How can plasmon-initiated charge injection from metallic particles into semiconductors compete with energy losses and charge recombination if the particles possess virtually no energy gaps? We show that the injection mechanism depends on particle-semiconductor interaction chemistry and system morphology and that the traditional mechanism, involving the rapid decay of plasmons into free electrons and subsequent charge injection, competes successfully with charge recombination in Au nanorods on the MoS$_2$ surface.
SUMMARY
Using nonadiabatic molecular dynamics simulations combined with time-domain density functional theory, we show that electron injection from gold nanorods into MoS2 by the traditional mechanism is still faster than energy relaxation causing charge recombination. Plasmon-like excitations decay into free-electron states within 30 fs after photoexcitation of gold nanorods. Electron transfer follows within less than 100 fs, whereas energy relaxation requires 200 fs. Surface plasmons couple to low-frequency phonons of gold, and free charges also couple to higher-frequency phonons of gold and MoS2. The contribution of the charge-transfer photoexcitation mechanism to plasmon-driven charge separation depends strongly on the type of donor-acceptor interaction, e.g., chemical versus van der Waals, and more weakly on contact area and system geometry. The simulation generates a detailed time-domain atomistic description of the interfacial plasmon-driven charge separation and relaxation that are fundamental to many applications.

INTRODUCTION
Two-dimensional transition-metal dichalcogenides (TMDs)1,2 have great potential for photocatalytic3–7 photovoltaic8–10 and optoelectronic11–13 applications because their high charge mobility, flexibility, and low cost.13,14 The applications are limited by weak light-matter interactions, including poor visible-light absorption, arising from atomic-scale thickness.15,16 This challenge has motivated intense research efforts focusing on enhancing light absorption by metallic particle sensitization and the resulting exciton-plasmon interactions.17–21 Excitation of many types of metal particles in the visible or ultraviolet (UV) frequency range stimulates collective motions of electrons, known as surface plasmons, that exhibit wave-like densities extending beyond the material surface. Such coherent oscillations of conduction band electrons induced by an electromagnetic field give rise to strong absorption and scattering resonances,22 driving charge separation at metal-semiconductor interfaces.

The advantageous properties of localized plasmon resonances have motivated many recent experiments focusing on the fabrication and characterization of various semiconductors sensitized with plasmonic particles, and showing promising photovoltaic and photocatalytic properties.16–21 Shi and co-workers demonstrated that monolayer MoS2 sensitized with gold nano-antennas exhibits a significantly enhanced photoresponse at the wavelength of the localized surface plasmon resonance.20 Chen and co-workers reported that plasmonic-MoS2 hybrids dramatically
improve the hydrogen evolution reaction with a significant increase of carrier density in MoS$_2$ caused by injection of photogenerated “hot” electrons from Au nanorods.$^{19}$ Recently, Fang and co-workers used pump-probe spectroscopy to characterize the dynamics of the ultrafast electron transfer (ET) from excited gold nano-antennas into the MoS$_2$ monolayer, indicating that the ET occurs within 200 fs. Surprisingly, one may expect a priori that photogenerated electrons rapidly dissipate energy to vibrations of metallic particles, which have dense electronic state manifolds all the way to Fermi energy. Electron-phonon relaxation leads to charge annihilation. Experiments defy this expectation and motivate theoretical studies of the mechanisms that allow ET to compete with energy relaxation. The extremely fast, sub-200 fs, non-equilibrium ET from gold nano-antennas into the MoS$_2$ monolayer$^{21}$ makes it difficult to involve traditional ET models, such as Marcus-Gerischer,$^{23,24}$ which operates under quasi-equilibrium assumptions and is applicable to sufficiently slow ET. Instead, explicit time-domain modeling of the ultrafast non-equilibrium charge separation and energy relaxation dynamics is necessary, preferably at the atomistic level of detail. A thorough understanding of the electron-vibrational dynamics that follows plasmon excitation and that is provided by time-domain atomistic simulation is essential for the rational design of high-performance optoelectronic, photocatalytic, and photovoltaic devices based on two-dimensional TMDs sensitized with plasmonic particles.

There has been a long discussion on why semiconductors sensitized by plasmonic metal particles show appealing photon-to-electron conversion efficiencies in photovoltaic and photocatalytic applications. Most explanations are attributed to enhanced light harvesting due to localized surface plasmon resonance. However, the question remains—why do electrons and holes generated in the metallic particles not recombine, but live sufficiently long to produce charge separation and/or drive photochemistry? In order to rationalize how plasmon-induced ET can compete with rapid electron-phonon energy relaxation and charge recombination in metallic particles, Long and Prezhdo$^{25}$ simulated the dynamics in an Au-TiO$_2$ system and showed that optical excitation at the plasmon wavelength can lead to instantaneous charge separation, bypassing energy losses inside the Au nanocrystal. The charge-transfer optical transition was possible because of the strong chemical-like interaction between Au and TiO$_2$, facilitated by the undercoordinated oxygen atoms on the TiO$_2$ surface. A charge-transfer optical transition satisfies two conditions. First, it is optically active with a non-negligible transition dipole moment. Overlap of the wavefunctions of the initial and final states is necessary but not sufficient for an excitation to be optically active. Second, during such excitation, a significant amount of charge is transferred from one part of the system to another, presently from a plasmonic nanosystem into a semiconductor. Because charge transfer implies that the final state is localized on a different part of the system than the initial state, it is not possible to satisfy both conditions perfectly. Typically, a charge-transfer optical transition leads to a partial charge transfer and is moderately optically active, although the activity can be strongly enhanced by coupling to plasmonic excitation. Following the theoretical prediction, the charge-transfer optical transition was demonstrated experimentally by Lian and co-workers in the Au-CdSe system.$^{26}$ Similarly to TiO$_2$, the CdSe surface contains undercoordinated atoms that interact strongly with Au. Still, most publications refer to the traditional charge separation mechanism, which involves the simultaneous presence of electrons and holes in the metallic particles. Can the traditional mechanism explain plasmon-induced charge separation if electrons and holes recombine rapidly in metals, or do all experiments have to be reinterpreted according to the new mechanism?

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The present work reports a time-domain *ab initio* simulation of the plasmon-driven charge separation and energy relaxation in a hybrid Au-MoS$_2$ system. The simulation demonstrates that the traditional mechanism, consisting of two distinct steps, can produce charge separation. Initially, plasmon-like excitations, photogenerated in the Au particle, decay rapidly into free electrons. Subsequently, an electron is injected into the MoS$_2$ conduction band. Most importantly, the simulation shows that electron injection by the traditional plasmon-driven mechanism is still faster than electron-phonon energy relaxation and charge recombination. Plasmon decay occurs within 30 fs in the simulated system; the subsequent electron injection requires 30–60 fs, and the electron-phonon energy relaxation proceeds on a 200 fs timescale. The energy relaxation is slow because it is facilitated primarily by low-frequency phonons of the heavy Au atoms. The ET times obtained are in excellent agreement with the available experimental data. The direct charge-transfer transition seen in the Au-TiO$_2$ and Au-CdSe systems is not observed in the present case because of weaker Au-MoS$_2$ interaction and different system geometry. The ET process competes successfully with the energy relaxation regardless of the excitation energy, indicating that “hot” electrons can be extracted from gold particles before cooling. The study establishes the principles underlying the ability of gold nanoparticles to enhance visible-light harvesting in MoS$_2$ and other semiconductors.

**RESULTS AND DISCUSSION**

The time-domain simulations of plasmon decay, charge separation, and energy relaxation in the Au-MoS$_2$ system provide a detailed atomistic picture of the movement of charge and energy at the interface. The simulations establish the ET mechanism, characterize the timescales of the competing processes, and identify the phonon modes that couple to the electronic degrees of freedom. The timescales obtained can be directly compared with the time-resolved experimental observations. In general, efficient light-to-electron energy conversion requires charge separation to proceed faster than energy relaxation. The discussion in the following subsections focuses on several closely related aspects of the electron-vibrational dynamics, including the geometric and electronic structure of the Au-MoS$_2$ system, electron-phonon interactions, plasmon decay into bulk electrons, ET from Au into MoS$_2$, and electron-vibrational energy relaxation.

**Geometry and Electronic Structure of the Au$_{100}$-MoS$_2$ System**

Interactions between the Au$_{100}$ nanorod and the MoS$_2$ monolayer influence the electronic donor-acceptor coupling, ET time and mechanism, and ET efficiency in competition with energy relaxation. Figure 1 shows the geometry of the combined system relaxed at 0 K (top) and a representative geometry from the molecular dynamics (MD) trajectory run at 300 K (bottom). As the temperature increases, the...
The separation between the two subsystems increases as well, from 2.712 Å to 3.420 Å. The donor-acceptor interaction is dominantly van der Waals. The increased separation between Au100 and MoS2 at room temperature weakens the donor-acceptor coupling further. Thermal effects have little influence on the MoS2 monolayer on the scale of the simulation cell. In contrast, the gold nanorod undergoes significant deformations. The extended system experiences long-wavelength fluctuations, and the nanorod ends undergo structural reconstruction. Despite the significant change in the arrangement of Au100 atoms near MoS2, the Au-MoS2 interaction does not become stronger. The nanorod ends reconstruct to minimize the free energy of the nanorod itself, as demonstrated by the similarity of the reconstructions at the ends that are near and far from MoS2. It is quite common that surfaces, edges, and tips of nanoscale structures undergo reconstruction to minimize the free energy, as demonstrated by the pioneering work of Galli and co-workers, who have shown that Cd33Se33 can “self-heal” via surface reconstruction to stabilize the nanoparticle structure. A similar feature of gold nanorods was found by Hu et al. who used ab initio MD.

Figure 2 shows the projected density of states (PDOS) of the Au100-(MoS2)12 hybrid is split into contributions from the gold antenna and the MoS2 layer. The peaks marked by A and B correspond to the plasmon states whose charge densities are shown in Figures 3A and 3B, respectively.

The PDOS illustrates that the plasmon excitation band of Au100 is located well inside the MoS2 conduction band. It is perhaps surprising that the PDOS of the 36 atom (MoS2)12 layer, whose conduction band arises from atomic orbitals of only 12 Mo atoms, is comparable with and even larger than the PDOS of the 100 atom Au nanorod. The observation can be rationalized by the fact that the Au energy levels are formed by s atomic orbitals, whereas the MoS2 levels are due to d orbitals of Mo, and there are five times more d than s orbitals. This situation is favorable for efficient ET because the electron acceptor species contains more states per atom.

The strength of the donor-acceptor interaction is directly reflected in the amount of mixing between the donor and acceptor wave functions. Figures 3A and 3B shows the spatial distribution of electron densities (modulus squared) of the unoccupied Kohn-Sham (KS) orbital that describe the surface plasmon-like states taken at the energies of peaks A and B in Figure 2. The states are selected on the basis of localization of state densities with respect to Au nanorod atoms. Figure 3 demonstrates the distinction between plasmon-like and bulk states. Both plasmon-like excitations are
localized primarily on the Au\textsubscript{100} surface, and a small tail is delocalized onto MoS\textsubscript{2}. The excitation densities form smooth continuous waves that extend significantly outside the region occupied by the Au atoms. Interaction with MoS\textsubscript{2} has little effect on the symmetry of the densities, indicating that the donor-acceptor interaction is weak. The situation is different from the Au\textsubscript{20}-TiO\textsubscript{2} system,\textsuperscript{2} in which the surface plasmon-like state is shared by the Au\textsubscript{20} pyramid and TiO\textsubscript{2} surface, leading to instantaneous generation of the charge-separated state upon photoexcitation at the plasmon energy. The difference arises from both the nature of the donor-acceptor interaction and the system geometry. The surface of the TiO\textsubscript{2} acceptor\textsuperscript{2} contains undercoordinated oxygen atoms that can interact with the Au donor. Similarly, the surface of the CdSe acceptor studied experimentally\textsuperscript{2} also contains undercoordinated atoms. The Au cluster was grown on top of the CdSe nanorod, creating conditions for Au-CdSe chemical-type bonding. In comparison, all atoms in the MoS\textsubscript{2} acceptor used in the present calculation and corresponding experiment\textsuperscript{21} are fully

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**Figure 3. Charge Densities for a Narrow Au Rod**

(A–D) Plasmon-like states in the gold nanorod corresponding to peaks A and B in Figure 2 (A and B, respectively), the nanorod bulk-type state (C), and the electron acceptor state (D). The charge densities were obtained with the isosurface value of 0.00015 e/Bohr\textsuperscript{3}. Photoexcited charge separation involves the excitation of surface plasmon-like states (A and B) that decay rapidly into bulk states (C). Subsequently, an electron is transferred into an MoS\textsubscript{2} state (D). Note that both plasmon and bulk states are slightly delocalized onto MoS\textsubscript{2}, facilitating plasmon dephasing and charge transfer. The acceptor state is distributed on Mo atoms of the MoS\textsubscript{2} monolayer.

(E and F) Charge-density projections on the z (E) and y (F) axes demonstrate that plasmon-like states extend much more outside the Au rod and are much smoother than the bulk state.
coordinated, and all bonding requirements are satisfied, creating little opportunities for chemical donor-acceptor interaction.

Figure 3 also shows the density of a bulk-type Au state (Figure 3C) and MoS\textsubscript{2} acceptor state (Figure 3D). The bulk state of the Au\textsubscript{100} rod differs qualitatively from the plasmon-like states. Located within the same energy region as the plasmon-like states, the bulk-type state has many nodes and is localized on the Au atoms. In contrast, most of the plasmon-like state density is outside the nanorod.\textsuperscript{21} Similar observations have been made regarding plasmon-like and bulk states of Ag clusters.\textsuperscript{29,30} In thicker metallic particles, one can separate bulk-like states further into core and surface states on the basis of the state localization (see Figure 2 in Guo et al.).\textsuperscript{26} The bulk-type state represents the free-electron states into which plasmonic excitations decay or dephase. The bulk-type state has a small tail extending into MoS\textsubscript{2} and localized within the Mo layer. The tail enhances both electronic donor-acceptor and nonadiabatic electron-phonon couplings, facilitating ET. Generally, the lighter and faster S atoms can generate larger nonadiabatic coupling, which is proportional to the phonon velocity (Equation 7). However, S atoms do not contribute to the states of the electron (vacant KS orbitals) within the energy range of interest. Higher excitation energies are required to observe S atom contributions.\textsuperscript{31,32}

The electron acceptor state is localized fully on MoS\textsubscript{2} (Figure 3D), once again emphasizing the fact that the donor-acceptor interaction is weak in the present system. The state originates from atomic orbitals of Mo atoms, as expected for this energy range. Because of the weak donor-acceptor coupling, the oscillator strength for the plasmon-like optical transition involving charge transfer from Au to MoS\textsubscript{2} is very small, and the plasmon-driven ET proceeds by the traditional mechanism; i.e., plasmon-like excitations (Figures 3A and 3B) decay rapidly into free-electron states (Figure 3C), which then transfer the electron into MoS\textsubscript{2} (Figure 3D).

In order to emphasize the difference between the plasmon-like and bulk states further, we present projections of the states on the y and z axes (last two panels of Figure 3). The y projection (Figure 3F) demonstrates that the plasmon-like states (black and red lines) extend much farther outside the Au rod than the bulk state (blue line). The z projection (Figure 3E) shows that the plasmon-like state densities are much smoother than the bulk state density. It also demonstrates that the tail of the second plasmon state with a node in the middle extends into MoS\textsubscript{2} more significantly than the tail of the nodeless plasmon.

**Electron-Phonon Interactions**

Figure 4 presents the spectral densities obtained by Fourier transforms of the plasmon and bulk state energies (Figure 3), which fluctuate in time as a result of vibrational atomic motion. The vibrational modes that modulate the energy levels also generate electron-phonon coupling. In addition, thermal atomic fluctuations produce an ensemble of inhomogeneous initial conditions before the photoexcitation.

The spectral densities demonstrate that surface plasmons couple exclusively to low-frequency vibrational modes of gold (Figures 4A and 4B). The 100 cm\textsuperscript{-1} mode exhibits the largest amplitude and contributes most to nonadiabatic electron-phonon coupling. Because the plasmon-like excitations are delocalized over the whole gold nanorod surface and have very few nodes (Figures 3A and 3B), their density waves are sensitive primarily to low-frequency acoustic phonons that modulate the nanorod shape. In comparison, free electrons relaxing inside the gold nanorod interact...
with more phonon modes (Figure 4 C), including both lower and higher frequencies. Because bulk-type states extend slightly onto MoS$_2$ (Figure 3 C), one can also expect contributions from MoS$_2$ phonons. The signal seen at 380–410 cm$^{-1}$ in the spectral density of the bulk-type state (Figure 4 C) can be assigned to in-plane $E_{1g}$ and out-of-plane $A_{1g}$ vibrations of S–Mo bonds in MoS$_2$. The in-plane $E_{1g}$ mode is generated by S and Mo atoms moving in opposite directions. This vibration affects chemical bonding inside MoS$_2$, and hence energies of the MoS$_2$ acceptor states. The out-of-plane vibration changes the Au-MoS$_2$ donor-acceptor separation, and therefore influences the electronic donor-acceptor and nonadiabatic electron-phonon couplings.

### Plasmon Decay, Electron Transfer, and Energy Relaxation

The photoexcited state created at the plasmon energy is fully localized on the Au$_{100}$ surface, indicating that initial photoexcitation of the gold nanorod antenna does not lead to a charge-separated state as a result of weak donor-acceptor interaction between Au$_{100}$ and MoS$_2$. Instead, the plasmon-like state has to decay into free-electron states localized inside the nanorod, before the ET can happen. Figures 5 A and 5B describe decay of the two chosen plasmon-like states A and B (Figures 2, 3A, and 3B) into multiple bulk states. The timescales reported in the figure are obtained by fitting the population of the initial state to a Gaussian model (Equation 1).

$$P(t) = \exp \left(-0.5(t/\tau)^2\right)$$  \hspace{1cm} (Equation 1)

The simulated plasmon decay into free-electron states occurs on a sub-30 fs timescale for both initial conditions. The multiple bulk states populated by plasmon decay have densities of the type represented by Figure 3C; i.e., plasmon-like excitation decays into states that are localized predominantly inside Au$_{100}$ with a very small tail extending into MoS$_2$. This process constitutes the first step of the electron-phonon dynamics initiated by photoexcitation at the plasmon energy.

In order to estimate the timescales of electron injection from the bulk states into MoS$_2$, we consider the broadening of the plasmon (peaks A and B) and bulk (peak C) states in Au$_{100}$ due to interaction with MoS$_2$ (Figure 6). This method is often used to estimate ET timescales. Evaluating ET times by the current implementation of nonadiabatic MD is problematic because of the extremely weak donor-acceptor coupling, which leads to the so-called trivial or unavoided crossings problem in evaluating the nonadiabatic coupling matrix elements, requiring additional numerical tools.

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**Figure 4. Spectral Density**

Spectral density obtained by Fourier transform of the energies of the initial plasmon-like states (A) peak A and (B) peak B in Figure 2 and (C) the bulk state. The state densities are shown in Figures 3A–3C. Surface plasmons couple only to low-frequency phonons of gold, and gold bulk states also interact with higher frequency phonons.
The left-hand panels of Figures 6B–6D present the fragment analysis of density of states (DOS) near the plasmon (peaks A and B) and bulk (peak C) states (Figure 6A). The vertical black lines represent the energies of the KS orbitals in isolated Au\textsubscript{100}. Each orbital splits into two orbitals when Au\textsubscript{100} interacts with MoS\textsubscript{2} (red vertical lines). The height of the red lines represents the fraction of the KS orbitals localized on Au\textsubscript{100}. The corresponding orbital charge densities, as denoted by the arrows, are shown in the right panels. The energy splitting between the two peaks characterizes the strength of the Au\textsubscript{100}-MoS\textsubscript{2} interaction. The timescales of ET from Au\textsubscript{100} into MoS\textsubscript{2} are determined by computing the peak broadening, $D_{\text{ET}}$, in the Au\textsubscript{100}-MoS\textsubscript{2} system, and converting it to time: $\tau = h/\Delta E$. Here, $h$ is the reduced Planck’s constant. The peak broadening and corresponding ET timescales are summarized in Table 1. In all cases, the calculated ET timescales are sub-100 fs, in agreement with the experimentally determined sub-200 fs values.\textsuperscript{21} The energy splitting correlates directly with the extent of the charge density tail extending onto MoS\textsubscript{2} (Figure 3).

The gold nanorod used in the simulation is smaller than those used in the experiments.\textsuperscript{21} Therefore, the donor and acceptor states have more overlap and stronger coupling, leading to faster ET than in the experiment. This situation also leads to slower decay of the plasmon-like excitation into free electrons as a result of lower DOS. The accepted plasmon dephasing times are sub-20 fs\textsuperscript{43} and even sub-10 fs.\textsuperscript{44}

Typically, electrons and holes generated in a metal rapidly dissipate excess energy to heat and annihilate. Photovoltaics and photocatalysis require charge separation to be faster than charge relaxation and annihilation. Therefore, it is important to investigate the competition between plasmon decay and ET on the one hand and electron-vibrational energy relaxation on the other.

Figure 7 presents the evolution of the energy of the photogenerated electron for the two initial excitations (Figure 2 or 6). In each case, the data are fitted by Equation 2:

$$E(t) = E(0) \exp(-t/\tau) + E(\infty),$$

(Equation 2)

where $\tau$ is the energy relaxation time, $E(0)$ is the initial energy, and $E(\infty)$ is determined by the energy range included in the calculations. The simulated ~200 fs electronic energy relaxation is faster than the 1–1.5 ps timescales of the experimental observations for gold particles.\textsuperscript{35,46} The difference arises primarily as a result of the small size of the current gold nanorod because electron-phonon coupling is generally stronger in smaller systems with less extended electronic states.
Importantly, the energy relaxation times are longer than the ET timescales in both cases (Table 1), indicating that ET can occur before electronic energy relaxation and charge recombination, regardless of the excitation energy. This fact is critical for photovoltaic and photocatalytic applications of semiconductors sensitized with plasmonic particles, because “hot” electrons can be extracted from the metallic particles before they lose energy to heat and disappear.

**The Effects of Contact Area and System Geometry**

Further systematic investigations are required in order to establish the effects of donor-acceptor interactions and system morphology on the mechanism of plasmon-driven charge separation. The current study focused on a metallic nanorod interacting via its tip with a chemically inert semiconductor. Here, ET occurs by the traditional mechanism. The system studied earlier included a pyramidal particle with one of its bases in contact with a chemically unsaturated surface. There, ET took place by photoexcitation of a charge-separated state. The two situations represented extreme cases. In order to provide further tests, we studied the properties of plasmon-like states in contact with MoS₂ for the Au₂₀ pyramid, investigated earlier in contact with TiO₂, and a Au₂₇ rod, which has an aspect ratio (2.3) similar to that in the experiments (2.4). Figure 8 demonstrates that, just as in the...
Au100-MoS2 system, the gold-MoS2 interaction is weak, and the tails of the plasmon states extending into MoS2 are small. The charge-transfer character of the plasmon-like excitation, characterized by the tail magnitude, increases with increasing Au-MoS2 contact area. Nevertheless, it remains much smaller than in the Au20-TiO2 system. Consequently, the interaction type, chemical versus van der Waals, and the contact area and system morphology are important in determining the plasmon-driven charge injection mechanism. Surface defects, ligands, and temperature may play important roles as well.

Conclusions

The mechanism of injection of “hot” electrons, generated by plasmonic excitations in gold nanorods, into two-dimensional MoS2 has been characterized by a state-of-the-art atomistic time-domain simulation combining ab initio real-time TDDFT and nonadiabatic MD. The simulation mimics directly recent time-resolved experiments and provides detailed information on the geometric and electronic structure of the Au-MoS2 system, the role of thermal fluctuations, plasmon decay into free-electron states, charge injection, and electron-phonon energy relaxation, generating a comprehensive picture of charge and energy flow at the nanoscale interface.

The simulation demonstrates that the mechanism of the hot electron injection is different in the Au-MoS2 system from that in the Au-TiO2 system. The charge-transfer photoexcitation predicted in Au-TiO2 and demonstrated in Au-CdSe is not possible in the Au-MoS2 system because of the weak donor-acceptor interaction and different morphology. Donor-acceptor coupling is stronger in Au-TiO2 and Au-CdSe, because both TiO2 and CdSe contain undercoordinated surface atoms that are in contact with Au. In contrast, all atoms in MoS2 are fully coordinated. Compared with Au-MoS2, the morphologies of the Au-TiO2 and Au-CdSe systems result in a large donor-acceptor contact area, because the base of the Au pyramid is planar. In contrast, the Au nanorods interact with MoS2 only at one end, and most of the surface supporting plasmons is far from the electron acceptor. Because charge-transfer photoexcitation is not possible in Au-MoS2, plasmon-driven injection of hot electrons proceeds by the traditional two-step mechanism, involving rapid decay of plasmons into free-electron states, followed by electron injection.

Our time-domain ab initio study demonstrates theoretically that injection of plasmon-generated hot electrons by the traditional mechanism is still faster than energy losses. The simulations show that plasmon decays into free electrons within 30 fs, electron injection takes less than 100 fs, and electron-phonon energy relaxation occurs on a 200 fs timescale. The simulation shows that plasmon excitations couple only to low-frequency acoustic phonons of Au. In comparison, free electrons also couple to higher frequency phonons of Au and even MoS2, because corresponding states have small tails extending onto MoS2. Stemming from the small size of the Au nanorod, compared with the experimental system, the plasmon decay time is most

<table>
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<th>Peak</th>
<th>Broadening (meV)</th>
<th>ET time (fs)</th>
<th>Peak B</th>
<th>Broadening (meV)</th>
<th>ET time (fs)</th>
<th>Peak C</th>
<th>Broadening (meV)</th>
<th>ET time (fs)</th>
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<td>24.1</td>
<td>19.5</td>
<td>64</td>
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Also see Figure 6. The electron-transfer timescales are estimated from the broadening as \( \tau = h / \Delta E \). Electron injection is slower than plasmon decay (Figure 5) but faster than energy relaxation (Figure 7).
likely overestimated because of a lower density of free-electron states. At the same time, the electron injection and electron-phonon relaxation times are underestimated because of closer proximity of donor and acceptor states and stronger electron-phonon coupling in smaller systems.

Our simulations establish that efficient injection of plasmon-generated hot electrons is possible by both traditional and direct photoexcitation mechanisms, and that the mechanism depends on the strength of the interfacial interaction and system morphology. Such robust electron injection, outpacing charge relaxation and recombination, rationalizes why semiconductors sensitized with plasmonic particles can lead to efficient visible-light photovoltaic and photocatalytic devices.

**EXPERIMENTAL PROCEDURES**

The simulation of plasmon-driven ET and energy relaxation dynamics was performed by the mixed quantum-classical approach\(^4\),\(^5\) implementing fewest-switching surface hopping (FSSH)\(^6\) within real-time TDDFT in the KS representation.\(^7\) The light electrons were treated quantum mechanically, and the heavy ionic cores were classical. The method has been applied successfully to study photoinduced processes in a broad spectrum of systems, including TiO\(_2\) sensitized by metallic\(^2\) and semiconducting\(^3\) particles, graphene,\(^4\) graphene quantum dots,\(^5\) van der Waals TMD heterojunctions,\(^6\) polymers interfaced with carbon nanotubes,\(^7\) quantum dots,\(^8\) and other nanoscale materials.\(^9\) A detailed description of this approach can be found in Akimov and Prezhdo.\(^10\) Here, we outline the calculation procedure and provide simulation details.

**Time-Dependent Kohn-Sham Theory for Electron-Vibrational Dynamics**

The total electron density, \(\rho(r, t)\), is expressed as the sum of the densities of single-electron KS orbitals, \(\varphi_i(r, t)\), occupied by \(N_e\) electrons:

\[
\rho(r, t) = \sum_{i=1}^{N_e} |\varphi_i(r, t)|^2. \tag{Equation 3}
\]

Application of the time-dependent variational principle to the KS energy leads to a set of single-electron equations for the evolution of the electron density:\(^5\)

\[
\hbar \frac{\partial \varphi_i(r, t)}{\partial t} = H(r, R, t)\varphi_i(r, t). \tag{Equation 4}
\]
The equations are coupled through the dependence of the DFT Hamiltonian, i.e., the functional, \( H(r,R,t) \), on the electron density. The electron-vibrational coupling enters the Hamiltonian through the external potential created by atoms. The time-dependent single-electron orbitals in Equation 4 are expressed in the current implementation of real-time TDDFT\(^{36,37,47} \) on the basis of adiabatic KS orbitals, \( \tilde{\psi}_j(r,R(t)) \), which are calculated for the current atomic positions \( R \):

\[
\psi_i(r,t) = \sum_{j=1}^{N_a} c_i(t) |\tilde{\psi}_j(r,R(t))\rangle. \tag{Equation 5}
\]

Insertion of Equation 5 into Equation 4 gives a set of equations describing the evolution of the adiabatic expansion coefficients:

\[
\frac{\hbar}{i} \frac{\partial}{\partial t} c_i(t) = \sum_{j=1}^{N_a} c_j(t) \left( \hat{E}_j \delta_{ij} + \mathbf{d}_{jk} \cdot \dot{\mathbf{R}} \right), \tag{Equation 6}
\]

where \( \hat{E}_j \) is the energy of the adiabatic one-electron state \( k \), and \( \mathbf{d}_{jk} \cdot \dot{\mathbf{R}} \) is the nonadiabatic coupling between orbitals \( j \) and \( k \). The nonadiabatic coupling is generated by atomic motions and characterizes electron-vibrational interactions. Presently, it is calculated numerically as the overlap between adiabatic orbitals \( j \) and \( k \) at sequential time steps:\(^{64} \)

\[
\mathbf{d}_{jk} \cdot \dot{\mathbf{R}} = - \frac{\hbar}{2\Delta t} \left( \langle \phi_j(t)|\phi_k(t+\Delta t)\rangle - \langle \phi_j(t+\Delta t)|\phi_k(t)\rangle \right).
\tag{Equation 7}
\]

The adiabatic representation shifts the main computational efforts to solving the time-independent DFT problem. The significantly lower computational cost than that of other implementations\(^{67-69} \) is particularly useful for application in large-scale condensed phase systems. The adiabatic representation of nonadiabatic dynamics suffers from the so-called trivial\(^{38} \) or unavoidable\(^{39} \) crossing problem. The many-particle generalization of the above KS equations is presented in Akimov and Prezhdo.\(^{36} \) It has been shown that \textit{ab initio} TDDFT gives an accurate description of plasmon-like excitations in metallic particles composed of tens to hundreds of atoms.\(^{70} \)
Nonadiabatic MD with FSSH

The dependence of the electronic Hamiltonian on nuclear coordinates (Equation 6) 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 the most popular description for the back reaction. FSSH can be viewed as a stochastic Monte-Carlo algorithm that introduces branching of classical trajectories, satisfying detailed balance between transitions upward and downward in energy. The latter property is not satisfied by many quantum-classical schemes, including the most basic Ehrenfest dynamics; it is required for proper description of electron-vibrational energy exchange and approach to thermodynamics equilibrium.

The probability of a transition between states $j$ and $k$ within the time interval $\Delta t$ is given in FSSH by

$$g_{jk}(t, \Delta t) = \max \left\{ 0, \frac{b_{jk} \Delta t}{a_{jk}} \right\}$$

(Equation 8)

where

$$a_{jk} = c_j \ast (t) c_k(t)$$

and

$$b_{jk} = 2 \hbar^{-1} \text{Im} \left( a_{jk} \bar{\Phi}_j | H | \Phi_k \right) - 2 \text{Re} \left( a_{jk}^* \mathbf{d}_k \cdot \mathbf{R} \right).$$

(Equation 9)

If $g_{jk}(t, \Delta t)$ is negative, the hopping probability is set to zero. A hop from state $k$ to state $j$ can occur only when the electronic occupation of state $k$ decreases and the occupation of state $j$ increases. Although more advanced versions of nonadiabatic dynamics have been developed to account for phonon-induced decoherence and super-exchange or many-particle transitions and been implemented in Pyxaid, FSSH is appropriate in the present case because the dynamics involves hops within a dense manifold of electronic states.

To conserve the total electron-vibrational energy after a hop, the original FSSH technique rescales the atomic velocities along the direction of nonadiabatic coupling. If a nonadiabatic transition to a higher energy electronic state is predicted by Equation 8, but 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 and hop rejection gives the detailed balance between the transitions upward and downward in energy, leading to Boltzmann statistic and quantum-classical thermodynamics equilibrium. To achieve more efficient calculations, we applied the classical path approximation to FSSH. The approximation avoids the need to calculate multiple excited-state trajectories and allows one to simulate nonadiabatic dynamics of electrons by using a single, typically ground-state trajectory. The approximation is justified if thermal fluctuations in the atomic coordinates are stronger than the differences between the excited- and ground-state geometries. This is indeed the case in the present system. Figure 1 demonstrates that thermal fluctuations in the nanorod geometry are significant. Further, we optimized the geometry of the system in the first excited state by using the delta self-consistent field approach, i.e., by promoting and constraining the electron from the highest occupied molecular orbital to the lowest unoccupied molecular orbital. Compared with the ground-state geometry shown at the top of Figure 1, the changes in the system geometry were small and undetectable visually.
Simulation Details

Considering the experimental geometry of the Au-MoS₂ hybrids, we interfaced a gold nanorod with the MoS₂ monolayer in a periodic supercell. The nanorod contained 100 gold atoms cleaved from the Au (111) surface. It was placed perpendicular to the MoS₂ monolayer composed of 24 S and 12 Mo atoms. An additional 30 Å of vacuum was added to the simulation cell in the direction perpendicular to the surface in order to screen off the artificial interactions between periodically replicated images. The distance between the gold rods was 9 Å. The simulation cell is shown in Figure 1.

The geometry optimization, electronic structure, and adiabatic MD calculations were carried out with the Vienna ab initio simulation package. The electron exchange and correlation terms were described with the Perdew-Burke-Ernzerhof functional on the basis of the generalized gradient approximation. The projector augment wave method was used to describe the valence electron-ion interaction. Gaussian smearing with the default parameter value was used to accelerate the convergence, because the gold nanorod-MoS₂ system is highly metallic. The van der Waals interaction between the gold nanorod and MoS₂ is described by the DFT-D3 method of Grimme with Becke-Jonson damping.

After relaxing the geometry at 0 K, repeated velocity rescaling was used to bring the temperature of the Au₁₀₀(MoS₂)₁₂ system to 300 K, corresponding to the temperature in the experiment. Then, a 4 ps adiabatic MD simulation was performed in the microcanonical ensemble with a 1 fs atomic time step. The adiabatic state energies and nonadiabatic couplings were calculated for each step of the MD trajectory. To simulate the electron-phonon dynamics according to optical excitation of plasmon-like states, 500 system geometries were selected randomly from the first 3 ps of the adiabatic MD trajectory and used to solve the TD-KS equations, coupled to the FSSH Monte-Carlo type algorithm. The TD-KS equations were solved with the second-order differencing scheme with a 10⁻³ fs time step. The stochastic FSSH sampling was performed every 1 fs.

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AUTHOR CONTRIBUTIONS

Z.Z. performed calculations. L.L., W.-H.F., and M.V.T. analyzed the data. R.L. and O.V.P. supervised the project. R.L. drafted the manuscript. R.L. and O.V.P. edited the manuscript.

DECLARATION OF INTERESTS

The authors declare no competing financial interest.

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REFERENCES AND NOTES


