the hole transfer. Elevated temperatures amplify thermal agitation effects, overcoming hydrogen bond-mediated constraints on water mobility. At higher temperatures, the inhibitory role of hydrogen bonding diminishes, leading to enhanced surface water dynamics, stronger non-

adiabatic coupling, and faster hole transfer processes. Our simulations unveil the fundamental physical mechanism underlying how water molecules modulate the charge carrier dynamics.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpclett.5c01994>.

Averaged bond lengths of Ti–O bond; averaged standard deviations in positions of the atoms; averaged nonadiabatic couplings between states for hole transfer; top view of representative snapshots; time evolutions of Kohn–Sham eigenstates of TiO₂@LW, TiO₂@MW, and TiO₂@HW at 100 K, 300 K, 500 K (PDF)

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Notes

The authors declare no competing financial interest.

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