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Excited State Dynamics of Ru₁₀ Cluster Interfacing Anatase TiO₂(101) Surface and Liquid Water

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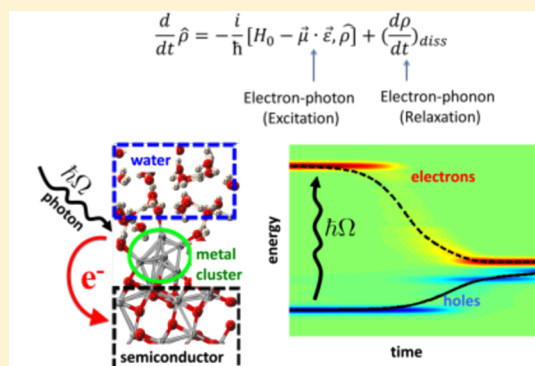
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S Supporting Information

ABSTRACT: Charge transfer dynamics at the interface of supported metal nanocluster and liquid water by GGA+U calculations combined with density matrix formalism is considered. The Ru₁₀ cluster introduces new states into the band gap of TiO₂ surface, narrows the band gap of TiO₂, and enhances the absorption strength. The H₂O adsorption significantly enhances the intensity of photon absorption, which is due to the formation of Ti–O(water) and Ru–O(water) bonds at the interfaces. The Ru₁₀ cluster promotes the dissociation of water, facilitates charge transfer, and increases the relaxation rates of holes and electrons. We expect that our results are helpful in understanding basic processes contributing to photoelectrochemical water splitting.

SECTION: Spectroscopy, Photochemistry, and Excited States



Transition metal complexes^{1,2} and clusters serve as heterogeneous catalysts by capturing reactants and lowering the activation barrier of a target reaction. The activation barrier is often lowered by charge transfer between adsorbing site and reactant. The understanding and prediction of direction, rate, and efficiency of photoinduced charge transfer to/from the catalytic site is an open challenge of ultimate practical importance for photoelectrochemical water splitting.

Nonbiological, molecular level conversion of water to hydrogen fuel using sunlight is still a great challenge because the reaction is thermodynamically uphill. Fujishima and Honda first reported water splitting with TiO₂ photoelectrodes under UV illumination in 1972.³ The visible portion of sunlight constitutes nearly half of the total radiation received at the surface of the Earth. A widely used photocatalyst for splitting water into H₂ and O₂ should have a sufficiently narrow band gap to harvest visible photons. In the past decade, many materials have been reported as visible-light-driven photocatalysts capable of producing both H₂ and O₂ under visible light.^{4,5}

The anatase and rutile TiO₂ have large band gaps, more than 3.0 eV, away from the visible light region. Several approaches have been used to narrow the band gap. Typical approaches to tune the band gap and enhance the absorption in visible light region are surface doping and functionalization, such as sensitizing the surface of TiO₂ with metallic nanoparticles or different kinds of organic dye molecules.^{6,7}

Metal nanoclusters supported by semiconductor surface attract close attention due to their catalytic properties,^{8–10} with

specific interest to metal clusters at TiO₂ surfaces.¹¹ Metal nanoparticles can also sensitize light absorption, analogous to organic dyes in dye-sensitized solar cell.¹²

Ru-based catalysts are important in many reactions, including ammonia synthesis and decomposition, hydrogenation, CO oxidation, CO/CO₂ methanation. Ru/TiO₂ catalysts exhibit excellent catalytic performance in many important chemical processes. The Ru surface deposited on oxide supports are much more active for catalyzing CO oxidation than single-crystal surface.^{13,14} The ultrasmall Ru clusters (~1.5 nm) deposited on TiO₂ have good thermal stability and excellent catalytic activity for the hydrogenation of CO₂ to methane.¹⁵

The charge transfer between semiconductor and metal cluster is important in efficient separating electron–hole pairs.^{16–18} The separated electron or hole reduces or oxidizes the adsorbates such as water molecules to produce hydrogen and oxygen. The relaxation pathways and rates of electron and hole have significant effects on photocatalytic processes. High charge generation rate and low charge relaxation or recombination rate are beneficial to improve photoelectrochemical yields. The Ru nanoparticle–TiO₂ composites can overcome the lack of visible light response of TiO₂ and promote TiO₂ photocatalytic activity.

The interaction of water with solid surfaces plays a vital role in catalysis. Feibelman shows that water adsorbed on Ru(0001) is partially dissociated, with one OH bond broken and the

Received: June 13, 2014

Accepted: July 22, 2014

Published: July 22, 2014

isolated H atoms bonded directly to the metal surface, which is the key step for catalytic generation of a clean energy source of hydrogen.¹⁹

Understanding the charge transfer mechanism and carrier relaxation rates is of critical importance for a wide variety of applications. Experimentally, various types of time-resolved spectroscopy, such as time-resolved two-photon photoemission spectroscopy²⁰ and time-resolved fluorescence spectroscopy,²¹ have been developed for studying the carrier excitation, relaxation, and charge transfer processes. Typical values of measured charge transfer rates between metal particle and semiconductor are <240 fs for Au/TiO₂¹⁶ and on a sub-20 fs time scale for CdS–Au nanocrystals.²²

Atomistic description of charge transfer can be based on several approaches, such as surface hopping and multilevel Redfield theory.^{23–32} There are several theoretical works focused on charge transfer dynamics at molecule, water layer, graphene layer, and quantum dot (QD)–TiO₂ surfaces.^{33–38} The most recent report of computed charge transfer between Au₂₀ and rutile TiO₂ in vacuum shows a sub-100 fs time scale.¹¹ In most materials, the relaxation rate of photoexcitation scales inverse to the excitation energy, according to “energy gap law”.^{39,40}

Computationally assisting in the design of new materials or systems for photocatalysis is challenging. It is split into two global components: (1) photophysics, i.e., optimize light absorption and charge transfer and (2) photochemistry, i.e., optimize catalytic activity. Current work contributes to addressing the first challenge. We believe that exploration of various compositions, shapes, and sizes of metal clusters at TiO₂ surfaces promises a versatile control of direction, rate, efficiency, and lifetime of charge transfer. This work reports a case study of one possible example of a cluster while design of efficient catalyst would include screening of numerous clusters.

In this work, the charge transfer dynamics between three kinds of interfaces—TiO₂/Ru₁₀, TiO₂/H₂O, and Ru₁₀/H₂O—were investigated based on ab initio electronic structure calculations and density matrix formalism^{7,32} (see Supporting Information for methods).

The anatase (101) surface was selected, represented by a $p(3 \times 4)$ slab¹⁴ with a thickness of four Ti layers. The anatase phase is more efficient and more widely used in catalysis and photoelectrochemistry, while the (101) facet is the most stable with the lowest surface energy. The structure of Ru₁₀ cluster selected is the same as shown in ref 14. Figure 1 shows the side views of our model. The bottom surface of (101) is saturated with water molecules, and the top surface is decorated by a Ru₁₀ cluster and water molecules. The water molecules are used to simulate the aqueous environment. After the geometry optimization at 0 K, the Ru cluster is well stabilized and anchored on the (101) surface via Ru–O bonding, and the H₂O molecules are found to be molecularly adsorbed on the (101) TiO₂ surface and Ru₁₀ cluster. During molecular dynamics (MD), the water molecules rotate, break old hydrogen bonds and form new ones. Some water molecules escape from the surface and others move toward the surface. After heating and during the MD simulation, a single water molecule on the top (101) anatase surface and the surface of Ru₁₀ cluster dissociates into OH and H. The H bonds to a surface O atom of the anatase surface, and the OH bonds to both a surface Ti and a surface Ru atom. No water molecules in the bottom surface dissociate during MD, indicating that the Ru₁₀ cluster promotes the dissociation of water. A trajectory

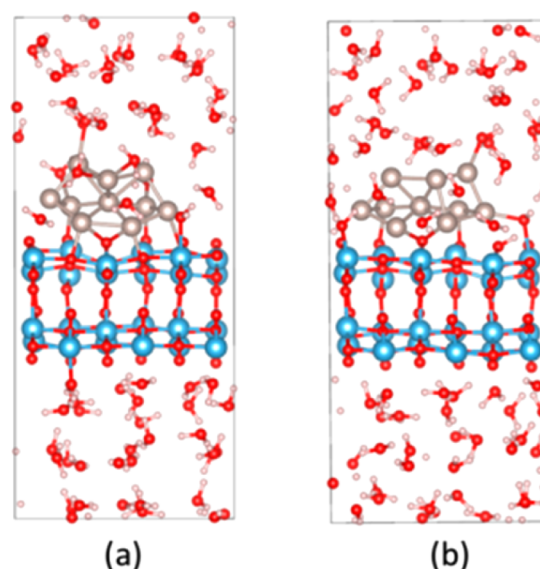


Figure 1. Side views of H₂O–Ru₁₀–(101) TiO₂. (a) The optimized structure at 0 K. (b) The structure at $t = 500$ fs during MD simulations at 300 K. The blue, red, gray, and white balls represent Ti, O, Ru, and H atoms.

with no dissociated H₂O molecules would lead to major steps of electron dynamics involving TiO₂ and Ru cluster. A trajectory, where dissociated molecules exist would involve charge density exploring spatial regions away from catalysts, at dissociated radicals. Such states can play a 2-fold role: (a) speed up the relaxation, as they make orbital's energies denser or (b) serve as traps and retain charge on radicals for longer time. Dynamics of further water splitting photochemistry needs methods focusing on changes in nuclear trajectory induced by electronic excitations, such as time-dependent excited-state molecular dynamics (TDESMD).⁴¹

The total density of states (TDOS) and partial density of states (PDOS) of H₂O–Ru₁₀–(101) TiO₂ are illustrated in Figure 2a (see Figure S2, Supporting Information, for comparison to bare (101) and Ru₁₀–(101) TiO₂). For bare (101) surface, the top of valence band (VB) is dominated by O-2p states and the bottom of conduction bands are due to Ti-3d states. The calculated band gap is about 3.23 eV, which is close to the experimental value of bulk anatase (3.2 eV). The GGA +U method enhances the band gap obtained by GGA (2.66 eV). After the adsorption of Ru₁₀ cluster, the band gap almost disappeared. The calculated gap for Ru₁₀–TiO₂ (101) is 0.12 eV. The hybridization of Ru-4d with O-2p and Ti-3d states at $-5 \sim -3$ eV indicates Ru–O bonding and Ru–Ti interaction at the interface. In the H₂O–Ru₁₀–(101) TiO₂, the O atoms from water hybridize with Ru-4d and Ti-3d states at $-5 \sim -3$ eV, indicating the formation of Ti–O(water) and Ru–O(water) coordination bonds at the interfaces. The calculated gap for H₂O–Ru₁₀–(101) TiO₂ is 0.15 eV. The states introduced by the Ru cluster become the dominant centers for optical excitation and relaxation. In the VB region, the substantial contribution of atomic O-2p oxygen orbitals to KS-orbitals in dissociated water appears at higher energy compared with the nondissociated water. This indicates that for the dissociated water, there are additional states introduced near the top of VB, where the photohole can be transferred (Figure S3). Nondissociated H₂O molecules away from surfaces provide occupied orbitals well below the highest occupied orbital (HO) and unoccupied

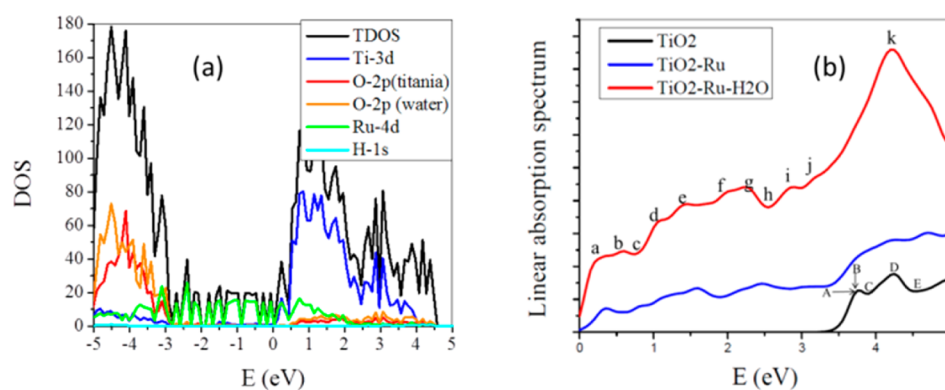


Figure 2. (a) The TDOS and PDOS of H₂O-Ru₁₀-(101) TiO₂. (b) The calculated absorption spectra of (101) anatase TiO₂ surface, Ru₁₀-(101) TiO₂, and H₂O-Ru₁₀-(101) TiO₂. Transitions contributing to labeled peaks are used as initial states for electron dynamics.

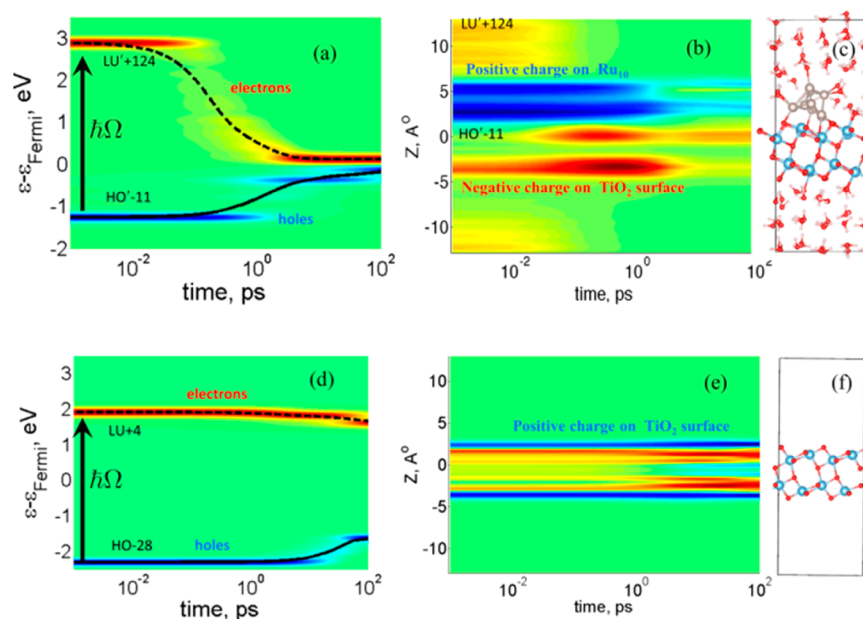


Figure 3. (a,b) Nonadiabatic relaxation dynamics of H₂O-Ru₁₀-(101) TiO₂ for the initial condition corresponding to the feature k in Figure 2b. Here, red, green, and blue colored areas label the distribution for gain, no change, and loss, respectively, in comparison with the equilibrium distribution. (c) The structure of H₂O-Ru₁₀-(101) TiO₂ was scaled with the Z in (b). (d,e) Nonadiabatic relaxation dynamics of (101) TiO₂ for the initial condition corresponding to the feature D in Figure 2b. (f) The structure of (101) TiO₂ was scaled with the Z in panel e. (a,d) Distribution in energy vs time; (b,e) distribution in space versus time.

orbitals substantially above the lowest unoccupied orbital (LU). These orbitals cannot be accessed by low-energy optical excitation and do not lead to water splitting. Water molecules near the surface, and especially dissociated H₂O contribute to orbitals near the top of VB (Figure S4). These orbitals can be populated upon visible excitation and reorganization of nuclei, following such excitation, could serve as important intermediate step for water splitting.

We find absorption spectra in the basis of noninteracting one electron orbital approximation. Absorption by an approximate method using noninteracting orbitals is highlighted in contrast to time-dependent density functional theory (TDDFT) and Bethe-Salpeter equation (BSE) approach,⁴² where bound states are formed due to interaction of particles and holes. Often, in multiple cases such as semiconductor nanostructures, the excitonic correction to the excitation energy is a constant, providing systematic shift of the spectrum. Here, the interaction of electrons is described through the Kohn-Sham (KS) procedure, leading to a set of auxiliary KS orbitals for ground

state. Then, matrix elements of electron-photon interaction in the basis of such orbitals approximately describe optical properties of the model, in the lower order approximation. This approximation is valid in the case where a photoexcitation introduces a negligible change into total density, into orbitals, and into matrix elements for ground state, which allows an adequate analysis of optical properties.

The calculated absorption spectra in Figure 2b show that the introduction of Ru₁₀ cluster on the (101) anatase surface induces the absorption in the visible light region and doubles the original absorption strength, which may be due to the surface plasmon effect of Ru₁₀ cluster. The H₂O adsorption provides additional significant enhancement of the photon absorption intensity both in the visible, IR, and UV light regions. The A-E features in the bare surface originate from the transitions from O-2p to Ti-3d states. The absorption of H₂O-Ru₁₀-(101) TiO₂ is contributed by transitions of different nature. Specifically, the features a, b, d and f are due to d-d transitions of Ru. The c, g, h, i, and j features are dominated by

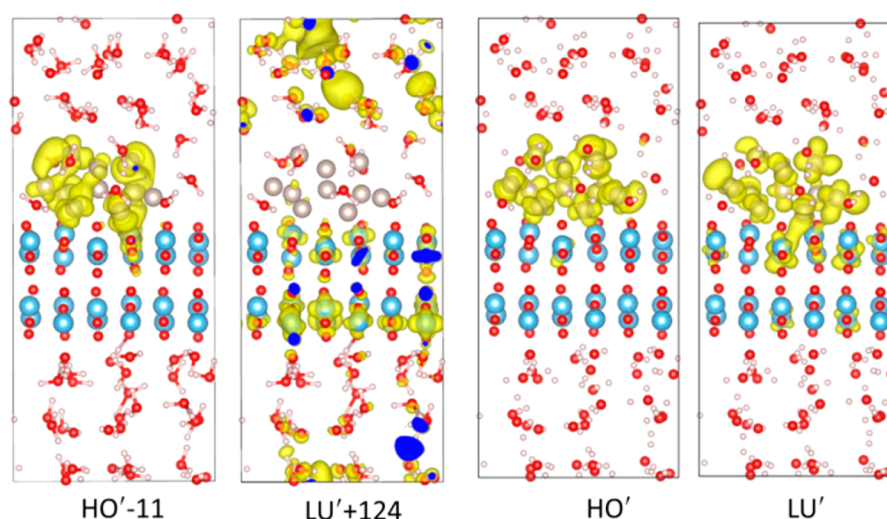


Figure 4. Partial charge densities of HO'-11, LU'+124, HO', and LU' orbitals of H₂O-Ru₁₀-(101) TiO₂ at the Γ point. The blue, red, gray, and white balls represent Ti, O, Ru, and H atoms. Yellow clouds represent charge density isocontours.

the transitions from Ru-4d to Ti-3d states. The feature ϵ is a mixture of d-d transitions of Ru and the Ru-4d \rightarrow Ti-3d transition. The transitions from Ru-4d to Ti-3d and from Ru-4d to O-2p (water) states contributed to the feature k . The absorption at ~ 3.47 and ~ 3.81 eV are due to the transitions from O-2p to Ti-3d, from O-2p to Ru-4d, and the d-d transition of Ru.

In order to study electron-nuclear interaction, the model was explored at finite temperatures modeled by microcanonical ensemble represented by a trajectory of positions of ions. The size of the model is at the lower edge of applicability of microcanonical ensemble for modeling finite temperature. Due to the small size of the model, the kinetic energy fluctuates around its energy as $T = \bar{T} \pm \Delta T$, $\bar{T} \approx 309.6$ K, $\Delta T \approx \pm 26$ K (Figure S5). A minimization of amplitude of fluctuations can be achieved by (i) smaller time step, (ii) longer equilibration with thermostat, and (iii) by increasing the size of the model.

The orthogonality of electronic states breaks due to dynamics of positions of ions. A mixing of electronic states originates from quantum operator of kinetic energy of ions. An on-the-fly nonadiabatic coupling is a measure of such mixture. Upon averaging over the ensemble, the influence of ions onto electrons is dominated by the second-order term in the time-dependent perturbation theory, represented by the autocorrelation functions of nonadiabatic coupling. A time average of the autocorrelation function (eq S3a) of the electron-to-lattice nonadiabatic couplings (eq S2) provides Redfield coefficients of electronic transitions (eq S4b) that enter into the equation of motion for the electronic degrees of freedom (eq S1a). Specifically, autocorrelations for representative pairs of orbitals rapidly decay within the first several femtoseconds for both models, as shown in Figure S6a,b. The Redfield tensor elements demonstrated in Figure S6c,d are related to population transfer for a given pair of orbitals k,j . The most intense transitions occur between pairs of orbitals with similar indices $j = k \pm 1$ with several other transitions being nonvanishing. The values of the Redfield tensor elements for CB ($j,k > \text{HO}$) are larger than the ones for VB ($j,k < \text{LU}$). Also the values of the Redfield tensor elements for the intense transitions for H₂O-Ru₁₀-(101) TiO₂ are larger than that of (101) TiO₂.

Figure 3 visualizes representative examples of photoinduced dynamics triggered by initial excitation at energy 4.22 eV for

both models. Such excitation is represented by the relevant initial condition $i\text{H} = \text{HO}'\text{-11}$, $i\text{E} = \text{LU}'\text{+124}$ (feature k in Figure 2b) in Ru-cluster interfacing water and semiconductor substrate and by the initial condition $i\text{H} = \text{HO}\text{-28}$, $i\text{E} = \text{LU}\text{+4}$ (feature D in Figure 2b) in bare semiconductor surface. The left panels (a and d) show distribution of charge as a function of energy and time. The electronic part of the excitation relaxes to LU and the hole part of excitation relaxes to HO. The electron relaxation is faster than hole relaxation for both models. For H₂O-Ru₁₀-(101) TiO₂, the electron generated in the transition of 4.22 eV loses energy by coupling to phonons and relaxes within 548 fs, compared to 2643 fs for bare surface. This is longer than those observed for the Au:TiO₂ interface due to showing the whole process, contributed by several subsequent elementary charge transfer events.

Considered electron dynamics are presented for a time interval until 100 ps labeled as 10^2 and as \log_{10} (time, ps). By this time, most of charge rearrangements are complete as seen in Figure 3. Beyond this range the system would experience only recombination and chemical reaction dynamics, which needs more advanced methodology focusing on dissociative limit of coupled electron nuclear dynamics.⁴¹ We anticipate that the smaller time step would lead to the same trends in nonadiabatic couplings, the same pattern of Redfield tensor, and very similar charge dynamics.

The KS orbitals corresponding to the considered transition (HO'-11 \rightarrow LU'+124) of H₂O-Ru₁₀-(101) TiO₂ are shown in Figure 4. For LU'+124, the charge density is distributed on Ti atoms, O atoms of water, and some on H atoms. The HO'-11, HO', and LU' are dominated by Ru-4d orbitals. At the initial excitation, the electron is distributed on Ti atoms, O atoms of water, and some of H atoms, and the hole is located at the Ru cluster. After the nonadiabatic relaxation, the hole is relaxed from HO'-11 to HO', during which only Ru-4d orbitals partly hybridized with oxygen (Figure S3) are involved; the electron is relaxed from LU'+124 to LU', during which the electron transfers from Ti atoms, O atoms of water, and some of the H atoms to Ru atoms.

The middle panels (b and e) of Figure 3 show distribution of charge as a function of space and time. The geometry structures in right panels (c and f) were added for scale. For H₂O-Ru₁₀-(101) TiO₂, at $t < 0.01$ ps, the electron distributes in water and

TiO₂. At 0.01 ps < t < 1 ps, one can see a partial electron transfer from water to the interface between the Ru₁₀ cluster and TiO₂. At $t \leq 1$ ps, the charge transfer state is most pronounced. At $t > 1$ ps, most of the electron distribution is localized at the interface between the Ru₁₀ cluster and TiO₂. For the bare surface, after excitation, the positive charge accumulates at the surface.

Tables S1 and S2 summarize the most probable photo-excitations and their relaxation rates of nonequilibrium dynamics of (101) TiO₂ and H₂O–Ru₁₀–(101) TiO₂, respectively. For the bare surface, the bright transition energies are higher than the optical band gap energies. For H₂O–Ru₁₀–(101) TiO₂, the transitions at low energy region are contributed by the d–d transitions inside Ru or between Ru and Ti.

Figure 5 compares the computed relaxation rates of electron K_e and hole K_h for (101) TiO₂ and H₂O–Ru₁₀–(101) TiO₂.

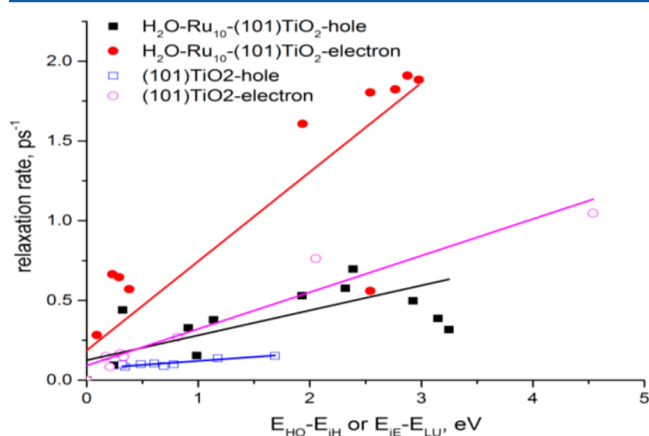


Figure 5. Relaxation rates of electron K_e and hole K_h for (101) TiO₂ and H₂O–Ru₁₀–(101) TiO₂. The x axis shows the value of the difference of initial and final energies $E_{HO}-E_{IH}$ for hole and $E_{IE}-E_{LU}$ for electron. For bare (101) TiO₂, $dK_e/dE = 0.23 \text{ ps}^{-1} \text{ eV}^{-1}$, $dK_h/dE = 0.05 \text{ ps}^{-1} \text{ eV}^{-1}$. For H₂O–Ru₁₀–(101) TiO₂, $dK_e'/dE = 0.56 \text{ ps}^{-1} \text{ eV}^{-1}$, $dK_h'/dE = 0.16 \text{ ps}^{-1} \text{ eV}^{-1}$.

The electron and hole relaxation rates of H₂O–Ru₁₀–(101) TiO₂ are higher than the ones of (101) TiO₂. The interactions among H₂O, TiO₂, and Ru₁₀ provide additional channels for electron and hole relaxation. For both models, the electron relaxation is quicker than the hole relaxation, due to different spacing of orbital energies in valence bands and conduction bands. Electron and hole relaxations exhibit the same type of dependence on energy, different from the results of TiO₂ nanowire.⁴³ Specifically, higher excitations relax more quickly, going against the energy gap law.^{39,40} Exception to the energy gap law is also found for lanthanide luminescence.⁴⁴ This observation may originate from relaxation taking additional pathways, i.e., in addition to subsequent relaxation between neighboring states $i \rightarrow i-1 \rightarrow i-2$, system may experience “over the neighbor” transitions $i \rightarrow i-2$, illustrated by nonzero Redfield tensor off-diagonal elements in Figure S6.

Photocatalytic water splitting using sunlight to form hydrogen and oxygen is still challenging. The GGA+U calculations combined with density matrix formalism were employed to investigate the effects of the adsorption of Ru₁₀ cluster on the electronic and optical properties of the wet (101) anatase TiO₂ surface for practical design of materials for sunlight energy harvesting. The applied theoretical method

provides atomistic details of changes in electronic structure introduced by interfaces and electrons interacting with lattice vibrations and light. The approximations used in this work are as follows: ions are considered as point charges, lattice vibrations instantaneously equilibrate with a thermostat, coupling autocorrelation functions decay abruptly leading to Markov approximation, vibrational reorganization is neglected, and excited state potential energy surfaces are assumed to have the same shape as the ground state, corresponding to negligible Huang–Rhys factors.

The Ru₁₀ cluster introduces states into the band gap of TiO₂ surface, narrows the band gap, and enhances the absorption strength. The H₂O adsorption further significantly enhances the strength of absorption spectra, due to the formation of Ti–O(H₂) and Ru–O(H₂) bonds at the interfaces. The Ru₁₀ cluster facilitates charge transfer and increases the relaxation rates of holes and electrons.

In the studied model, ruthenium metal cluster functions as an efficient photocathode which has the potential to facilitate water oxidation reaction, and photoexcitations of higher energy show quicker nonradiative relaxation, breaking the expected “energy gap law” behavior. This is a model combining all critical components for a photoelectrochemical cell. Results can be used for identifying mechanisms of charge transfer and developing new materials for energy.

■ ASSOCIATED CONTENT

Supporting Information

Details of computational methods, DOS, partial charge densities, autocorrelation functions, elements of Redfield tensor, fluctuation of temperature and total energies during MD, and carrier relaxation data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research was supported by NSF awards EPS-0903804 and CHE-1413614 and by the U.S. Department of Energy (DOE), BES – Chemical Sciences, NERSC Contract No. DE-AC02-05CH11231, allocation Award 86185, “Computational Modeling of Photo-catalysis and Photoinduced Charge Transfer Dynamics on Surfaces.” This work was performed, in part, at the Center for Integrated Nanotechnologies, an Office of Science User Facility operated for the DOE Office of Science by Los Alamos National Laboratory (Contract DE-AC52-06NA25396) and Sandia National Laboratories (Contract DE-AC04-94AL85000). S.H. and D.S.K. acknowledge Computational resources of USD High Performance Computing facilities operated by Doug Jennewein. T.M.I. thanks the Center for Computational Materials Science, Institute for Materials Research, Tohoku University (Sendai, Japan) for their continuous support of the SR16000 M1 supercomputing system. The authors thank Stephanie Jensen for Editorial Comments and Q. Meng, G. Yao, Y. Han, D. J. Vogel for discussions. D.S.K. thanks S. Kilina, O. Prezhdo, S. Tretiak, and S. Hammes-Schiffer for discussions of details of nonadiabatic dynamics.

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