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Electron transfer governed by light–matter interaction at metal–semiconductor interface

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The photoexcitation of heterostructures consisting of metallic nanoclusters and a semiconductor has been extensively investigated in relation to interests in photocatalysis and optical devices. The optoelectronic functions of the heterostructures originate from localized surface plasmon resonance, which can induce electron and resonance energy transfers. While it is well known that photoinduced electronic interaction between a metallic nanocluster and a semiconductor is responsible for the resonance energy transfer, the electron transfer associated with the photoinduced electronic interaction has not been discussed. In this paper, we elucidate the photoexcitation dynamics of a silver nanocluster/TiO₂ heterostructure using an original first-principles computational approach that explicitly deals with light–matter interactions. It is shown that the photoinduced silver–TiO₂ electronic interaction causes excited electrons to be directly transferred from the silver nanocluster to the TiO₂ layer without passing through the conduction band of the silver nanocluster.

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INTRODUCTION

The photoexcitation of heterostructures consisting of metallic nanoclusters and a semiconductor has been extensively investigated in relation to interests in optically functional materials, such as photonic devices, solar cells, and photocatalysis.^{1–4} The localized surface plasmon resonance (LSPR) of metallic nanoclusters plays a central role in the optoelectronic functions of these heterostructures. The collective electron oscillation of LSPR generates an intense electric field that is much larger than that of an incident laser. Because of the generated electric field, the photoinduced electronic interaction between metallic nanoclusters and a semiconductor remarkably enhances the photoexcitation intensity of the semiconductor while diminishing the collective electron oscillation; that is, LSPR causes resonance energy transfer from the metallic nanoclusters to the semiconductor.^{1,3} Meanwhile, photoabsorption by LSPR largely generates excited electrons that transfer from a metallic nanocluster to its surrounding materials.^{2,4} This excited-electron transfer by LSPR has been discussed separately from the photoinduced electronic interaction; however, the two can be simultaneously induced. In practice, experimental studies of heterostructures consisting of silver nanoclusters and TiO₂ have reported both electron transfer and resonance energy transfer caused by the photoinduced electronic interaction.^{5,6} In addition, the strong electronic coupling at the metal–semiconductor interface and the mixing of their electronic states is thought to induce direct metal-to-semiconductor electron transfer, and suppress the loss of excited electrons.⁷ In this context, it is increasingly necessary to investigate the role of the photoinduced electronic interaction at the metal–semiconductor interface in electron transfer by LSPR.

Extensive theoretical and computational studies have attempted to elucidate optical phenomena such as LSPR. Metallic nanoclusters are often approximated as a macroscopic classical model characterized by a complex dielectric function for describing the electric field of LSPR.^{8–10} Although first-principles calculations of photoinduced electron transfer in nanomaterials have gradually become more popular,^{11,12} the number of such studies is still severely

limited comparing to those on small molecules and bulk materials due to the large computational cost. In particular, to calculate LSPR of a noble metal nanocluster is difficult because a large number of electrons (i.e., s- and d-electrons) should be explicitly treated.¹³ So far, the electron transfer by LSPR associated with light–matter interactions has not been investigated with the electronic relaxation after the termination of a laser pulse being the main focus of previous first-principles studies. Indeed, to deal with light–matter interactions is essential for describing the electric field of LSPR, which is the collective electron oscillation synchronized with the incident laser field. Because the electron transfer and electronic interaction induced by LSPR have been studied individually, the relationship between the two is not understood.

In this study, we elucidate the mechanism of photoexcited electron transfer in a silver nanocluster/TiO₂ heterostructure using a first-principles computational program developed by our group.¹⁴ In this program, the electron dynamics caused by light–matter interactions is directly simulated in real time; thus, various optical processes including the photocurrent generation of nanomaterials can be described.^{13,15,16} Furthermore, because of the high parallel efficiency, this program can be applied to nanomaterials such as a heterostructure consisting of a silver nanocluster and a TiO₂ layer. It is shown that the electron transfer is governed by the photoinduced electronic interaction between a silver nanocluster and a TiO₂ layer, and has a substantially different mechanism from that of the conventional electron transfer by LSPR. Insights into this mechanism can be applied in the design of various optically functional materials with high light-energy conversion efficiency.

RESULTS

Simulated systems

Figure 1a shows the optimized structure of a silver/TiO₂ heterostructure, which consists of an Ag₂₀ nanocluster and a TiO₂ layer. We employ the slab model of TiO₂(110) that has been

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Fig. 1 $\text{Ag}_{20}/\text{TiO}_2$ heterostructures employed in this study. (a) Fully optimized system A, and (b) ideal system B in which the Ag_{20} nanocluster and the TiO_2 layer are individually optimized. Ag, Ti, and O are colored gray, aqua, and red, respectively.

utilized in previous studies.^{17,18} The Ag–O bond distances are 2.1–2.5 Å, which is close to previous computational results for heterostructures consisting of a silver nanocluster and a TiO_2 layer.^{19,20} In the following, the fully optimized $\text{Ag}_{20}/\text{TiO}_2$ heterostructure is denoted as system A. We also calculated two ideal $\text{Ag}_{20}/\text{TiO}_2$ systems (B and C), in which the Ag_{20} nanocluster and the TiO_2 layer were separately optimized. The isolated Ag_{20} nanocluster has the tetrahedral geometrical structure that has previously been used to investigate optical responses involving the LSPR of a silver nanocluster.^{21,22} We consider this tetrahedral structure to be better than a spherical one for modeling an adsorbed metallic nanocluster that tends to form a planar structure. The Ag–O bond distances for ideal system B (Fig. 1b) are 3.0–3.3 Å, which is about 1 Å longer than that for system A. As the Ag_{20} nanocluster becomes closer to the TiO_2 layer, electronic transitions that are not found in system A become noticeable (Supplementary Sec. 1). Ideal system C is almost the same as system B (and is thus omitted from Fig. 1), except that the Ag–O bond distances are 4.0–4.2 Å, slightly larger than the sum of the van der Waals radii of ~3.7 Å.²³ System C is used to investigate the electron transfer associated with the photoinduced electronic interaction between the silver nanocluster and the TiO_2 layer. Although we calculate a larger $\text{Ag}_{84}/\text{TiO}_2$ heterostructure system, no remarkable dependence on the nanocluster size is observed in the electron transfer mechanism described below. Thus, we mainly discuss the $\text{Ag}_{20}/\text{TiO}_2$ heterostructures in the following text.

For the systems considered in this paper, we calculate the photoexcited electron dynamics using our original computational program SALMON (Scalable Ab-initio Light–Matter simulator for Optics and Nanoscience), in which the time-dependent Kohn–Sham equation is calculated explicitly dealing with light–matter interactions in real time and real space.¹⁴ The laser intensity and the pulse duration are set to 10^9 W cm^{-2} and 30 fs, respectively.

Fundamental electronic and optical properties

Figure 2a shows a map of the two-dimensional (2D) local density of states (LDOS) of system A. The horizontal axis is the z -direction perpendicular to the TiO_2 layer. The TiO_2 and silver moieties are in the left and right, respectively. The Ag_{20} – TiO_2 interface is at $z \approx 13$ – 14 Å. The vertical axis is the band energy E relative to the Fermi level. Valence band states in the silver moiety from -1 to 0 eV are occupied by ~10 electrons, and analogous states are recognized from the isolated silver nanocluster. Localized states in the TiO_2 moiety around -0.3 eV are absent from the isolated TiO_2 layer, and are regarded as gap states created by Ag–O chemical bonds. Although evanescent metal states caused by a surface

Fig. 2 Fundamental electronic and optical properties. (a) 2D LDOS map of system A in which values larger than the threshold are set to the same color as the maximum value, and (b) optical absorption spectra of a tetrahedral Ag_{20} nanocluster, TiO_2 layer, system A, and ideal system B.

termination can generate delocalized gap states,²⁴ such gap states play a minor role in photoexcitation discussed below. The further details of the electronic structure are given in Supplementary Sec. 2. In the conduction band, the LDOS in the silver moiety is lower than that in the TiO_2 moiety. Therefore, photoexcited electrons tend to transfer into the conduction band of TiO_2 , that is, into a high-DOS region. Although this tendency is observed in our first-principles simulation of the photoexcited electron dynamics shown below, the feature of the electron transfer cannot be rationalized solely by the character of the DOS.

Figure 2b shows the optical absorption spectra with x -polarization for the tetrahedral Ag_{20} nanocluster, TiO_2 layer, system A, and ideal system B. The edge of the optical absorption energy of the TiO_2 layer is ~2.7 eV, ~0.3 eV lower than that of bulk rutile TiO_2 .²⁵ This underestimation is a result of employing the conventional Perdew–Burke–Ernzerhof (PBE) functional. Note that the purpose of this study is to elucidate the mechanism of electron transfer in the silver nanocluster/ TiO_2 heterostructure related with the photoinduced electronic interaction between the silver nanocluster and the TiO_2 layer. Because the absorption spectrum of the Ag_{20} nanocluster has a peak at ~3 eV, our approach can reproduce the experimental condition whereby a silver nanocluster and a TiO_2 layer are simultaneously excited by a laser pulse with an energy of ~3 eV.⁶ Thus, we consider that the

dependence on the functional of the density functional theory (DFT) does not affect the discussion at the qualitative level. In the following, we mainly discuss the photoexcited electron dynamics by a 3.0-eV laser. It is noted that we change the laser frequency from 3.0 eV to 2.8 eV at which system A has the absorption peak, and confirmed that the mechanism of the photoexcited electron transfer in system A is qualitatively unchanged.

Photoexcited electron dynamics

Figure 3 shows 2D maps of the variation in the electron occupation number at $t = 30$ fs induced by an x-polarized laser pulse with an energy of 3.0 eV. The definition of the horizontal and vertical axes is the same as that of Fig. 2a. The red and blue distributions indicate that the electron occupation numbers are greater and less than that in the ground state, respectively. Thus, electrons are excited from blue areas to red areas. White arrows depict an energy gap of 3.0 eV, which is equal to the incident laser energy. In the isolated TiO_2 layer (Fig. 3a), 3.0-eV electronic transitions take place. As seen from Fig. 3b, a number of distributions are found in the conduction band of the Ag_{20} nanocluster truncated from system A. These distributions are also

attributed to 3.0-eV electronic transitions (the white arrows). Figure 3c illustrates the 2D map for system A. A remarkable change caused by the silver– TiO_2 contact can be observed in the silver moiety; no electron occupation is found in the conduction band at all (white rounded box), even though the occupation numbers decrease in the valence band. A recent experimental study on a heterostructure with silver nanoclusters and TiO_2 also reported that excited electrons are almost absent from the conduction band of the silver moiety.⁶ In Fig. 3c, small electronic excitation from the gap states ~ -0.3 eV is found, and an analogous result has been also reported in the experimental study. Figure 3d shows possible electronic transition paths for a silver nanocluster/ TiO_2 heterostructure. The change in electronic transitions caused by the silver– TiO_2 contact exhibited in Fig. 3 indicates that direct electron transfer from the silver moiety to the TiO_2 layer (path III) is induced while excited-electron generation in the silver moiety (path II) substantially diminishes. Indeed, as the time-dependent photoexcitation process proceeds, no excited electrons are found in the conduction band of the silver moiety (Supplementary Fig. 4).

Fig. 3 Variations in the electron occupation number caused by photoexcitation. (a) Isolated TiO_2 layer, (b) Ag_{20} nanocluster truncated from system A, (c) system A, and (d) possible paths of electronic transition in a silver nanocluster/ TiO_2 heterostructure. A distribution whose value is larger (smaller) than the threshold value is set to the same color as the maximum (minimum) value.

Fig. 4 Dependence on the Ag_{20} - TiO_2 distance. Variation in the occupation number on the distance between the tetrahedral Ag_{20} nanocluster and the TiO_2 layer for (a) system B and (b) system C. A distribution whose value is larger (smaller) than the threshold value is set to the same color as the maximum (minimum) value.

For comparison, we further investigate the dependence of the photoexcitation on the distance between the Ag_{20} nanocluster and the TiO_2 layer using the ideal systems. The variation in the occupation number at $t = 30$ fs is shown in Fig. 4. The direct electron transfer is also induced in system B (Fig. 4a), in which the Ag_{20} nanocluster rather weakly contacts with the TiO_2 layer compared with system A. Furthermore, a larger heterostructure consisting of Ag_{84} and TiO_2 yields the direct electron transfer (Supplementary Fig. 8). Therefore, the direct electron transfer is not a singular phenomenon caused by atomistic details of Ag–O chemical bonds or by a small silver nanocluster. For system C (Fig. 4b), in which Ag–O distances are slightly longer than the van der Waals contact distance, excited electrons clearly accumulate in the silver nanocluster, and the conventional LSPR-induced electron transfer from the silver nanocluster to the TiO_2 layer (i.e., path IV in Fig. 3d) takes place. Figures 3 and 4 show that the direct electron transfer is significantly different from the conventional electron transfer that has been discussed in previous studies. The difference between systems A, B, and C can be made clearer by numerically evaluating the variation in the occupation number. The occupation number in the valence band of the silver moiety decreases by 1.2×10^{-2} , 3.4×10^{-2} , and 3.3×10^{-2} for systems A, B, and C, respectively. In the conduction band, the occupation number in the silver moiety increases by 8.6×10^{-4} , 4.6×10^{-3} , and 1.4×10^{-2} for systems A, B, and C, respectively. It is clearly shown that photoexcited electrons almost completely transfer from the silver moiety into the TiO_2 moiety for systems A and B, whereas remains in the silver moiety as excited electrons for system C.

The difference in the direct electron transfer from the conventional LSPR-induced case is reflected in the photoexcited electron dynamics. Figure 5 shows the z component of the time-dependent electronic polarization, $P_z(t)$ defined by Eq. (6), where the z is the direction perpendicular to the TiO_2 layer. As time elapses, a negative electronic polarization is induced by the laser field, and is attributed to the electron transfer from the silver moiety to the TiO_2 layer. Although the magnitude of the polarization for system A is smaller than that for the ideal systems, this is simply because the photoexcitation intensity of the silver moiety in system A is smaller than that of the tetrahedral Ag_{20} nanocluster. Independent of the difference in the geometrical structure, the electron transfer is almost terminated just after the incident laser is switched off ($t = 30$ fs) in systems A and B. In contrast, for system C, the polarization continues to increase, even after the laser is switched off. The time-dependence reflects the mechanism of the electron transfer: the direct electron transfer occurs simultaneously with the electronic transition, whereas the conventional LSPR-induced electron transfer takes place after the

Fig. 5 Photoexcited electron dynamics. Time-dependent electronic polarization perpendicular to the TiO_2 layer caused by photoexcitation for system A (black), system B (red), and system C (blue).

electronic transition in the silver nanocluster. An analogous time-dependence to Fig. 5 can be obtained by analyzing the electron density and the variation in the occupation number (Supplementary Figs 4–7, 9).

Note that our simulation do not take into account the energy relaxation of excited electrons originating from electron–electron and electron–phonon scatterings. The electron–electron scattering due to the large electron oscillation of LSPR causes the fast decay of the electronic excitation in ~ 10 fs.^{2,4} Because our approach cannot describe inelastic electron–electron scattering, the conventional LSPR-induced electron transfer is probably overestimated compared with the direct electron transfer. A many-body description such as the GW approximation is required to describe the inelastic electron–electron scattering.²⁶ The relaxation by the electron–phonon coupling occurs on time scales from 100 fs to 1 ps,^{2,4} which are clearly longer than the experimental decay rate for a silver nanocluster/ TiO_2 system, ~ 10 fs.⁶ Thus, the electron–phonon coupling would play a minor role in the direct electron transfer although is important after the direct electron transfer is completed (e.g., in carrier recombination and carrier transport in TiO_2).

Photoinduced electronic interaction

To reveal the driving force of the direct electron transfer, it is important to analyze the photoinduced electronic interaction

under light irradiation. This is because LSPR is primarily ascribed to the photoinduced electronic interaction rather than interband transitions.^{27,28} Furthermore, LSPR induces various optical phenomena that are not realized only by small molecules and bulk materials.^{29,30} Indeed, the direct electron transfer of the present systems is not readily rationalized from transition dipole moments; even though not directly induced by the *x*-polarized field, the electronic transition along the *z*-direction is preferentially induced over the conventional electronic transition inside the silver moiety. To reveal the mechanism of the electron transfer, Fig. 6a shows the real part of the *z* component of the Fourier-transformed photoinduced electric field. This field is coherent in phase with the incident laser field, namely, it is governed by light–matter interactions. The red and blue colors indicate that the respective electric fields are turned to the opposite direction to each other. The electric field is substantially distributed in the Ag–O contact region (green dotted circles). This is attributed to the mutual electronic polarization of the silver nanocluster and the TiO₂ layer, as schematically illustrated in Fig. 6b. Because of the difference in DOS between the silver and TiO₂ moieties (Fig. 2a), the electric field along the *z*-direction mainly induces electronic transitions

from the silver moiety to the TiO₂ moiety (green arrows in Fig. 6b). As the silver–TiO₂ distance increases, the mutual electronic polarization becomes weaker; thus, the direct electron transfer does not occur for system C, in which the photogenerated electric field is smaller than that in system B (Supplementary Fig. 10). In other words, the direct electron transfer is governed by the light–matter interaction that causes the photoinduced electronic interaction in the silver–TiO₂ interfacial region.

DISCUSSION

In numerous studies on the photoexcitation of heterostructures consisting of metallic nanoclusters and a semiconductor, it has been assumed that electrons pass through the conduction band of the metallic nanoclusters.^{2,4} The excited electrons accumulated in metallic nanoclusters lose their energy through electron–phonon and electron–electron scatterings, seriously reducing the efficiency of electron transfer into a semiconductor. Thus, direct electron transfer is capable of yielding high-efficiency light-energy conversion.

If a metal is in close contact with a semiconductor, electronic transitions occur between interfacial states, resulting in direct electron transfer.^{31,32} However, because interfacial states are delocalized in both the metal and semiconductor moieties, excited electrons are partially generated in the metal moiety. In contrast, the present electron transfer is induced in ideal system B with a weak silver–TiO₂ contact, and excited electrons are not found in the silver moiety. Furthermore, electronic states participating in the electron transfer are recognized from the isolated silver nanocluster and the TiO₂ layer. Therefore, the direct electron transfer revealed in this study is significantly different from that between interfacial states.

Although interfacial gap states do not participate in the electron transfer for the present employed systems, it is expected that the interface modification alters the efficiency of the direct electron transfer. For instance, gap-state-assisted electron transfer^{31,32} would be induced by modifying the interfacial region. It is also noted that to select a metallic species suitable for photocurrent generation requires detailed considerations. For example, to replace silver with gold is favorable for preventing carrier recombination by the band bending in a semiconductor near the Schottky barrier because of the higher vacuum level of gold than that of silver. However, the photogenerated electric field from gold is smaller than that from silver; that is, to replace silver with gold is inappropriate for inducing the direct electron transfer. Because of these complex factors, for improving the efficiency of photocurrent generation, it is needed to carefully design the details of the system (e.g., the size and shape of nanoclusters, and an employed semiconductor).

In conclusion, we have elucidated photoexcited electron transfer in heterostructures consisting of a silver nanocluster and a TiO₂ layer using our original first-principles computational approach, which explicitly deals with light–matter interactions. Excited electrons transfer from the silver nanocluster to the TiO₂ layer without passing through the conduction band of silver. The photoinduced electronic interaction at the silver–TiO₂ interface is responsible for direct electron transfer with a mechanism that is significantly different from the conventional LSPR-induced electron transfer. While the proposed mechanism is new, we believe that the direct electron transfer would have occurred in previous experimental studies without being recognized. This is because no singular interfacial electronic state is needed—it is only necessary to make the distance between a silver nanocluster and a TiO₂ layer shorter than the van der Waals contact distance. According to this rather lax requirement, analogous direct electron transfer would be induced in metal/semiconductor heterostructures other than silver/TiO₂ systems. By actively developing metal/semiconductor heterostructures on the basis of the insights reported in this

Fig. 6 Photoinduced electronic interaction. (a) Cross-section of the real part of the Fourier-transformed electric field for system A seen from the direction perpendicular to the *x*–*z* plane, and (b) scheme of the photoinduced electronic polarization in a silver nanocluster/TiO₂ heterostructure.

paper, the efficiency of light-energy conversion should be improved. In this regard, this study provides a general concept that can be applied in the design of optically functional materials consisting of metal/semiconductor heterostructures. For further improving the functionality of these materials, it would be required to obtain deeper atomic-scale insights into the interfacial region. To obtain the insights, our first-principles approach is highly useful because of the wide applicability, for example, to the variation in optical functions depending on defects and contaminants at the interface.

METHODS

Theoretical formula

In SALMON, the photoexcited electron dynamics is simulated by solving the time-dependent Kohn–Sham equation.¹⁴

$$i\frac{\partial}{\partial t}\psi_{jk}(\mathbf{r}, t) = \left[-\frac{1}{2}\nabla^2 - i\mathbf{A}(t) \cdot \nabla + \frac{1}{2}\mathbf{A}^2(t) + v_{\text{nuc}}(\mathbf{r}) + v_{\text{H}}(\mathbf{r}, t) + v_{\text{XC}}(\mathbf{r}, t) \right] \psi_{jk}(\mathbf{r}, t), \quad (1)$$

where v_{nuc} is the nuclear attraction potential, v_{XC} is the exchange correlation (XC) potential, v_{H} is the Hartree potential, and $\mathbf{A}$ is the vector potential of an external field. Equation (1) is directly solved at three-dimensional Cartesian grid points by a nine-point finite-difference formula in the space derivatives.^{33,34} The time propagation is evaluated by the fourth-order Taylor expansion method. Because of the simplicity of this algorithm, the program has high parallel efficiency and can be applied to nanometer-scale heterostructures by carrying out massively parallel calculations.

From the time-dependent wave function, the electric conductivity σ_a ($a \in x, y, z$) and dielectric function ϵ_a are obtained from the following formulas:

$$\sigma_a(\omega) = \frac{\int dt e^{i\omega t} J_a(t)}{\int dt e^{i\omega t} E_{\text{ext}}(t)}, \quad (2)$$

$$\epsilon_a(\omega) = 1 + \frac{4\pi i \sigma_a(\omega)}{\omega}. \quad (3)$$

Here, $E_{\text{ext}}(t)$ is the electric field of the laser pulse polarized along the a direction, and $J_a(t)$ is electric current following through the unit cell defined as^{35,36}

$$J_a(t) = \frac{1}{\Omega} \int_{\Omega} \sum_{jk} \text{Re} \left[\psi_{jk}^*(\mathbf{r}, t) \left(-i\nabla_a + \frac{1}{c} \mathbf{A}_a(t) \right) \psi_{jk}(\mathbf{r}, t) \right] + i \sum_{jk} \int d\mathbf{r} d\mathbf{r}' \psi_{jk}^*(\mathbf{r}, t) \{ V_{\text{nonloc}}(\mathbf{r}, \mathbf{r}') \mathbf{r}'_a - \mathbf{r}_a V_{\text{nonloc}}(\mathbf{r}, \mathbf{r}') \} \psi_{jk}(\mathbf{r}, t), \quad (4)$$

where Ω is the system volume, and V_{nonloc} is caused by the nonlocality of the pseudopotential. We define the optical absorption intensity as $a_2 \equiv z_s \text{Im}[c]/(4\pi)$, where z_s is the supercell length perpendicular to the TiO_2 layer. When the vacuum region is sufficiently large, a_2 is almost independent of the unit cell size.³⁷

We calculate the electron dynamics using a laser pulse with an electric field given by

$$\mathbf{E}_{\text{ext}}(t) = E_0 \hat{\mathbf{u}} \cos(\omega t) \sin^2(\pi t/\tau), \quad (5)$$

where $\hat{\mathbf{u}}$ is a unit vector along the Cartesian axis, ω is the laser frequency, E_0 is the amplitude of the incident laser field, and τ is the pulse width. The laser intensity I (W cm^{-2}) is given with E_0 (V m^{-1}) as $E_0 = 27.45\sqrt{I}$. The vector potential $\mathbf{A}$ is defined with $\mathbf{E}_{\text{ext}}$ as $\mathbf{A}(t) = -\int_0^t \mathbf{E}_{\text{ext}}(t') dt'$.¹⁴ The time-dependent electronic polarization $P(t)$ induced by the external laser field is then evaluated using the following formula:

$$P_a(t) = \int_0^t J_a(t') dt'. \quad (6)$$

Equation (6) is available for both the perpendicular and parallel polarizations to the TiO_2 layer.

The variation in the electron occupation number is defined by the following equations:¹⁵

$$c_{jk}(t) = f_{jk}(t=0) |\langle \psi_{jk}(\mathbf{r}, t) | \psi_{jk}(\mathbf{r}, t=0) \rangle|^2, \quad (7)$$

$$\mathcal{D}_{lk}(E \equiv \epsilon_{lk}, z, t) = \sum_j c_{jk}(t) \int |\psi_{jk}(\mathbf{r}, t=0)|^2 dx dy, \quad (8)$$

$$\Delta \mathcal{D}_{lk}(E, z, t) = \mathcal{D}_{lk}(E, z, t) - \mathcal{D}_{lk}(E, z, t=0). \quad (9)$$

Here, ϵ is a band energy in the ground state, and f_{jk} is the electron occupation number defined by the Fermi–Dirac distribution. In Eq. (7), the photoexcited orbital $\psi_{jk}(\mathbf{r}, t)$ is projected onto the ground-state orbital $\psi_{jk}(\mathbf{r}, t=0)$.³⁸ By integrating over the x and y directions in Eq. (8), the electronic excitation is illustrated along the z -direction, which is perpendicular to the TiO_2 layer. Equation (9) gives the variation in $\mathcal{D}_{lk}$ caused by the laser field. The $\Delta \mathcal{D}_{lk}$ are summed with respect to l and k after Lorentzian broadening has been applied to $\Delta \mathcal{D}_{lk}$; thereby, we obtain the variation in the electron occupation number.

The Kohn–Sham orbitals are, strictly speaking, just an auxiliary construct for obtaining the total electron density.^{39,40} However, the photoexcited electron transfer cannot be fully investigated by only analyzing the electron density. This is because electrons remaining in the valence band also transfer due to an electric field generated by excited electrons. Thus, from the electron density, we can evaluate only the total electron transfer in which electrons in both the valence and conduction bands participate. It is noted that the Kohn–Sham orbitals have been widely utilized to get qualitative interpretations.³⁹ Therefore, the analysis based on Eqs. (7)–(9) is valuable, at least, for obtaining insights into the mechanism of the photoexcited electron transfer.

The photoinduced electronic interaction is analyzed using the Fourier-transformed electric field at the incident laser frequency.⁴¹

$$\Delta \mathcal{E}(\mathbf{r}, \omega) \equiv \int_0^T \{ \rho(\mathbf{r}', t) - \rho(\mathbf{r}', 0) \} \cdot \frac{\mathbf{r} - \mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|^3} \cdot \left\{ 1 - 3(t/T)^2 + 2(t/T)^3 \right\} e^{i\omega t} dt d\mathbf{r}', \quad (10)$$

where the cubed and squared terms reduce the numerical noise due to the Fourier transformation,⁴² and T is set to the pulse width, i.e., 30 fs. As a cosine-type laser field is employed (Eq. (5)), the real part (i.e., the cosine component) of $\Delta \mathcal{E}$ is attributed to electronic polarization by the incident laser field, whereas the imaginary part (i.e., the sine component) reflects the photoabsorption.⁴¹

To obtain the 2D LDOS, we calculate the following quantity:

$$\mathcal{D}_{lk}(E \equiv \epsilon_{lk}, z) = f_{jk}(t=0) \int |\psi_{jk}(\mathbf{r}, t=0)|^2 dx dy. \quad (11)$$

Then, Lorentzian broadening is applied to $\mathcal{D}_{lk}$, and the sum with respect to l and k is performed.

Computational details

Geometry optimization was performed using the Quantum Espresso program package.⁴³ A rutile $\text{TiO}_2(110)$ surface was employed and the cell size was fixed to that of the bulk system. We further calculated a twice thicker $\text{TiO}_2(110)$ layer, which was also utilized in the previous study,¹⁸ and confirmed that the results are, at least, qualitatively unchanged in terms of the discussions given in this study (Supplementary Sec. 8). The dispersion-corrected PBE functional was employed to calculate the exchange correlation potential to take into account van der Waals interactions.^{44–47}

The optimized systems were used in calculating the optical response with SALMON.¹⁴ The grid spacings were set to ~ 0.25 Å, in accordance with the unit cell size. The supercell length along the direction perpendicular to the TiO_2 layer was set to 30 Å. This makes the width of the vacuum region ~ 12 Å. The PBE functional was used in the SALMON calculations. Comparing the computational and experimental results of optical absorption, we concluded that the functional dependence has a qualitatively negligible influence on the discussion of this study (see also the Results section). It is noted that the dispersion-corrected functional employed in the geometrical optimization semiempirically corrects the total energy by utilizing a geometrical structure, and does not directly modify optical properties when the geometrical structure is fixed in the photoexcitation process. Effective core potentials were obtained using the Troullier–Martins scheme implemented in the fhi98PP program.^{48,49} Visualizations were performed with the VESTA program package.⁵⁰

In this study, the x-polarized excitation is mainly discussed. Due to the finiteness of the employed system, the absorption intensity by the z-polarized field is several times smaller than that by the x-polarized field (Supplementary Secs. 7, 8). It is noted that the direct electron transfer is also induced by the z-polarized field, as well as the experimental study.⁶ Thus, we consider that the discussion of this study is, at least, qualitatively in accord with the experimental study.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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AUTHOR CONTRIBUTIONS

K.I. performed all calculations and wrote the paper. M.N. developed the core part of the computational program to carry out the nanomaterial calculations, helped the analysis of the computational result, and reviewed the paper.

COMPETING INTERESTS

The authors declare no competing interests.

ADDITIONAL INFORMATION

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