Instantaneous Generation of Charge-Separated State on TiO$_2$ Surface Sensitized with Plasmonic Nanoparticles

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ABSTRACT: Photoexcitation of the plasmon band in metallic nanoparticles adsorbed on a TiO$_2$ surface initiates many important photovoltaic and photocatalytic processes. The traditional view on the photoinduced charge separation involves excitation of a surface plasmon, its subsequent dephasing into electron–hole pairs, followed by electron transfer (ET) from the metal nanoparticle into TiO$_2$. We use nonadiabatic molecular dynamics combined with time-domain density functional theory to demonstrate that an electron appears inside TiO$_2$ immediately upon photoexcitation with a high probability (~50%), bypassing the intermediate step of electron–hole thermalization inside the nanoparticle. By providing a detailed, atomistic description of the charge separation, energy relaxation, and electron–hole recombination processes, the simulation rationalizes why the experimentally observed ultrafast photoinduced ET in an Au–TiO$_2$ system is possible in spite of the fast energy relaxation. The simulation shows that the photogenerated plasmon is highly delocalized onto TiO$_2$ and thus, it is shared by the electron donor and acceptor materials. In the 50% of the cases remaining after the instantaneous photogeneration of the charge-separated state, the electron injects into TiO$_2$ on a sub-100 fs time scale by the nonadiabatic mechanism due to high density of acceptor states. The electron–phonon relaxation parallels the injection and is slower, resulting in a transient heating of the TiO$_2$ surface by 40 K. Driven by entropy, the electron moves further into TiO$_2$ bulk. If the electron remains trapped at the TiO$_2$ surface, it recombines with the hole on a picosecond time scale. The obtained ET and recombination times are in excellent agreement with the experiment. The delocalized plasmon state observed in our study establishes a novel concept for plasmonic photosensitization of wide band gap semiconductors, leading to efficient conversion of photons to charge carriers and to hybrid materials with a wide variety of applications in photocatalysis and photovoltaics.

1. INTRODUCTION

The prominent catalytic properties of gold nanoparticles on well-ordered metal oxide substrates$^1$–$^4$ stimulate extensive research activities. These systems combine the light-harvesting ability of semiconductor nanocrystals$^5$ with the catalytic activity of small metal particles,$^6$ showing great promise in photocatalysis, such as light-driven hydrogen production.$^7$–$^9$ Interfacial electron transfer (ET)$^{10}$ is key to light-induced activity, because the latter depends on the ability of a catalyst to create and efficiently separate electron–hole pairs. The photoinduced electron–hole separation facilitates redox reactions via formation of adsorbed radicals on semiconductor surface. Many factors affect photocatalytic processes, especially those concerning the fate of the carriers that have reached the catalytic surface: do these charges directly react with adsorbates, or are they first trapped by surface species and then transferred to the reactants? High photochemical yields require that the charge generation rate far exceeds the rates of charge relaxation and recombination.

Solar cells based on semiconductor sensitization with metal nanoparticles$^{1,11}$–$^{16}$ have attracted significant attention because of the unique electronic and optical properties of metallic clusters. The exciting optical physics of metal nanoparticles arises from the resonant interaction of conduction band electrons and the electromagnetic field.$^{17}$–$^{23}$ The collective excitations, usually known as plasmons, are responsible for the specific light extinction and high local fields. Surface plasmons are propagating electron density waves occurring at the interface between metal and dielectric. They can be viewed as electromagnetic waves strongly bound to the interface. In particular, the physical origin of the light absorption by metal nanoparticles is the coherent oscillation of the conduction band electrons induced by the electromagnetic field. The oscillation modes that comprise an electromagnetic field coupled to the oscillations of the conduction band electrons are called surface plasmons.$^{24}$ Plasmon excitations trigger nontrivial electron–phonon dynamics. In optical, electronic, and photovoltaic devices, electron–phonon coupling causes nonradiative energy loss and system heating and should be avoided. At the same time, rapid electron–vibrational relaxation is key to applications of metal nanoparticles in photothermal therapy, in which the absorbed photon energy is converted into heat.$^{25}$–$^{27}$ Similarly,
fast electron—phonon relaxation shortens the response time of electro-optic switches. 28

Gold nanoparticles deposited onto TiO2 can increase the power-conversion efficiency of the dye-sensitized solar cell. The localized surface-plasmon resonance enhances light absorption of molecular chromophores. 29,30 Alternatively, excitation of the surface plasmon band can be exploited directly, bypassing the need for traditional dyes. Gold nanoparticle—TiO2 systems exhibit efficient light-to-charge conversion under excitation at the wavelength of the plasmon band. 11,16,31 The gold nanoparticle—TiO2 composites can overcome the lack of visible light response of TiO2 and promote TiO2 photocatalytic activity. Recently, Kilin and co-workers investigated the electron and hole relaxation dynamics at the Au/Si metal-semiconductor nanointerface co-doped by aluminum and phosphorus. 32 In contrast to molecular and semiconductor quantum dot (QD) chromophores, metallic particles exhibit small or zero band gap, allowing for rapid electron—hole recombination. In order to achieve the photovoltaic and photocatalytic activity, the electron injection from the gold nanoparticles into the TiO2 substrate should be faster than the recombination. These phenomena provide strong motivation for investigation of microscopic details of the charge- and energy-transfer dynamics at the gold nanoparticle—TiO2 interface.

Figure 1a presents a diagram of the energy levels in a gold nanoparticle—TiO2 system, while Figure 1b demonstrates the commonly assumed sequence of events. Absorption of a photon by the nanoparticle surface plasmon is particularly strong near the sharp features of the nanoparticle. The collective plasmonic excitation dephases into electron—hole pairs on a sub-10 fs time scale. The holes are substantially lower in energy than the valence band states of TiO2 and remain inside the particle. (Note that hole energy rises as one proceeds down in energy along the occupied orbital manifold.) The electrons inside the metal particles are in energetic resonance with the TiO2 conduction band states, and therefore, the electrons are injected into TiO2. Simultaneously, electrons and holes relax in energy by coupling to vibrational motions of the nanoparticle and TiO2 atoms. If the electron is able to lose its energy to phonons and recombine with the hole faster than the injection, the absorbed photon energy is lost to heat. The injection leads to a charge-separated state, with the electrons at the bottom of the TiO2 conduction band and the holes near the gold nanoparticle Fermi level. At this point, the electrons can delocalize into TiO2 bulk or again recombine with the holes. Once in the bulk, the electrons diffuse inside TiO2 toward an electrode or a chemical reaction site. If an electron that has already reached the bulk returns to the surface and recombines with the hole, the photon-to-charge conversion yield is reduced. Therefore, it is critical for photovoltaic and photocatalytic applications that charge separation across the metal particle—TiO2 interface occurs rapidly.

Figure 1c demonstrates an alternative mechanism for the photoinduced charge separation in the Au—TiO2 system. Here, the plasmon excitation exhibits a strong delocalization into TiO2 surface. As a result, there exists a significant probability for the electron to find itself inside TiO2 immediately upon the photoexcitation. According to this scenario, the charge-separated state is generated instantaneously. The high density of TiO2 states ensures that the electron delocalizes into TiO2 bulk very rapidly, and the time-scale of the charge-phonon relaxation and electron—hole recombination becomes essentially irrelevant for the photovoltaic and photocatalytic response.

Furube et al. employed a femtosecond transient absorption spectroscopy with an IR probe to report ultrafast extraction of electrons from excited gold nanoparticles into the TiO2 semiconductor. 11 The extraction occurred within <240 fs, as limited by the experimental time resolution. At the same time, the electron—hole recombination exhibited a broad range of time scales, from 1 ps to nanoseconds. The extremely fast, sub-240 fs, nonequilibrium ET from the gold nanoparticles into the TiO2 surface makes it difficult to invoke traditional ET models, such as the Marcus theory. The latter makes a quasi-equilibrium assumption, and therefore, it is applicable to sufficiently slow ET, which allow for energy redistribution.

The present work applies the state-of-the-art theoretical technique developed in our group and combining time-domain density functional theory (TDDFT) with nonadiabatic molecular dynamics (MD) to investigate the nonequilibrium, plasmon-driven dynamics at the gold nanoparticle—TiO2 interface. The work of Schatz, Jensen, and Aikens 21 showed how collective plasmon excitations arise in TDDFT from single particle transitions between Kohn—Sham (KS) orbitals, as the size of a metallic particle grows. Individual single-electron transitions form a broad excitation band, matching the plasmon band of metals particles several nanometers in size. Other techniques, such as the electron-driven discrete-dipole approximation (e-DDA), developed recently by Masiello and co-workers, 36 can be used to study plasmon excitations in large systems with arbitrary geometries. At the same time, it is not trivial to extend e-DDA method to time-domain modeling, as in the current work. Our simulation gives a novel perspective on the electron- and energy-transfer dynamics, focusing on the geometric structure of the nanoparticle—TiO2 system, its
electronic properties, the nuclear dynamics and electron–vibrational coupling, the mechanisms responsible for the electron injection, the electron–phonon relaxation process, and the electron–hole recombination. The results show excellent agreement with the available experimental data. Perhaps most importantly, the simulation demonstrates that charge separation occurs simultaneously with the photoexcitation of the plasmon band in 50% of the cases. The traditional ET mechanism, Figure 1b, operates in the remaining 50% of the time and is faster than the electron–phonon relaxation.

2. THEORETICAL METHODOLOGIES

The nonadiabatic MD simulation of ET dynamics is carried out using the mixed quantum-classical approach,37 implementing the fewest switches surface hopping (FSSH) technique38–40 within TDDFT41–43 in the KS representation.44 The electrons are treated quantum mechanically, and the nuclei are treated semiclassically, since they are much heavier and slower. The decoherence correction44 to FSSH is used to study the electron–hole recombination. The following subsections outline the TDDFT-nonadiabatic MD and FSSH methods and provide the technical details of the standard DFT and MD techniques,45 underlying the more advanced methodologies.

2.1. Time-Dependent KS Theory for Electron–Nuclear Dynamics. The ET dynamics including the nonadiabatic effects46 are described by real-time TDDFT within the KS approach.47,48 The electron density, $\rho(r, t)$, is expressed by the sum of the densities of the occupied time-dependent single-electron KS orbitals, $\psi_k(r, t)$.

$$\rho(r, t) = \sum_{p=1}^{N_e} \rho_p(r, t)$$  (1)

The evolution of the electron density is determined by the time-dependent variational principle, leading to a set of single-particle equations for the evolution of the KS orbitals:

$$i\hbar \frac{\partial \rho_p(r, t)}{\partial t} = H(r, R, t) \psi_p(r, t); \quad p = 1, 2, ..., N_e$$  (2)

The equations are coupled, because the DFT Hamiltonian $H$ depends on the overall electron density. The electron–vibrational interaction enters the Hamiltonian $H$ through the external potential created by the nuclei. The time-dependent single-electron orbitals in eq 2 are expressed in the basis of the adiabatic KS orbitals, $\tilde{\psi}_k(R(t))$, which are calculated for the current atomic positions $R$. The focus is on the evolution of the orbital $\psi_{PE}$ occupied by the photoexcited electron. As discussed previously,47–50 the ET dynamics are well described by the evolution of the photoexcited electron, which involves unoccupied orbitals of the gold cluster and TiO$_2$ conduction band states. The populations of the other orbitals do not change over the course of the simulation: The hole resides near the Fermi energy, in particular, the Au$_{20}$ highest occupied molecular orbital (HOMO), while the rest of the Au$_{20}$ valence band orbitals and all TiO$_2$ valence band orbitals are occupied.

The adiabatic representation of the time-dependent KS orbital occupied by the photoexcited electron is given in eq 3:

$$\psi_{PE}(r, t) = \sum_k c_k(t) \psi_k(r; R(t))$$  (3)

Inserting eq 3 into eq 2 leads to the equation describing the evolution of the expansion coefficients:

$$i\hbar \frac{\partial c_k(t)}{\partial t} = \sum_i c_i(t) (\epsilon_i \delta_{ki} + d_{ki})$$  (4)

where $\epsilon_k$ is the energy of the adiabatic state $k$, and $d_{ki}$ is the nonadiabatic coupling between states $k$ and $j$. The nonadiabatic coupling is created by motion of atoms and represents the electron–vibrational interaction. It is calculated numerically as the overlap of orbitals $j$ and $k$ at sequential time steps:

$$d_{kj} = -i\hbar \langle \phi_j | \nabla R | \phi_k \rangle \frac{dR}{dt} = -i\hbar \langle \phi_j | \frac{\partial}{\partial t} \phi_k \rangle$$

$$\approx -i\frac{\hbar}{2\Delta t} \left( \langle \psi_j(t) | \psi_k(t+\Delta t) \rangle - \langle \psi_j(t) + \Delta t | \psi_k(t) \rangle \right)$$  (5)

2.2. ET Mechanisms. The extent of ET from the gold nanoparticle to the TiO$_2$ surface is computed by integrating the photoexcited electron density over the region of the simulation cell occupied by the Au$_{20}$ QD, Figure 2:

$$\int_{QD} \rho_{PE}(r, t) dr = \int_{QD} |\psi_{PE}(r, t)|^2 dr$$

$$= \sum_{k,j} c_k^* (t) c_j (t) \int_{QD} |\psi_k^*(r, R(t)) \psi_j (r, R(t))| dr$$  (6)

The time-derivative of eq 6 gives expressions for the adiabatic and nonadiabatic ET contributions:

Figure 2. Top and side views of the simulation cell showing the geometry of the rutile TiO$_2$-[110]-Au$_{20}$ system optimized at 0 K (left) and during the molecular dynamics run at 300 K (right). No chemical bonding between the subsystems is seen, and only minor thermal fluctuations in the system geometry are observed at ambient temperature.
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\[
\frac{d}{dt} \int_{QD} \rho_{PE}(r, t) dr = \sum_{k} \left\{ \frac{d(\epsilon_{i}^{k} \epsilon_{j}^{k})}{dt} \int_{QD} \phi_{i}^{k} \phi_{j}^{k} dr + \epsilon_{j}^{k} \frac{d}{dt} \int_{QD} \phi_{i}^{k} \phi_{j}^{k} dr \right\}
\]

(7)

The first term has fixed localizations of adiabatic states, \( \int_{QD} \phi_{i}^{k} \phi_{j}^{k} dr \), but changing expansion coefficients, \( \epsilon_{i}^{k} \epsilon_{j}^{k} \), defining state occupations. The second term has fixed adiabatic state occupations but changing localizations. The first and second terms correspond to nonadiabatic ET and adiabatic ET, respectively. The adiabatic ET proceeds by a change in the localizations of the photoexcited state from the gold QD to the TiO\(_2\) surface, induced by atomic motions. To undergo a nonadiabatic transfer, the photoexcited electron has to hop into a TiO\(_2\) state, causing a change in the state occupations.

The ET mechanisms carry different implications for the variation of the interface conductance and solar cell voltage with system properties. Direct ET usually requires strong donor–acceptor coupling, and the photoexcited state is shared by donor and acceptor materials. Direct electron injection implies that positive and negative charges are created at the energy of the absorbed photon. This fact can be used to avoid energy and voltage losses to heat. Adiabatic ET also requires strong donor–acceptor interaction as well as an energy fluctuation that can drive the system along the reaction coordinate and across the transition state. Adiabatic electron injection can take place near the edge of TiO\(_2\) conduction band, potentially avoiding energy losses to heat.\(^{50}\) Nonadiabatic ET does not require strong donor–acceptor interaction and, therefore, occurs in a broader range of systems. Nonadiabatic ET can be ultrafast in the presence of a high density of acceptor states. As the distance between the donor and acceptor species increases and the donor–acceptor coupling decreases, adiabatic ET becomes insignificant, and ET proceeds by the nonadiabatic mechanism, showing exponential dependence on the distance. The adiabatic and nonadiabatic mechanisms represent opposite limits are described by different analytic formulas and exhibit dissimilar dependence of the ET rate on system properties. Therefore, establishing the ET mechanism is of both fundamental and practical importance. A more detailed discussion of the ET mechanisms can be found in our recent work on the graphene–TiO\(_2\) system\(^{51}\) and a number of reviews.\(^{52}–^{54}\)

2.3. Fewest Switches Surface Hopping. The dependence of the electronic Hamiltonian on nuclear coordinates, eq 2, determines the influence of vibrational motions on the electronic evolution. The opposite effect, the back-reaction of electrons onto the nuclei, constitutes an essential part of a nonadiabatic MD algorithm. FSSH provides a prescription for the back-reaction, both allowing for branching between alternative reaction pathways\(^{58}\) and satisfying detailed balance between transitions upward and downward in energy.\(^{44}\) The latter is required for proper treatment of electron–vibration energy exchange.\(^{55}\)

The probability of a transition from an initial state \( i \) to another state \( j \) within the time interval \( \delta t \) is given in FSSH by\(^{58}\)

\[
g_{ij}(t, \delta t) = \max \left\{ 0, \frac{b_{ij}(\delta t)}{a_{ij}(t)} \right\}
\]

(8)

where

\[
a_{ij}(t) = \epsilon_{j}(t)\epsilon_{j}(t)
\]

and

\[
b_{ij} = 2\hbar^{-1} \text{Im} \langle a_{ij} | \hat{H}_{\text{eff}} | \hat{\psi}_{j} \rangle - 2\text{Re}(a_{ij} d_{ij})
\]

(9)

If the calculated \( g_{ij} \) is negative, the hopping probability is set to zero; a hop from state \( j \) to state \( k \) can take place only when the electronic occupation of state \( j \) decreases and the occupation of state \( k \) increases. To conserve the total electron–nuclear energy after a hop, the original FSSH technique rescues the nuclear velocities along the direction of the nonadiabatic coupling. If a nonadiabatic transition to a higher energy electronic state is predicted by eq 8 and the kinetic energy available in the nuclear coordinates along the direction of the nonadiabatic coupling is insufficient to accommodate the increase in the electronic energy, then the hop is rejected. The velocity rescaling and hop rejection give the detailed balance between the upward and downward transitions in energy.\(^{44}\) The current simulation uses a simplified version of FSSH, as described in ref 56. If the energy exchanged between the electronic and nuclear degrees of freedom during a hop is rapidly exchanged among all nuclear modes, the energy distribution is Boltzmann at all times. Then, the velocity rescaling and hop rejection can be replaced by multiplying the probability, eq 8, for transitions upward in energy by the Boltzmann factor.

2.4. Decoherence Correction in Surface Hopping. The original FSSH\(^{58}\) does not involve decoherence that takes place in the electronic subsystem due to coupling to quantum vibrations.\(^{53,57,58}\) Decoherence can be ignored if it is slower than the time of quantum transitions.\(^{77}\) This condition is satisfied for ET from the Au\(_{20}\) nanocluster to the TiO\(_2\) surface, since it involves multiple rapid hops between closely spaced electronic states. In contrast, the return of the injected electron to the gold QD involves an electronic transition across a wide energy gap. It takes place on picosecond time scale,\(^{11}\) which is significantly longer than the decoherence time. Therefore, a semiclassical decoherence correction should be included with SH.\(^{46,55,57,58}\) In the current simulation, the time-dependent KS wave function \( \hat{\psi}_{\text{eff}}(t, \mathbf{r}) \) is collapsed to an adiabatic eigenstate \( \hat{\psi}_{\text{a}}(\mathbf{r}, \mathbf{R}(t)) \), eq 3, on the decoherence time scale, as implemented in ref 34. The collapse procedure is equivalent to resetting to zero the off-diagonal matrix elements \( a_{ij} \), eq 9, entering the FSSH transition rate, eq 8. The collapse times are determined by a sequence of random numbers sampled from the Poisson distribution with the characteristic time determined by the decoherence time. The probability of collapse onto eigenstate \( k \) is given by the square of the coefficient \( \epsilon_{k}(t) \) at the collapse time. The decoherence time was computed as the time of quantum transitions.37,50 This condition is satisfied in the current simulation, the time-dependent KS wave function \( \hat{\psi}_{\text{eff}}(t, \mathbf{r}) \) is collapsed to an adiabatic eigenstate \( \hat{\psi}_{\text{a}}(\mathbf{r}, \mathbf{R}(t)) \), eq 3, on the decoherence time scale, as implemented in ref 34. The collapse procedure is equivalent to resetting to zero the off-diagonal matrix elements \( a_{ij} \), eq 9, entering the FSSH transition rate, eq 8. The collapse times are determined by a sequence of random numbers sampled from the Poisson distribution with the characteristic time determined by the decoherence time. The probability of collapse onto eigenstate \( k \) is given by the square of the coefficient \( \epsilon_{k}(t) \) at the collapse time. The decoherence time was computed as the time of quantum transitions.37,50 This condition is satisfied in the current simulation, the time-dependent KS wave function \( \hat{\psi}_{\text{eff}}(t, \mathbf{r}) \) is collapsed to an adiabatic eigenstate \( \hat{\psi}_{\text{a}}(\mathbf{r}, \mathbf{R}(t)) \), eq 3, on the decoherence time scale, as implemented in ref 34. The collapse procedure is equivalent to resetting to zero the off-diagonal matrix elements \( a_{ij} \), eq 9, entering the FSSH transition rate, eq 8. The collapse times are determined by a sequence of random numbers sampled from the Poisson distribution with the characteristic time determined by the decoherence time. The probability of collapse onto eigenstate \( k \) is given by the square of the coefficient \( \epsilon_{k}(t) \) at the collapse time. The decoherence time was computed as the time of quantum transitions.37,50
The pure-dephasing function is computed using the second-order cumulant expansion to the optical response function, as described, for example, in ref 59:

\[ \rho_{\text{LUMO}}(t) = \exp(-g(t)) \]  
where \( g(t) \)

\[ g(t) = \int_0^t dt_1 \int_0^t dt_2 C(r_2) \] 

Typically for condensed phase systems, the cumulant representation of the pure-dephasing function converges rapidly and gives an accurate description.\(^{60,61}\) Fast convergence is important for \( ab\) \( initio \) simulations, which are limited to picoseconds. Fitting eq 12 by a suitable analytic function, typically Gaussian, gives the pure-dephasing time.

2.5. Simulation Details. The simulation uses the stoichiometric rutile (110) surface, since it is most stable among the low index surfaces of rutile TiO\(_2\).\(^{62}\) The 120-atom (5 \( \times \) 2) surface region was modeled with a periodically repeated slab, comprised of six atomic layers of TiO\(_2\) with the bottom three layers frozen in the bulk configuration. The slab was separated from its periodic image along the surface normal by a large, 20 Å vacuum region. The tetrahedral Au\(_{20}\) cluster, chosen due to its high symmetry (\( T_d \)) and stability, represented the gold QD.\(^{63,64}\) The cluster geometry corresponds to fcc bulk gold, with the cluster surfaces forming the (111) planes. The Au\(_{20}\) cluster preserves the semiconductor bulk structure during both geometry optimization and finite-temperature MD simulation. Initially, the gold atoms in the bottom plane of Au\(_{20}\) connect to six bridging oxygen atoms of the TiO\(_2\) (110) surface. This setup maximizes the number of direct Au\(_{20}\)–TiO\(_2\) interactions and creates the most stable configuration.

The geometry optimization, electronic structure, and adiabatic MD calculations are performed using the projector augment wave method implemented in the Vienna \( ab\) \( initio \) simulation package (VASP).\(^{65}\) The electron exchange and correlation terms are treated with the Perdew–Burke–Ernzerhof (PBE) functional.\(^{66}\) The DFT+U approach is used to describe the TiO\(_2\) properties. The on-site \( U \) = 6.0 eV and \( J \) = 0.5 eV values are applied to treat the 3d electrons of Ti atoms.\(^{67}\) After relaxing the geometry at 0 K, repeated velocity rescaling is used to bring the temperature of the Au\(_{20}\)–TiO\(_2\) system to 300 K, corresponding to the temperature in the experiment.\(^{11}\) After that, a 3 ps adiabatic MD simulation is performed in the microcanonical ensemble with a 1 fs atomic time-step.

To simulate the photoinduced ET dynamics, 100 initial system geometries are selected randomly from the 3 ps adiabatic MD trajectory. An electron is promoted to the orbital corresponding to the lowest energy plasmonic excitation of Au\(_{20}\), and its evolution is tracked by solving eq 4, using the second-order differencing scheme and a 10\(^{-3}\) fs electronic time-step. This procedure is applied to study the competing ET and energy relaxation processes within the manifold of Au\(_{20}\) and TiO\(_2\) conduction band states. The electronic energy is computed as the standard quantum mechanical expectation value, averaged canonically over multiple nonadiabatic MD runs. The electron–hole recombination is simulated with the decoherence-corrected nonadiabatic MD-FSSH scheme, outlined in the previous subsection. Since the ET and electron–phonon energy relaxation occur much faster than the electron–hole recombination, it is assumed that the electron had relaxed to the lowest energy unoccupied molecular orbital (LUMO) prior to the recombination. The recombination process is modeled within the two-state HOMO–LUMO approximation, requiring evaluation of only one pure-dephasing time scale. This time scale determines the homogeneous luminescence line-width and can be tested experimentally, as done previously for a variety of systems.\(^{69–73}\)

3. RESULTS AND DISCUSSION

The time-domain \( ab\) \( initio \) simulations of the plasmon-driven electron injection and recombination in the Au\(_{20}\)–TiO\(_2\) system provide a detailed real-time atomistic picture of the electron and energy transfer, energy relaxation, and electron–hole recombination dynamics at the interface. The nonadiabatic MD simulation allows us to explore and identify directly the ET mechanisms, the time scales of various competing processes, the elastic and inelastic electron–vibrational interactions, and the phonon modes that couple to the electronic subsystem. The simulation results can be compared directly with the corresponding time-resolved experiments. The simulation establishes that the direct photoexcitation mechanism generates a large contribution to the photoinduced charge separation in the plasmonic system. The discussion in the following subsections emphasizes a number of issues related to the electron–vibrational dynamics, including the geometric and electronic structure of the interface, vibrational dynamics, plasmon-driven ET from the gold nanoparticle into the TiO\(_2\) conduction band, electron–vibrational energy relaxation, and electron–hole recombination.

3.1. Geometric Structure of the Au\(_{20}\)–TiO\(_2\) System. The interaction between the Au\(_{20}\) nanocluster and the TiO\(_2\) surface determines the rates and mechanisms of the electron- and energy-transfer processes.\(^{74–76}\) The Au\(_{20}\)–TiO\(_2\) geometry and separation characterize the strength of the interfacial interaction. The simulation uses the most common (110) surface of rutile TiO\(_2\) and a medium size gold nanoparticle that is thermodynamically stable and preserves the topology of bulk gold. Figure 2 shows the top and side views of the systems relaxed at 0 K (left panel) and a geometry from the MD run at 300 K (right panel). The Au\(_{20}\) nanoparticle remains bound to the TiO\(_2\) substrate at room temperature, even though thermal fluctuations affect the combined system geometry. In either case, the Au\(_{20}\) particle remains relatively close to the TiO\(_2\) surface, although no directional, covalent-type bonds are formed between the subsystems. This behavior differs from all previously studies cases, including the molecule–semiconductor interfaces,\(^{49,52,77–80}\) the wet-electron system,\(^{48}\) the PbSe QD–TiO\(_2\) interface,\(^{47}\) and the graphene–TiO\(_2\) composite.\(^{51}\) While the molecules sensitizing TiO\(_2\) are designed to bind covalently, neither the PbSe QD nor graphene systems include bridging chemical groups. Nevertheless, the Pb atoms formed strong bonds with the bridging oxygens of the rutile TiO\(_2\) (110) surface,\(^{27}\) and some of the graphene six-membered rings rearranged, freeing \( p_z \) electrons from the \( \pi \)-conjugated network and allowing them to interact with the TiO\(_2\) oxygens.

The largest scale motion at ambient temperature is associated with in-plane oxygen atom displacements in the first layer of the TiO\(_2\) surface and nanocluster movement perpendicular to the TiO\(_2\) (110) surface. The displacements of the bridging oxygen atoms can be seen in the top views of the simulation cell, Figure 2. The movement of the nanocluster is demonstrated by the side views. The nanocluster becomes slightly more spherical at the elevated temperature. The average separation between Au\(_{20}\) and the surface increases from 2.125
to 2.431 Å as temperature is raised from 0 to 300K. The increasing Au20−TiO2 separation serves to decrease the donor−acceptor coupling strength. This decrease can have a notable effect on the ET mechanism and may be partially responsible for nonadiabatic ET being the dominant mechanism, as shown below. Adiabatic ET requires a strong donor−acceptor interaction, while nonadiabatic ET operates in cases with a weaker interaction. Nonadiabatic ET is similar to tunneling and shows exponential dependence on the donor−acceptor separation.

3.2. Electronic Structure of the Au20−TiO2 Interface.

Figure 3a shows the density of states (DOS) of the combined system, separated into the contribution from Au20 (black line) and the TiO2 (110) slab (red line). The DOS of the isolated Au20 cluster and TiO2 surface are shown in Figure S1. Since most pure DFT functionals, such as PBE used here, underestimate band gaps due to the self-interaction error,66 the band gap of the current system was scaled to the experimental value of 1.1 eV.11 The DOS demonstrates that the plasmon excitation band of the metallic nanocluster is well inside the TiO2 conduction band. The high density of TiO2 acceptor states available at the plasmon excitation energy facilitates efficient ET and favors the nonadiabatic ET mechanism. The Au20 DOS is low at energies from 1 to 2 eV above the Fermi energy and rises rapidly at 2.25 eV, coinciding with the onset of the plasmon band.11 Comparing the combined DOS given in Figure 3a with the DOS of the individual subsystems shown Figure S1, we observe that the combined DOS resembles the sum of the DOS of the isolated subsystems. The peaks of the individual DOS are broadened by the interaction, and some small new features appear. The key bands present in the isolated subsystem DOS are also present in the combined DOS. The Fermi energy of TiO2 is lower by about 2 eV relative to the Fermi energy of Au20.

The DOS of the Au20−TiO2 (110) system, Figure 3a, gives rise to the absorption spectrum, shown in Figure S2. The strongest peak at 2.3 eV corresponds to the plasmon excitation of the Au20 particle. It is excitation of this peak that is sampled in the reported time-domain simulation, as illustrated by the black points in Figure 3b. The LUMO of the combined Au20−TiO2 system is due to TiO2, while the HOMO arises from Au20, Figure 3a. This setup indicates that the lowest electronically excited state of the system is a charge-transfer state. Indeed, the absorption spectrum, Figure S2, shows a lower intensity peak at 1.7 eV, corresponding to the charge-transfer excitation. The peaks in the spectrum at 2.7 eV and higher have contributions from both TiO2 and Au20.

Following the plasmon-initiated ET process, the system will evolve to the lowest excited state on a subpicosecond time scale as a result of phonon-induced relaxation of the electron to the conduction band edge. Further electron−phonon relaxation can lead to electron−hole recombination, which competes with electron delocalization into TiO2 bulk and constitutes the primary source of losses in the photoinduced current and photocatalytic efficiency. These processes are accounted for in the time-domain simulation discussed below.

Figure 3. (a) DOS of the TiO2(110) surface (red line) and Au20 nanocluster (black line). The Fermi level is set to zero. (b) TiO2 DOS in the excitation energy range (red line) and localization of the plasmon excitation on the Au20 cluster (black squares). About 50% of the plasmon density extends onto TiO2.

Figure 4. Charge densities of (a) plasmon, (b) TiO2 acceptor state, and (c) HOMO of the Au20−TiO2 system. The excited surface plasmon, state (a), is delocalized significantly onto TiO2, leading to instantaneous generation of the charge-separated state upon photoexcitation at the plasmon energy. Entropy drives the electron into TiO2 bulk, exemplified by state (b). Following electron−vibrational relaxation, the electron can recombine with the hole, residing in state (c), on a picosecond time scale.
In the continuous-wave excitation limit describing sunlight absorption, a system is excited to an adiabatic state, i.e., an eigenstate of the electronic Hamiltonian for fixed nuclear positions. If the donor and acceptor state energies are in near resonance and the donor–acceptor coupling is significant, the adiabatic state becomes a superposition of the donor and acceptor states. The coupling occurs due to interaction of the Au 5d orbitals with the 3d orbitals of the under-coordinated Ti atoms of the surface, facilitated by the surface oxygens. Figure 3b shows localization of the excited state on the Au20 donor (black dots), indicating that continuous-wave light generates a state that is already about 50% delocalized onto the TiO2 acceptor. Figure 4 presents the spatial distribution of electron densities of the donor and acceptor states for electron injection process. The donor state is distributed about equally between the Au20 pyramid and the TiO2 substrate, Figure 4a. This result indicates that in 50% of the cases, excitation of the plasmon band instantaneously generates the charge-separated state. This characteristic is different from a typical plasmon, with the majority of the density localized on the nanoparticle surface and in regions of high curvature, on top of the Au20 pyramid. The acceptor state is spread nearly uniformly across the TiO2 and in regions of high curvature, on top of the Au20 pyramid.

The Fourier transforms of the time-dependent photoexcited state energy and localization identify the phonon modes that are coupled to the electronic subsystem. The Fourier transforms are shown in Figure 5, together with the normalized autocorrelation functions of the state energy and localization. The nonadiabatic electron–phonon coupling is directly related to the second derivative of the energy along the nuclear trajectory. Therefore, the vibrational modes that most strongly modulate the energy levels create the largest coupling. The autocorrelation function describes how the energy at a particular time depends on its value at earlier times. Poorly correlated, random motions result in autocorrelation functions that decrease rapidly from 1 to 0. Well-correlated, periodic motions lead to autocorrelation functions that oscillate between 1 and −1.

The Fourier transforms show that low-frequency vibrational modes couple to the electronic excitation more strongly than high-frequency modes, Figure 5. This is in agreement with the previous studies. Phonon modes with frequencies <400 cm\(^{-1}\) dominate both Fourier transforms. The localization Fourier transform has largest amplitude in the region between 100 and 300 cm\(^{-1}\). Notable contributions from vibrations around 800 cm\(^{-1}\) are seen in both spectra. In particular, the mode at 700 cm\(^{-1}\) is responsible for the persistent oscillation of the energy autocorrelation function, Figure 5a. Since the plasmon excitation is delocalized onto the nanoparticle surface and the TiO2 substrate, Figure 4a, its wave function is sensitive primarily to low-frequency acoustic phonons that modulate the size and shape of the nanoparticle. High-frequency optical modes involve local displacements of atoms, having little effect on the plasmon excitation. They couple to the photoexcited state primarily due to the state delocalization onto the TiO2 substrate. High-frequency TiO2 vibrations change dipole moments of the polar Ti–O bonds, and therefore, they couple to the electronic subsystem.

The peaks in the calculated Fourier transforms can be assigned to the following vibrations. The peak around 50 cm\(^{-1}\) is seen in both spectra shown in Figure 5. It is particularly strong in the low-frequency 1E mode of Au20. The energy Fourier transform also shows several moderate peaks at middle and high frequencies, arising from a series of transverse acoustic (TA), transverse optical (TO), and longitudinal optical (LO) modes. For example, the peak at 250 cm\(^{-1}\) corresponds to the coupled LO modes of rutile. The higher frequency signals are overtone combinations of the lower frequency phonons. The TiO2 modes contribute to the calculated Fourier transform spectra, since the photoexcited state delocalizes onto the TiO2 slab.

The modes seen in the Fourier transform spectrum for the photoexcited state localization are somewhat different from the phonons that modulate the state energy. The localization is more sensitive to changes in the wave function than the energy, since the energy is computed by averaging over the whole wave function. The localization Fourier transform shows a strong peak around 135 cm\(^{-1}\), a slightly weaker peak at 270 cm\(^{-1}\), and a few weak signals in the range between 400 and 800 cm\(^{-1}\). The
135 cm\(^{-1}\) peak corresponds to the triply generate vibration \(t_2\) in bare Au\(_{20}\) with \(T_d\) symmetry.\(^{64}\) In a perfectly symmetric cluster, the vibration is at 148 cm\(^{-1}\).\(^{64}\) Here, minor dilation and distortion of the Au\(_{20}\) cluster, arising due to heating and interaction with TiO\(_2\), lead to a small blue shift. The peak at 270 cm\(^{-1}\) is the double overtone of the main vibration at 135 cm\(^{-1}\). This mode is also close to the coupled LO modes of TiO\(_2\) at 255 cm\(^{-1}\).\(^{68}\)

Thermal fluctuations of atomic coordinates create an inhomogeneous ensemble of initial conditions for the plasmon-driven dynamics. The black dots in Figure 3b present the distribution of the photoexcited state energy. Its width is several tenths of eV, on the order of the plasmon resonance line-width.\(^{11}\) The distribution starts at 2.25 eV, coinciding with the onset of the plasmon band.\(^{11}\) Figure 3b also presents the TiO\(_2\) DOS within the energy region containing the photoexcited state. The TiO\(_2\) DOS varies slowly, indicating that states in the plasmon band interact, on average, with the same number of TiO\(_2\) surface states, rationalizing why the donor–acceptor state mixing and the photoexcited state localization are virtually independent of energy.

The autocorrelation functions of the photoexcited state energy and localization, insets in Figure 5, decay quite rapidly; nevertheless, there are substantial differences between the two functions. The initial decay in the energy autocorrelation function occurs within 25 fs. The initial decay of the localization autocorrelation function requires only 10 fs. On the longer time scale, the energy autocorrelation function continues to oscillate with a 50 fs period for several periods, while the localization autocorrelation function shows only one minor recurrence. The comparison indicates that the electronic donor–acceptor coupling, determining the extent of the photoexcited state delocalization between the gold nanoparticle and the TiO\(_2\) surface, is more sensitive to the positions of the nuclei than the state energy.

### 3.4. Electron Transfer Dynamics

The delocalization of the photoexcited state between Au\(_{20}\) and TiO\(_2\) indicates that the charge-separated state is created upon excitation of the Au\(_{20}\) plasmon band with a 50% probability. The remaining 50% of the cases involve a distinct ET step. The simulated ET occurs on a 40 fs time scale, Figure 6a, in agreement with the experimentally determined 240 fs upper bound.\(^{11}\) The gold nanocluster used in the simulation is smaller than those employed in experiments, and therefore, one can expect more significant overlap and stronger coupling between the donor and acceptor states, leading to faster ET.

Both the contribution of direct ET by photoexcitation and the time needed to transfer remaining fraction of the photoexcited electron from Au\(_{20}\) cluster to TiO\(_2\) depend on the donor–acceptor interaction. The ET coordinate is defined by integrating the photoexcited electron density over the region of the simulation cell occupied by the electron acceptor, that is, TiO\(_2\), eq 6. The initial ET coordinate shown in the y-axis of Figure 6a gives the contribution of the direct ET mechanism, Figure 6b, to the overall ET process. The time scales and relative amounts of adiabatic and nonadiabatic electron injection are calculated by separating the overall evolution of the ET coordinate into the contributions due to changes in the localization and occupation, respectively, according to eq 7. Figure 6a demonstrates that nonadiabatic ET is the dominant mechanism, responsible for about 75% of the ET amplitude. The adiabatic mechanism contributes around 25%. Adiabatic ET relies on strong electron–phonon coupling, while nonadiabatic ET can operate with weaker coupling and is accelerated by a high density of acceptor states. The coupling is relatively weak in the present system, since no chemical bonds exist between the gold nanoparticle and the TiO\(_2\) substrate. At the same time, the DOS of the TiO\(_2\) acceptor is high. These two factors rationalize the nonadiabatic mechanism. The situation is similar to that in the graphene–TiO\(_2\) system.\(^{51}\)

The time scales, \(\tau\), of the total, adiabatic and nonadiabatic ET were obtained by fitting the data with the exponential function

\[
f(t) = f_0 + A\exp(-t/\tau)
\]

The time scales are reported in Figure 7a. The time of ET from the Au\(_{20}\) particle to the TiO\(_2\) surface is longer than the time required for a collective surface plasmon excitation to separate into electron–hole pairs. The latter process occurs on a 10 fs time scale.\(^{29}\) Thus, the sequence of events leading to the plasmon-driven charge separation at the interface between a gold nanocluster and a TiO\(_2\) surface starts by excitation of a gold surface plasmon exhibiting notable delocalization onto the TiO\(_2\) surface. In 50% of the cases, the plasmon separates into electron–hole pairs on a 10 fs time scale, and on a 40 fs time scale the electron transfers into TiO\(_2\). These processes are
accompanying by electronic energy loss to heat due to coupling to phonons, as discussed in the next section.

The conclusions drawn about the plasmon-induced ET dynamics on the basis of the above calculations may be affected by a number of factors, including approximations made during the calculations and the experimental conditions. To test the former, we employed a more advanced DFT functional. To test the latter, we incorporated defects within both subsystems. Using the range-separated hybrid functional HSE06, we optimized the geometry of the Au–TiO2 system and carried out a short MD trajectory. Figure S3 shows the excited plasmon densities obtained with the HSE06 functional at 0 K and at ambient temperature. Similarly to Figure 4a, the densities extend from the gold nanoparticles onto the TiO2 surface, supporting the conclusion that there exists a significant probability of ET immediately during photoexcitation of a plasmonic particle.

Realistic systems often contain defects. To mimic this situation, we created defects in each subsystem. We removed a bridging oxygen atom from the TiO2 surface to create an oxygen vacancy. Separately, we removed gold atoms from the TiO2 surface to create a situation, we created defects in each subsystem. We removed a gold atom from a bridging oxygen atom from the TiO2 surface to create an oxygen vacancy. Consequently, we removed a gold atom from a bridging oxygen atom from the TiO2 surface to create an oxygen vacancy. The unsaturated chemical bonds arising due to the missing atoms increase the donor–acceptor interaction, leading to further delocalization of the plasmon excitation onto TiO2. Thus, defects create favorable conditions for ET from the nanoparticle to the substrate already during excitation of the plasmon band. Defects should also accelerate ET if it occurs subsequent to the photoexcitation.91

3.5. Energy Relaxation. Electron–phonon relaxation parallels the ET process and results in electronic energy loss to heat. In gold and other metals, all electronic energy is rapidly deposited into vibrations, and photogenerated electrons and holes quickly recombine, in the absence of a bias voltage. Semiconductors, such as TiO2, have a gap between the conduction and valence bands. As a result, electrons and holes decay to the edges of the corresponding bands and survive for long times. The metallic Au20 cluster is sufficiently small to exhibit a band gap due to quantum confinement.
Figure 4b,c depicts the orbital densities of LUMO and HOMO, which constitute the initial and final states for the electron–hole recombination. The LUMO is spread nearly uniformly across the TiO$_2$ slab. The HOMO is localized on Au$_{20}$ and extends into the TiO$_2$ substrate. The HOMO delocalization into TiO$_2$ is required to create the nonadiabatic coupling and to achieve the electron–hole recombination. Both elastic and inelastic electron–phonon scattering affects the recombination process. Inelastic scattering accommodates the energy lost by the electron as it makes a transition from the LUMO to the HOMO. Elastic interactions introduce more subtle effects. In particular, they destroy coherence formed between HOMO and LUMO. The elastic electron–phonon interaction is known as pure dephasing in optical measurements.$^{93,94}$ It determines the line-width of single particle luminescence. Luminescence from LUMO to HOMO is unlikely in the present system, since HOMO and LUMO are localized on different parts of the system, Figure 4b,c, and the relevant transition dipole moment is small. Instead, the LUMO to HOMO transitions occurs nonradiatively.

Figure 8a presents the Fourier transform of the HOMO–LUMO energy gap. The gap autocorrelation function is shown as an inset. The autocorrelation function is similar to that for the electron injection, inset of Figure 5a. However, the spectrum shows a significantly stronger contribution from the midfrequency vibrations in the 300–500 cm$^{-1}$ energy window. This is to be expected, since the Au$_{20}$ state involved in the electron–hole recombination is an ordinary bulk state localized directly on Au atoms. In contrast, the Au$_{20}$ state participating in the initial ET is a delocalized surface plasmon. As shown earlier,$^{40}$ bulk-like states couple to higher frequency phonons than plasmons. The signal seen in the mid-frequency range can also be assigned, to the 366 and 430 cm$^{-1}$ phonons, which are detected in rutile TiO$_2$. Since TiO$_2$ has higher frequency phonons compared to Au, due to the presence of light O atoms, and since higher frequency motions generate stronger nonadiabatic coupling, the vibrational modes of TiO$_2$ contribute strongly to the back-ET process.

The current simulation treats phonons classically, necessitating a semiclassical decoherence correction for the simulation of the electron–hole recombination.$^{34}$ The correction is needed here, because the elastic (pure-dephasing) time is significantly shorter than the quantum transition time. The situation is opposite for the initial ET process: multiple quantum transitions take place within the 40 fs time scale of the delocalized plasmon-driven ET. The pure-dephasing time for the electron–hole recombination is computed with the cumulant expansion, eqs 12 and 13. The resulting dephasing function is shown in inset of Figure 8b. It is fit with a combination of two Gaussians:

$$f(t) = B \exp(-0.5(t/\tau_a)^2) + (1-B)\exp(-0.5(t/\tau_b)^2)$$

The obtained times are $\tau_a = 11$ fs and $\tau_b = 27$ fs. $B$ gives the amplitude of the fast Gaussian. The pure-dephasing time is obtained by taking a weighted average of the two times:

$$T = B\tau_a + (1-B)\tau_b$$

The 17 fs pure-dephasing time is significantly shorter than the 1 ps electron–hole recombination time reported in the experiment,$^{11}$ as should be expected for transitions across large energy gaps. The time-resolved electron–hole recombination signal is shown in Figure 8b. The calculated 1.2 ps time, obtained using the exponential fit, eq 14, agrees very well with the experimental data.$^{11}$ A similar back-ET time was found, for instance, in the alizarin–TiO$_2$ system.$^{52}$ The presented analysis shows that the 1 ps time scale reported in the experiments arises from recombination of the hole, remaining on the gold nanoparticle after the plasmon-driven ET, and the electron confined at the TiO$_2$ surface. In a realistic system, electrons are trapped near the surface by defect states. The current simulation includes no defects. One can expect that a defect state will accelerate the recombination, both because its energy will be somewhat below the TiO$_2$ conduction band edge and since localized states tend to create stronger electron–phonon nonadiabatic coupling.$^{34}$ Localized states exhibit higher frequency vibrations and hence larger nuclear velocity at a given temperature, eq 5. One can expect a larger value for the electronic overlap term as well, since the wave function of a surface trap should be closer to the nanoparticle than the wave function of a delocalized TiO$_2$ state.

4. CONCLUSIONS

In this paper, we reported a time-domain atomistic study of plasmon-driven ET, electron–phonon energy relaxation, and electron–hole recombination at the Au$_{20}$–TiO$_2$ interface. The simulations connect directly with the time-resolved experimental data. The obtained ET and electron–hole recombination time scales show excellent agreement with experiment. By performing atomistic simulations, we were able to provide a detailed analysis of the ET, relaxation and recombination processes, establish their mechanisms, characterize electronic states and phonon modes involved, and describe the interplay between the productive and unfavorable channels of photo-induced electron and energy flow.

We established that, with a 50% probability, the charge separation at the interface occurs immediately upon photo-excitation of the plasmon band. This novel mechanism of charge separation alters the traditional multistep description, in which the plasmonic excitation breaks into electron–hole pairs, and then electrons undergo charge transfer. Recent exper-
mental studies of H-doped black titania96 may provide another example of the instantaneous charge separation mechanism. There, the H-doped amorphous shell plays the same role as the metallic particles in the present system.

In the remaining 50% of the scenarios, the plasmon band excitation generates electron–hole pairs in the gold particle, and the electron is transferred to the TiO2 surface on a sub-100 fs time scale. Electron–phonon energy relaxation parallels the electron injection and is somewhat slower. Driven by entropy due to the high density of bulk TiO2 states, the electron overcomes the Coulombic electron–hole attraction and delocalizes into TiO2 bulk. Structural defects in the TiO2 surface can trap the injected electron near the gold nanoparticle, leading to a 1 ps electron–hole recombination.

Electrons that have been able to diffuse into bulk TiO2 can find their way back to the surface and recombine with the hole on a much longer time scale. The electron injection occurs primarily by the nonadiabatic mechanism, due to a relatively weak donor–acceptor coupling and a high density of TiO2 acceptor states. The recombination proceeds exclusively by the nonadiabatic mechanism, because of the large energy gap between the initial and final states in this case.

The interaction between Au30 and the bare rutile TiO2 (110) surface is noncovalent. This remains true at both zero and room temperature. Thermal atomic fluctuations, such as motions of TiO6 surface oxygens and acoustic modes of Au30, influence energies and wave functions of the electronic states. The energy of the surface plasmon is affected primarily by the acoustic modes of Au30, which alter the shape and size of the nanoparticle. The plasmon wave function is also influenced by the dipolar Ti–O bond vibrations, through the electrostatic interaction. TiO2 states and the Au30 HOMO are subject to higher frequency phonons than the plasmon.

The strong optical response of surface plasmon, rapid charge separation at the Au–TiO2 interface, and a significantly slower electron–hole recombination provide the fundamental basis for utilization of plasmon-sensitized TiO2 as an excellent photovoltaic material and a visible-light photocatalyst.

**ASSOCIATED CONTENT**

Supporting Information

DOS of the isolated Au30 particle and TiO2 slab, absorption spectrum of the Au–TiO2 system, and plasmonic excitation densities of the ideal system and the systems with O and Au vacancies computed using the hybrid HSE06 DFT functional. This material is available free of charge via Internet at http://pubs.acs.org.

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**Notes**

The authors declare no competing financial interest.

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