**Efficient hot-electron transfer by a plasmon-induced interfacial charge-transfer transition**

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Plasmon-induced hot-electron transfer from metal nanostructures is a potential new paradigm for solar energy conversion; however, the reported efficiencies of devices based on this concept are often low because of the loss of hot electrons via ultrafast electron-electron scattering. We propose a pathway, called the plasmon-induced interfacial charge-transfer transition (PICTT), that enables the decay of a plasmon by directly exciting an electron from the metal to a strongly coupled acceptor. We demonstrated this concept in cadmium selenide nanorods with gold tips, in which the gold plasmon was strongly damped by cadmium selenide through interfacial electron transfer. The quantum efficiency of the PICTT process was high (24%), independent of excitation photon energy. It competes with electron relaxation through rapid electron-electron scattering in the metal and is independent of the excitation polarization.

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**Fig. 1. Metal-to-semiconductor charge-separation pathways.** (A) Conventional PHET mechanism, in which a photoexcited plasmon (SP, blue ellipsoid) in the metal decays into a hot electron–hole pair (solid and open red circles in the dotted ellipsoids) through Landau damping, followed by injection of the hot electron into the CB of the semiconductor. The electron-hole pair has a broad distribution of initial electron and hole energies; only two are shown for clarity. (B) Optical excitation of an electron in the metal directly into the CB of the semiconductor through the DICTT pathway. (C) The newly demonstrated PICTT pathway, where the plasmon decays by directly creating an electron in the CB of the semiconductor and a hole in the metal. MB is the semiconductor valence band and hv indicates the excitation photons.
decay pathway: the direct generation of an electron in the semiconductor and an electron hole in the metal. This model is an extension of the chemical interface damping model that has been proposed to account for adsorbate-induced broadening of the plasmon bands of metal NPs (26–28).

We proposed and experimentally demonstrated the PICTT pathway in colloidal quantum-confined CdSe-Au nanorod (NR) heterostructures. Strong Au–CdSe interactions led to strong damping of the plasmon band in the Au tip. The proposed pathway was verified by observing highly efficient plasmon-induced Au-to-CdSe charge separation with >24% quantum efficiencies upon excitation of the Au tip. Measurements of transient absorption anisotropy showed more efficient Au-to-CdSe charge transfer when the plasmon was excited along the NR axis, consistent with the PICTT mechanism. The charge-separation efficiencies were independent of excitation photon energy, a result that is inconsistent with the conventional PHET mechanism and supports the proposed PICTT pathway.

Colloidal CdSe-Au NRs were synthesized according to a published procedure (29, 30). Representative transmission electron microscope (TEM) images of CdSe and CdSe-Au NRs (Fig. 2A and figs. S1 and S3) showed well-defined dumbbell-like morphologies for CdSe-Au, with two Au NPs at both ends of a single-crystalline CdSe NR. Static absorption spectra of CdSe and CdSe-Au NRs dispersed in chloroform are shown in Fig. 2B. The discrete absorption peaks of CdSe NRs at ~480 and ~582 nm are attributed to the 1s

Fig. 2. Plasmon-induced metal-to-semiconductor charge-transfer transition in CdSe-Au NRs. (A) A representative TEM image of CdSe-Au NRs (inset: a representative high-resolution TEM image). (B) Absorption spectra of CdSe NRs, CdSe-Au NRs, and CdSe QD-Au dimers dispersed in chloroform. The gray dashed line is the difference spectrum between the absorptions of the CdSe-Au NRs and the CdSe QD-Au dimers. (C) Absorption spectra (with the y axis plotted on a logarithmic scale and shifted by +0.1 to avoid negative values) of (i) isolated Au NPs and (ii) CdSe and CdSe-Au NRs with their first excitonic peak positions at 555, 582, and 605 nm. The absorption spectra of CdSe-Au NRs show an onset at ~1450 nm (0.85 eV). (D) Schematic electronic structure of a CdSe-Au NR, composed of a strongly damped Au tip with broadened electronic levels and a central region with relatively unperturbed discrete levels (1s, 1e). The green dashed arrow indicates the interband transition in the visible (Vis) spectrum, the red arrow indicates the intraband transition in the IR spectrum, and the green solid arrow indicates electron transport in the NR.

etching during the growth of the Au tips (29). Thus, the electronic structure of CdSe-Au NRs can be viewed as a combination of the strongly
interacting tip region, which resembles the CdSe QD-Au dimers (with strongly damped plasmon and exciton bands), and the center part, which is similar to the unperturbed CdSe NRs (Fig. 2D).

The broad, featureless, near-IR absorption spectra of the CdSe-Au NRs showed an onset at ~1450 nm (0.85 eV) for three NRs with Σ exciton bands at 553, 582, and 605 nm (with a corresponding shift of ~150 meV in the CB-edge position) (Fig. 2C). This suggests that the transition cannot be attributed to the DICTT mechanism (Fig. 1B), which should have an onset wavelength that shifts with the CdSe CB edge. Instead, we attribute the broad near-IR absorption feature to a strongly damped Au plasmon caused by the strong mixing of Au and CdSe electronic levels. Such strong interaction activates the PICTT plasmon decay pathway (Fig. 1C), which is not possible in isolated Au NPs.

In the PICTT pathway, the damped plasmon decays via direct excitation of an interfacial electron-hole pair (with an electron in CdSe and a hole in Au). Direct evidence to support this proposed mechanism was obtained through ultrafast transient absorption (TA) studies. In these studies, a pump laser with a photon energy below the CdSe band gap was used to excite the Au tip, and the electron transferred to the CdSe domain was probed through the bleaching of the Σ exciton band in the visible spectrum (caused by state filling of the ΣF level) and/or the ΣF to ΣE intraband absorption in the mid-IR spectrum (Fig. 2D) (35). The assignment of these spectral signatures was confirmed by comparing transient spectra of CdSe NRs and CdSe-benzoquinone (electron-acceptor) complexes.

The kinetics of the Σ exciton bleach at ~580 nm and the intraband absorption at ~3000 nm matched closely in free CdSe NRs, and electron transfer from CdSe to adsorbed electron acceptors led to a faster decay of both spectral features in the NR electron-acceptor complexes (fig. S4). The TA spectra of CdSe-Au NRs (Fig. 3A) showed a pronounced Σ-exciton-bleach feature at ~575 nm, indicating the formation of CdSe CB electrons through the excitation of the damped Au plasmon band at 800 nm. The bleach overlapped with a broad positive TA feature that was also present in the TA spectra of CdSe QD-Au dimers (fig. S6). This broad feature was subtracted from the total TA signal to obtain the TA spectra (fig. S8) and the kinetics of the Σ exciton bleach (Fig. 3C and fig. S8). Excitation at 800 nm also generated an intraband absorption feature at 3000 nm. The formation and decay kinetics of this signal and the Σ-exciton-bleach signal agreed well (Fig. 3B), further confirming the presence of CB electrons in CdSe.

These intra- and interband signatures were absent in control samples composed of a mixture of CdSe NRs and Au NPs (Fig. 3B and fig. S7). Fitting these kinetics yielded a formation time of ~20 ± 10 fs and a biexponential decay with a half-life of ~1.45 ± 0.15 ps, which corresponded to plasmon-induced hot-electron transfer and charge-recombination times, respectively (35). Such an ultrafast charge-separation time is consistent with the PICTT mechanism, in which the decay of a plasmon instantaneously generates an electron in CdSe (giving rise to the observed inter- and intraband features) and a hole in Au near the CdSe/Au interface. The injected electron quickly relaxes back to the Au with a recombination time of 1.45 ps, which indicates a negligible band-bending-induced recombination barrier at the CdSe/Au interface.

The transient quantum yields (QY) of Au-to-CdSe charge separation as a function of excitation wavelength are shown in Fig. 4. These QY values were determined by the peak amplitude of the CdSe intraband absorption signal (which averaged between 0.2 and 0.4 ps; see the supplementary materials for details). The pump wavelength (energy) was tuned over a >1-eV range below the band gap of CdSe NRs: 670 nm (1.85 eV), 710 nm (1.75 eV), 750 nm (1.65 eV), 800 nm (1.55 eV), 1160 nm (1.07 eV), 1340 nm (0.92 eV), and 1550 nm (0.80 eV). Within experimental errors, the measured QY values were constant (~24%) above ~0.85 eV (Fig. 4), the onset of the near-IR absorption feature shown in Fig. 2B. Below the onset, no measurable electron signals were observed because of a lack of photon absorption.

In the conventional PHET mechanism (Fig. 1A), the excitation energy dependence of the charge-separation QY has been shown to follow Fowler’s equation (36)

\[
QY(\omega) = \frac{\hbar \omega - E_E}{4E_F \hbar \omega} = \frac{\hbar \omega - E_E}{4E_F \hbar \omega}
\]

where \(\hbar \omega\) is the energy of the excitation photon, \(E_E\) is the barrier height between the metal and the semiconductor, and \(E_F\) is the Fermi energy of the metal. Most devices based on hot-electron transfer reported to date have been shown to follow this model (37–39). For small NPs, QY values of metal-to-semiconductor photoemission generally follow the same functional form, but they can be enhanced by a factor \(C\) through a geometric effect (40, 41) and a lowering of the escape barrier (42)

\[
QY(\omega) = C \frac{\hbar \omega - E_E}{4E_F \hbar \omega} = C \frac{\hbar \omega - E_E}{4E_F \hbar \omega}
\]

Recently, it has also been found that the momentum conservation requirement can be relaxed if electrons only scatter at the semiconductor/metal interface (43). Under this condition, QY is determined by

\[
QY(\omega) = \frac{\hbar \omega - E_E}{2\hbar \omega} = \frac{\hbar \omega - E_E}{2\hbar \omega}
\]

The predicted QY values according to Eqs. 1 to 3 are shown in Fig. 4. For Eq. 2, we chose the value of \(C\) so that the predicted QY at 1.85 eV agreed with the experimental results. The estimated value of \(E_E\) was 0.7 to 1.4 V because of uncertainty in the reported band-edge positions (30). We used a value of 0.85 V to allow more convenient comparison with the experimental results. The Fowler-type conventional hot-electron transfer models predict an increasing QY at higher excitation energies (because of the increase in hot
electrons with energies above the semiconductor CB edge) and are inconsistent with our experimental data.

The measured QY values are consistent with the PICTT pathway. In this pathway, the plasmon decays by direct excitation of an electron from Au to CdSe, and the QY is independent of the excess energy of the electron above the CB edge. The strongly damped plasmon bandwidth is probably dominated by homogeneous broadening: As long as the excitation energy is above the absorption threshold (~0.65 eV), the same plasmon is excited, and therefore the charge-separation QY is independent of excitation energy. The estimated full width at half maximum of the damped plasmon band, ~1.6 eV (fig. S11), corresponds to a plasmon dephasing time of ~0.8 fs, which is consistent with the observed fast hot-electron transfer time. Furthermore, the observed QY is about an order of magnitude higher than the reported value for CdSe-Au NRs (2.75%) (35). In CdS-Au NRs, the Au plasmon band is weakly perturbed, and the plasmon-induced hot-electron transfer occurs through the conventional PHET pathway (Fig. 1A), where the competition of hot-electron transfer with ultrafast relaxation reduces its efficiency. Compared with CdSe-Au NRs, the hot-electron transfer time in CdS-Au NRs is noticeably slower (90 ± 20 fs) (fig. S9). The microscopic origin of the dramatic differences in plasmon damping and hot-electron transfer between CdSe-Au and CdSe-Au NRs remains unclear and will be examined in future studies.

The observed QY values in CdSe-Au NRs are less than unity for at least two reasons. First, PICTT is probably not the exclusive decay channel for the strongly damped plasmon. The plasmon could also be damped in the Au domain, thereby proceeding via the less efficient conventional PHET pathway (35). Second, the electron generated in CdSe could either quickly relax back into the Au or escape into the center of the CdSe NR (and recombine on the 1.4-ps time scale); only the latter process was detected in our measurements. Thus, the measured QY values represent a lower limit of plasmon-induced electron transfer in this system.

Further insight into the nature of the PICTT pathway can also be obtained through polarization-dependent TA studies. Plasmons polarized in the direction parallel to the NR may be more strongly coupled to the CdSe than those polarized in the direction perpendicular to the NR. Because the optical transition in the CdSe NRs is strongly polarized (31, 44), the TA signal should depend on the relative polarization of the pump and the probe beams. This polarization dependence can be quantified by the anisotropy (r) of the TA signals, so that r = (SHH − SVH)/(SHH + 2SVH), where SHH and SVH are TA signals with the polarizations of the pump and probe beams parallel (SHH) or perpendicular (SVH) to each other. For band-edge (590-nm) excitation of free CdSe NRs (without Au tips), the 12-exciton-bleach signal amplitude for SHH was larger than for SVH (Fig. 5A). The calculated anisotropy was 0.12 and showed negligible decay over 10 ps (Fig. 5A, inset), which indicates that the band-edge-absorption transition dipole has 70% axial and 30% radial components (fig. S12; see the supplementary materials for details), consistent with previous reports (45). The intraband transition between 1s and 1p showed negligible anisotropy (fig. S13). Thus, we used the 1s exciton bleach to probe anisotropy in CdSe-Au NRs. For 800-nm excitation of CdSe-Au NRs, the resulting 1s-exciton-bleach signal amplitude for SHH was larger than for SVH, with an anisotropy value of 0.10 (Fig. 5B).

This result suggests a more efficient hot-electron transfer by plasmons polarized parallel to the NR axis, consistent with the PICTT mechanism. In contrast, in CdS-Au NRs where the conventional PHET mechanism dominates (35), we detected negligible anisotropy in the CdS 1s-exciton-bleach signal generated by exciting the Au plasmon band (fig. S15).

Finally, we showed that in the presence of sacrificial electron donors (S–), the electrons injected into CdSe could be used to reduce methyl viologen, a well-known redox mediator for solar fuel generation (46), with a steady-state QY of >0.75% (fig. S18; see the supplementary materials for details).

In light of the high QY values measured for transient charge separation (>24%), the relatively low steady-state QY can be attributed to ultrafast charge recombination. Charge recombination can be retarded by creating a built-in electric field at the semiconductor/metal interface using longer NRs (>100s nm) or by applying a large external bias (36).

Strong mixing of Au and TiO2 electronic levels has been reported in a recent computational study of Au-cluster–sensitized TiO2 NPs (47). Strongly broadened Au plasmon bands and efficient plasmon-induced hot-electron transfer were also observed in Au-NP–sensitized TiO2 nanocrystalline thin films (47). Thus, the PICTT mechanism reported here is potentially a general phenomenon at metal-semiconductor and/or metal/molecule interfaces. PICTT may present a new opportunity to circumvent energy-loss channels in metal nanostructures and greatly increase the efficiencies of devices based on plasmonic light-absorption materials.
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Efficient hot-electron transfer by a plasmon-induced interfacial charge-transfer transition

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Materials and Methods

Sample synthesis

**Synthesis of CdSe NRs.** CdSe NRs were synthesized by previously-reported procedures with slight modifications.\(^{(45,48)}\) Briefly, a mixture of 0.104 g Cadmium Oxide (CdO), 0.401 g octadecylphosphonic acid (ODPA), 0.07 g hexylphosphonic acid (HPA), and 1.43 g tri-n-octylphosphine oxide (TOPO) was degassed at 150 °C for 1 h and then heated to 320 °C under argon atmosphere until it turned clear. 0.136 g Se powder was dissolved in a mixture of 0.5 mL tri-n-butylphosphine (TBP) and 2.85 mL tri-n-octylphosphine (TOP) as the Se stock solution. At 320 °C, 1 mL of Se stock was swiftly injected, which brought the temperature down to 290 °C. The reaction was kept at 290 °C for 7 min for growth of CdSe NRs before it was stopped by removing the heating mantle. The resulting NRs had their first excitonic absorption peak at ~582 nm. NRs of other diameters were obtained by tuning the growth temperature and time, with higher temperature and longer time favoring formation of thicker NRs. Products were precipitated out of the reaction crudes by addition of toluene and ethanol. The precipitation processes were repeated for several times to remove excessive surfactants. Final products were dispersed in chloroform for optical measurements.

**Synthesis of Au tipped CdSe NRs.** Au tipped CdSe NRs were synthesized using the method of Banin and coworkers with slight modifications.\(^{(29)}\) Briefly, 1 mL of CdSe NRs with optical density (OD) of 2 at 582 nm (1 mm light pathlength) in chloroform was dried and re-dispersed in 4 mL toluene in a sealed vial and purged with Argon gas. The gold stock solution was prepared by dissolution of 33 mg gold(III) chloride (AuCl\(_3\)), 30 mg of didodecyldimethylammonium bromide (DDAB, 98%) and 115 mg of dodecylamine (DDA) in 9 mL toluene in another sealed vial. It was also purged with Argon before use. The Au deposition reaction was initiated by adding 3 mL of Au stock solution drop-wise to the CdSe NR solution over a period of 3 min in an ice bath. The ice bath was found to effectively suppress Au growth along the wall of NRs and preserve the well-defined exciton properties of NRs.\(^{(49)}\) After another 10 min, the reaction was stopped and ethanol was added to precipitate CdSe-Au NRs. Final products were dispersed in chloroform for optical measurements. Similar procedures were applied to synthesize QD-Au dimmers and CdSe-Au NRs with different NR diameters.

**Synthesis of Au tipped CdS NRs.** CdS NRs and Au tipped CdS NRs were synthesized using the procedures described in our previous work.\(^{(35)}\)

**Transient Absorption (TA) Spectroscopy set-ups**

**Visible Femtosecond Transient Absorption.** The ultrafast laser beams used in this study were derived from a regeneratively amplified Ti:sapphire laser system (Coherent Legend, 800 nm, 150 fs, 3 mJ/pulse, and 1 kHz repetition rate) and the signal acquisition was conducted by a Helios spectrometer (Ultrafast Systems LLC). A 50% beam splitter split the 800 nm output pulse of the amplifier in two parts. One part was used to pump an Optical Parametric Amplifier (Opera, Coherent) to generate two tunable near-IR pulses, signal and idler, from 1.1 to 2.5 μm. Signal and idler beams were separated with a dichroic mirror, and the former was used to generate 670 nm, 710 nm and 750 nm excitation beams by frequency-doubling in
a BBO crystal. 1140 nm, 1360 nm, and 1550 nm excitation beams were directly taken from the signal beam from OPA. 400 nm pump beam was made by frequency-doubling of 800 nm beam in a BBO crystal. A series of neutral-density filter wheels were used to adjust the power of the pump beam. The pump beam was focused at the sample with a beam waist of about 300 µm. A white light continuum (WLC) from 420 to 800 nm was generated by focusing ~10 µJ of the 800 nm pulse into a sapphire window. The WLC was split into probe and reference beams. The probe beam was focused with an Al parabolic reflector onto the sample (with a beam waist of ~150 µm at the sample). The reference and probe beams were focused into a fiber-coupled multichannel spectrometer with complementary metal-oxide-semiconductor (CMOS) sensors and detected at a frequency of 1 kHz. The intensities of the probe and reference beams were ratioed to correct for pulse-to-pulse fluctuation of the white-light continuum. The delay between the pump and probe pulses was controlled by a motorized delay stage. The pump beam was chopped by a synchronized chopper to 500 Hz. The change in absorbance for the pumped and unpumped samples was calculated. The instrument response function (IRF) of this system was measured to be ~170 fs by measuring solvent responses under the same experimental conditions (with the exception of a higher excitation power).

**Nanosecond Transient Absorption.** Nanosecond TA was performed with the EOS spectrometer (Ultrafast Systems LLC). The pump beam at 400 nm was generated in the same way as femtosecond TA experiments. The white light continuum (380-1700 nm, 0.5 ns pulse width, 20 kHz repetition rate) used here was generated by focusing a Nd:YAG laser into a photonic crystal fiber. The delay time between the pump and probe beam was controlled by a digital delay generator (CNT-90, Pendulum Instruments). The probe and reference beams were detected with the same multichannel spectrometers used in femtosecond TA experiments. The IRF of this system was measured to be ~280 ps.

**Mid-IR Femtosecond Transient Absorption.** A Clark-MXR IR optical parametric amplifier was pumped with 1 mJ/pulse of the 800 nm fundamental beam to generate two tunable near-IR pulses from 1.1 to 2.5 µm (signal and idler, respectively). They were combined in a 1-mm-thick AgGaS2 crystal to generate the mid-infrared probe pulses from 3 to 10 µm by difference frequency generation (DFG). The DFG signal was collimated with a 50 cm CaF2 lens before it was focused into a 0.5mm path length Harrick cell containing the sample, and near the focal point, it overlapped with the temporally delayed pump pulses with different wavelengths. The waist of the probe beam at the sample was 300 µm and the waists of the 400, 670, 710, 750, 800, 1140, 1340, and 1550 nm pump beams were determined to be ~640, 600, 680, 720, 680, 700, 660, and 680 µm respectively. The mid-IR probe was then dispersed in a monochromator and the intensity change of the IR light induced by photoexcitation was monitored as a function of time with a 32-element HgCdTe array detector. The pump beam was chopped by a Chopper at 500 Hz. The IRF of this spectrometer was determined to be ~260 fs by fitting signal formation time of quantum dots under band edge excitation.
Low magnification Transmission Electron Microscopy (TEM) images were obtained from Hitachi H-7500 Transmission Electron Microscope operated at 75 kV and the images of as-prepared CdSe (582 nm) and CdSe-Au NRs are shown in Figure S1a and S1b, respectively. The CdSe NRs have an average length and diameter (with standard deviations) of 18.2(±1.5) nm and 3.6(±0.2) nm, respectively. After deposition of Au tips with average diameter of 4.1(±0.4) nm, the NRs are slightly shorter and thinner, with average length and diameter of 13.0(±2.2) nm and 3.3(±0.3) nm, respectively, due to etching of NRs during Au growth. This etching has been attributed to dissolution of NRs in presence of dodecyl(dimethylammonium) bromide (DDAB) used for Au growth.(29)

High angle annular dark filed (HAADF) Scanning Transmission Electron Microscopy (STEM), energy-dispersive X-ray spectroscopy (EDS), and High-resolution transmission electron microscopy (HR-TEM) characterizations were performed on a FEI Tecnai Osiris operated at 200 kV. For the EDS mapping, we used a sub nanometer probe (~0.5 nm) and a beam current of 2.2 nA. Drift-corrected EDS maps were obtained using Bruker Esprit software. The map acquisition time was about 5 mins. STEM image of CdSe-Au NRs is shown in Figure S1c. The EDS map for selected area is shown in Figure S1d. HRTEM image is shown in Figure S1e. From these images, the Au deposition indeed only occurred on the tips of NRs, without discernible Au domains along the surfaces of NRs.

TEM images of CdSe QDs and QD-Au dimmers are shown in Figure S2a and S2b, respectively. The starting QDs have an average size of 3.5(±0.4) nm, corresponding to the first exciton peak absorption at ~575 nm and showing similar quantum confinement with the studied CdSe NRs (Figure S2c). After deposition of Au, most of particles appear as dimer structures with one domain showing higher contrast and the other lower contrast, as indicated in the inset of Figure S2b.

We also prepared two other NR samples with first excitonic peaks at 555 nm and 605 nm. The TEM images of corresponding CdSe-Au NRs are shown in Figure S3a and S3b, respectively. The CdSe (555 nm)-Au NRs have average NR length and diameter of 6.9(±1.3) and 2.6(±0.4) nm, respectively, and the average Au tip diameter is 2.7(±0.4) nm. The CdSe (605 nm)-Au NRs have average NR length and diameter of 10.5(±1.3) nm and 4.4(±0.5) nm, respectively, and the average Au tip diameter is 1.8(±0.3) nm. Although the Au tip size varies from 1.8 nm to 4.1 nm for these CdSe-Au NRs, their absorption onsets are the same in Figure 1B. It implies that the plasmon broadening induced by strong inter-domain coupling is much larger inhomogeneous broadening from Au particle size distributions.

Energetics estimation in CdSe-Au NRs

The reported electron affinity of bulk CdSe ranges from 4.1 eV to 4.8 eV (50). The work function of Au is 5.1 eV. (51) The quantum confinement effect in CdSe NR shift its band edges relative to bulk CdSe and the shifting can estimated using the simple model by Brus: (52,53)
\[ E_{1\sigma} = E_{CB} + \frac{m_e}{m_e + m_h} \left[ E_g(QD) + V_{e-h} - E_g(bulk) \right] \]  
\[ (S1a), \]

\[ E_{1\sigma} = E_{VB} - \frac{m_e}{m_e + m_h} \left[ E_g(QD) + V_{e-h} - E_g(bulk) \right] \]  
\[ (S1b), \]

where \( E_{CB}, E_{VB}, \) and \( E_g(bulk) \) are the conduction band (CB) edge, valence band edge (VB) and band gap of bulk CdS, \( E_g(QD) \) the lowest exciton energy in NRs, and \( m_h (m_e) \) the hole (electron) effective mass. The coulomb attraction \( V_{e-h} \) between electron and hole has been estimated to be \( \sim 150 \text{ meV} \) for CdSe NRs.\((30)\) Using these equations, the CB and VB edges have been estimated to between -3.7 eV to -4.4 eV and -6.0 eV to -6.7 eV \textit{versus} vacuum level, respectively. Therefore, the barrier between the Fermi level of Au and CB edge of CdSe is between 0.7 eV to 1.4 eV.

\[
E_{1\sigma} = E_{CB} + \frac{m_e}{m_e + m_h} \left[ E_g(QD) + V_{e-h} - E_g(bulk) \right]
\]
\[ (S1a), \]

\[
E_{1\sigma} = E_{VB} - \frac{m_e}{m_e + m_h} \left[ E_g(QD) + V_{e-h} - E_g(bulk) \right]
\]
\[ (S1b), \]

Interband and intraband kinetics of free CdSe NRs and CdSe NR-BQ complexes

\textbf{Interband kinetics.} The visible TA spectra of free CdSe NRs at indicated delays after 400 nm excitation are shown in Figure S4a. Previous TA studies on CdSe NRs have assigned the exciton bleach (XB) feature at \( \sim 580 \text{ nm} \) to state filling of \( 1\sigma_e \) electronic level.\((54,55)\) The XB kinetics is plotted in Figure S4b and fitted to the following multi-exponentials convoluted with the IRF:

\[
S_{XB} = S \cdot \left[ \sum_{i=1}^{3} a_i e^{-t/\tau_i} - e^{-t/\tau_f} \right] \otimes IRF
\]
\[ (S2), \]

where \( S \) is the signal size of XB, \( \tau_f \) is the formation time constant for the XB signal and \( a_i \) and \( \tau_i \) are amplitudes and time constants of the exponential decay components. The IRF of this measurement was determined to be \( \sim 170 \text{ fs} \) by measuring solvent responses. The fitting parameters and errors are listed in Table S1, from which the half-life of band edge electrons in CdSe NRs is determined to be \( 8.76 \pm 0.83 \text{ ns} \). In the presence of an electron acceptor, benzoquinone (BQ), XB recovery is faster due to electron transfer to BQ, as shown in Figure S4c. The kinetics of XB feature in NR-BQ (Figure S4d) can also be fitted to equation S1 and the fitting parameters are listed in Table S1. The electron transfer half-life is determined to be \( 70.9 \pm 2.5 \text{ ps} \).

\textbf{Intraband kinetics.} In addition to the interband XB, the dynamics of electrons in the conduction band of CdSe NRs and other quantum confined Cd chalcogenides can also be probed by intraband transition in the mid-IR regions.\((35,56,57)\) Indeed, as shown in Figure S4d, in both free CdSe NRs and CdSe NR-BQ complexes, the kinetics of intraband absorption at \( \sim 3000 \text{ nm} \) agree well with the XB feature, confirming that both signals can be used to follow band edge electron kinetics in CdSe NRs. The intraband signal provides a convenient probe to study plasmon-induced electron transfer from Au to CdSe in CdSe-Au NRs because it avoids spectral overlap with plasmon signals in the visible region.\((11, 35)\)
Charge separation and recombination in 400 nm excited CdSe-Au NRs

In a previous study of electron transfer from excited CdSe NRs to Au tip, it was reported that the initial XB amplitude in CdSe-Au NRs is only 10% of that for the free NRs because of ultrafast hot electron transfer to Au in <100fs. We also investigated this process in our CdSe-Au samples using 400 nm pump light, which could excite both CdSe NRs and inter-band transition of Au tips. The resulting TA spectra from 0.2 ps to 1 ns (Figure S5a) show much smaller initial XB signal amplitude (~13.5%) in CdSe-Au compared with free CdSe NRs (after normalizing the signals to correspond to the same number of absorbed photons by CdSe) and the formation of derivative-like features within 0.2 ps that can be assigned to charge separation induced stark effect signals. In addition, there is also strong broad absorption signal ranging from ~600 nm to the near IR, which is likely due to excitation of the Au tip or strongly-coupled CdSe-Au domains because a similar feature was also observed in CdSe QD-Au dimers (see below). Because this signal is nearly constant throughout the visible spectral window, it can be subtracted from the TA spectra to reveal the kinetics of the Stark effect spectral signatures (Figure S5c). Fitting these kinetics shows a formation time of ~46 fs (Table S2) followed by multi-exponential decays with half-life of ~0.90±0.15ps. We attribute the decay to charge recombination process (back electron transfer from Au tip to CdSe NR). The formation time (~46 fs) of charge separated states is much faster than the XB formation in free CdSe NRs (~308 fs), consistent with previous conclusion of ultrafast hot electron transfer from CdSe to Au. It should be noted that although the charge separated states was observed, the charge separation yield was not determined and the possibility of ultrafast energy transfer process (which would also lead to XB recovery) cannot be ruled out. Furthermore, although absorption at 400 nm is dominated by CdSe NRs, the XB bleach signal also contains contribution of Au-to-CdSe charge transfer resulted from the direct excitation of the Au tip, which can be best studied by exciting the NR below the CdSe band gap, as described in the main text.

Transient Absorption of CdSe QD-Au dimers

TA spectra of CdSe QD-Au dimers after 400 nm and 800 nm excitations are shown in Figure S6a and 6b, respectively. Typical TA feature of excited QDs (exciton bleach) and Au nanoparticles are absent. Instead, the TA spectra are dominated by a broad absorption feature throughout the whole probed spectral window. They are consistent with the absence of exciton bands of QDs and SPR band of Au on the static absorption spectrum of CdSe-QD dimers in Figure 1A. The kinetics of this broad absorption feature (averaged from 670 to 700 nm) for CdSe QD-Au dimers and CdSe-Au NRs are identical at both 400 nm and 800 nm excitations (FigureS6c). Fitting these kinetics reveals a formation process (~118±25 fs) followed by multi-exponential decays with a half-life of 2.3±0.1 ps (Table S3). This broad absorption feature is likely due to laser heating induced spectral changes of the strongly damped plasmon. In fact, the relaxation time scale (2.3 ps) is similar to previously-reported relaxation times of Au nanoparticles. Quantitative understanding of this feature is beyond the scope of this work.
Charge separation and recombination in 800 nm excited CdSe-Au NRs

In Figure 2A, direct excitation of the damped plasmon band of CdSe-Au NRs at 800 nm resulted in TA spectra with a broad-band absorption feature from ~500 nm to the near IR and a pronounced exciton bleach (XB) feature at ~575 nm. A control experiment using a mixture of isolated CdSe NRs and Au nanoparticles under the same excitation conditions showed only Au features without CdSe NR XB signature (Figure S7). The IR control experiment in Figure 2B does not show any noticeable absorption at 3000 nm either. Therefore, both XB and IR features observed in CdSe-Au NRs can be attributed to plasmon induced charge separation.

To more clearly show the XB feature in CdSe-Au NRs, we have subtracted the broad absorption from the total signal of CdSe-Au NR to yield the TA spectra in Figure S8a and the kinetics in Figure 2B. The subtracted spectra clearly show the XB signal in CdSe-Au, indicating the presence of electron at the 1σe level of CdSe NRs upon 800 nm excitation. However, XB kinetics shows a long-lived component after ~50 ps when mid-IR signal completely disappears (Figure S8b). As shown in Figure S8a, the long-lived component is a derivative feature of the exciton band. Its exact origin is unknown, although it may be attributed to heating induced shift of the NR exciton band. Fast decay of excited states converts the energy of the excitation photon into lattice phonons which heat up the nanorods. Due to this complication, we use the mid-IR signal to probe charge recombination kinetics. (35)

The mid-IR kinetics in Figure 2B can be fitted with the following multi-exponentials convoluted with the IRF:

\[ S_{\text{IR}} = S \cdot \left[ \sum_{i=1}^{2} e^{-t/\tau_i} - e^{-t/\tau_f} \right] \otimes \text{IRF} \]  

(35)

where \( \tau_f \) is the formation time constant for the mid-IR signal and \( a_i \) and \( \tau_i \) are amplitudes and time constants of the exponential decay components. The IRF ( ~260 fs ) and t=0 were determined by fitting the formation kinetics of mid-IR signal in Cd3P2 QDs under band edge resonant excitation (Figure S9a), where we have assumed that direct band edge excitation led to the instantaneous formation of 1S electron and its 1S-1P intraband absorption. Both IRF and time-zero from fitting Cd3P2 QDs are fixed in fitting the kinetics of CdSe-Au to ensure the accuracy of \( \tau_f \) (Figure S9a). The fitting parameters and errors are listed in Table S4. To demonstrate the accuracy of \( \tau_f \sim 20\pm10 \) fs, we also show the fitting results for different \( \tau_f \) of 10, 20, 30, 40, 60, 80, and 100 fs (with fixed IRF and time-zero) in Figure S9b. It is clear that our experimental data agree best with \( \tau_f \sim 20\pm10 \) fs.

In Figure S9c, we compare the fitting results for mid-IR formation kinetics in CdSe-Au and CdS-Au NRs. Again, both IRF and time-zero were independently determined in these fits. CdS-Au shows a considerably slower formation (90±20 fs) than CdSe-Au (20±10 fs), due to their different charge separation mechanisms.
Plasmon-induced charge separation yields in CdSe-Au NRs

**Calibration of signal sizes using QDs.** To accurately determine plasmon induced charge separation quantum yields (QY) in CdSe-Au NRs, we used near IR absorbing Cd$_3$P$_2$ and PbS QDs as internal calibration to correct for the uncertainties in pump beam size measurements. The absorption spectra of Cd$_3$P$_2$ and PbS QDs are shown in Figure S10a and their 1S excitonic absorption peaks are at 820 nm and 1320 nm, respectively. The former can be used to calibrate charge separation QY measurements in CdSe-Au NRs under 670 nm, 710 nm, 750 nm and 800 nm excitations, while the latter for 1140 nm, 1340 nm, and 1550 nm excitations.

Figure S10b shows the mid-IR intraband absorption signal sizes of Cd$_3$P$_2$ QDs (at 3000 nm) as a function of pump power for 400 nm and 800 nm excitations. The ratio of QYs for generating 1Se electrons using 800 nm and 400 nm pump lights can be calculated according to:

$$R = \frac{\Delta A(800nm)}{[1 - 10^{-\text{OD}(800nm)}] \cdot j(800nm)} / \frac{\Delta A(400nm)}{[1 - 10^{-\text{OD}(400nm)}] \cdot j(400nm)}$$  \hspace{1cm} (S4),

where OD(800 nm) and OD(400 nm) are optical densities of the samples at 800 nm and 400 nm, respectively. They were adjusted to be the same so that the pump-probe overlapping profiles are the same in these experiments. The ODs of free CdSe NRs at 400 nm and CdSe-Au NRs at 800 nm were also adjusted to the same value to ensure that the charge separation QY measurements in CdSe-Au are performed at exactly the same conditions as the calibration measurements. $j$(800 nm) and $j$(400 nm) are the photon fluxes of 800 nm and 400 nm pump beams, respectively, calculated according to the measured pump powers and beam sizes.

To increase the signal-to-noise ratio and also to ensure single-photon excitation processes, we can extract the slopes (in the unit of mOD/mW) $S(800nm)$ and $S(400nm)$ by linear fitting of the data points in Figure S10b. The ratio in equation S4 can be more conveniently calculated from the slopes and the photon flux per mW, $j'(800 nm, 1mW)$ and $j'(400 nm, 1mW)$, at 800 and 400 nm, respectively, using the following equation:

$$R = \frac{S(800nm)}{j'(800nm, 1mW)} / \frac{S(400nm)}{j'(400nm, 1mW)}$$  \hspace{1cm} (S5).

R should be 1 if the beam size measurements are accurate. It can be used to correct for the uncertainty in the measured beam sizes, as we will show later.

Figure S15c shows the mid-IR intraband absorption signal sizes as a function of pump power for 400 nm excited CdSe NRs and 800 nm excited CdSe-Au NRs. The QY of plasmon-induced charge separation by 800 nm excitation can be calculated by comparing the slopes of 800 nm excited CdSe-Au NRs $S(800 nm)$ with that of 400 nm excited free CdSe NRs $S(400 nm)$, according to the following equation:

$$QY(raw) = \frac{S(800nm)}{j'(800nm, 1mW)} / \frac{S(400nm)}{j'(400nm, 1mW)}$$  \hspace{1cm} (S6).

By taking the ratio between QY (raw) and R, we can correct for uncertainties in the beam size measurement:
Using this method, the charge separation QY of CdSe-Au NRs at 800 nm excitation was calculated to be 23.7(±0.5)%. Similar measurements were performed for 670 nm, 710 nm, and 750 nm excitations. For measurements at 1140 nm, 1340 nm, and 1550 nm excitations, PbS QDs were used as the calibration. In this case 400 nm pump was replaced by 580 nm to excite PbS QDs and CdSe NRs to avoid multiple exciton generation (MEG) effect in PbS QDs (which would make the theoretic R value in equation S5 smaller than 1). 400 nm and 580 nm pumps are 3.35 and 2.31 times the bandgap of PbS QDs, respectively. According to previous reports, 580 nm is below the threshold for MEG in PbS QDs (~3 times bandgap). (64)

**Excitation wavelength dependent QYs in the conventional mechanisms.** The charge transfer QY from excited metal to semiconductor in the conventional PHET mechanism was generally described by the Fowler’s formula (equation 1 in the main text): (35)

\[
QY(h\omega) = \left(\frac{h\omega - E_b}{2E_F}\right)^2 / 4E_F h\omega,
\]

where \(h\omega\) is the energy of excitation photons, \(E_b\) is the barrier height between metal and semiconductor, and \(E_F\) is the Fermi energy of Au (5.5 eV). Equation 1 can be derived by considering both energy and momentum conservations in the hot electron transfer process. (42) As shown in Scheme S1, the z-direction momentum of the hot electron has to be larger than onset momentum (\(P_{on} = \sqrt{2m(E_F + E_b)}\)). Therefore,

\[
\sqrt{2m(E + h\omega)} \cdot \cos \theta \geq \sqrt{2m(E_F + E_b)} \tag{S8}
\]

According to this equation, the range of electron energy E is:

\[
E_F \geq E \geq \frac{E_F + E_b}{2} - h\omega \tag{S9}
\]

and the range of angle \(\theta\) is:

\[
1 \geq \cos \theta \geq 1 - \frac{h\omega - E_b}{2E_F} \tag{S10}
\]

Note that in deriving S10, we have used the condition of \(E_F \gg E_b\) and \(h\omega\). Therefore, the QY of hot electron injection is:

\[
QY = \frac{1}{2N} \int_{-\frac{h\omega - E_b}{2E_F}}^1 d \cos \theta \int_{E_F + E_b - h\omega}^{E_F} \rho(E) dE \tag{S11}
\]

where \(\rho(E)\) is the density of state (DOS) of the conduction band of metal, N is the total number of available electrons near Fermi level that can be excited and the coefficient 1/2 accounts for half of the total electrons moving towards semiconductor. Since \(E_F \gg h\omega\), we
assume that the DOS is constant near Fermi level and therefore, \( N = \rho(E) \cdot h \omega \). With this assumption, the integral in equation S11 results in: 
\[
QY(h\omega) = \frac{(h\omega - E_b)^2}{4E_F h\omega}.
\]

It has been found that photoemission QYs from small nanoparticles are enhanced compared to planar bulk structures, possibly due to geometric effect \((40, 41)\) and lowering of escaping barrier \((42)\). In this case, the excitation energy dependence still follows Fowler’s function form except that a scaling factor (C) is added to account for the enhancement:
\[
QY(h\omega) = C \cdot \frac{(h\omega - E_b)^2}{4E_F h\omega},
\]
which is the equation 2 used in the main text.

If electron scattering only occurs at the metal/semiconductor interface, the momentum conservation can be relaxed and electrons transfer into semiconductor as long as:
\[
E + h\omega \geq E_F + E_b. \tag{S12}
\]
In this case, the QY of hot electron injection is:
\[
QY = \frac{1}{2N} \int_{E_F}^{E_F} \rho(E) dE = \frac{(h\omega - E_b)}{2h\omega} \tag{S13},
\]
which is the equation 3 in the main text.

**Estimation of the linewidth of damped plasmon bands**

To determine the line-width of damped plasmon in CdSe-Au dimers and NRs, we fit their absorption spectra using broadened excitonic and plasmonic bands. We start with fitting the absorption spectra of isolated Au nanoparticles, CdSe QDs and CdSe NRs. As shown in Figure S11a, the Au nanoparticle absorption spectrum was fitted to the sum of a surface plasmon band, using a Lorentzian lineshape, and an interband transition:
\[
Abs_{Au}(\omega) = I \left[ \frac{\gamma^2}{(h\omega - E_c)^2 + \gamma^2} \right] + f_{ib}(\omega) \tag{S14},
\]
where \( \omega \) is the transition frequency, \( I \) is the peak height, \( E_c \) is the peak center, \( \gamma \) is the half peak width, and \( f_{ib}(\omega) \) is a function describing interband absorption. The fitting parameters are listed in Table S5. Specifically, the plasmon peak width is 0.34 eV.

The absorption spectrum of CdSe QDs and NRs were fitted to sum of four excitonic bands using Gaussian lineshapes (Figure S11b&c):
\[
Abs_{CdSe}(\omega) = \sum_{i=1}^{4} I_i \cdot \exp\left[-\frac{(h\omega - E_{c,i})^2}{2\sigma_i^2}\right] \tag{S15},
\]
where \( I_i, E_{c,i}, \) and \( \sigma_i \) are the height, center, and half-width of the \( i \)th Gaussian bands. The fitting parameters are listed in Table S5.
The absorption spectrum of CdSe QD-Au dimers was fitted to the sum of broadened surface plasmon band of Au tips and excitonic bands of CdSe QDs (Figure S11d):

\[ \text{Abs}_{\text{Dimer}}(\omega) = I \left[ \frac{\gamma^2}{(\hbar \omega - E_\text{g})^2 + \gamma^2} \right] + f_{\text{b}}(\omega) + \sum_{i=1}^{4} I_i \cdot \exp \left[ -\frac{(\hbar \omega - E_{\text{e},i})^2}{2\sigma_i^2} \right] \]  

(S16).

In this fitting, the Lorentzian and Gaussians are broadened while the interband absorption of Au remains unchanged. In addition, the relative contributions of Au and CdSe to total absorption, i.e. the oscillator strength ratio between Au to CdSe, is fixed, which is determined by the reported extinction coefficients of CdSe QDs and Au nanoparticles of similar sizes.\((65, 66)\) The fitting parameters are listed in Table S5. The best fit gives a plasmon bandwidth of 1.6 eV.

The absorption spectrum of CdSe-Au NRs was fitted to the sum of broadened surface plasmon band of Au tips, broadened excitonic bands of the CdSe region near Au tip, and the unperturbed CdSe region near the NR center (Figure S11e):

\[ \text{Abs}_{\text{CdSe-AuNR}}(\omega) = I \left[ \frac{\gamma^2}{(\hbar \omega - E_\text{g})^2 + \gamma^2} \right] + f_{\text{b}}(\omega) + C_1 \sum_{i=1}^{4} I_i \cdot \exp \left[ -\frac{(\hbar \omega - E_{\text{e},i})^2}{2\sigma_i^2} \right] + C_2 \text{Abs}_{\text{CdSeQR}}(\omega) \]  

(S17).

In this fitting, the oscillator strength ratio between broadened and unperturbed CdSe regions, i.e. \(C_1/C_2\), is a new fitting parameter. But the sum of these two parts, i.e. total absorption of CdSe NRs, still has fixed contribution relative to Au, as determined by the extinction coefficient ratio between CdSe NRs and Au nanoparticles. The fitting parameters are listed in Table S5. The best fit gives an plasmon band width of 1.6 eV, identical to that in CdSe-Au dimers. The oscillator strength ratio between the broadened and unperturbed CdSe regions is 1:3.3. Considering the total length of 13.0 nm for CdSe NR, we can estimate that the strongly coupled regions extend \(~2\) nm from the CdSe/Au interface towards the NR center.

**Transient Absorption Anisotropy of CdSe and CdSe-Au NRs**

**Theory of TA anisotropy.** In TA anisotropy measurements, the polarization of the probe pulse was fixed while that of the pump pulse could be adjusted using a half-waveplate. We recorded the TA signals when the pump and probe pulses were either parallel or perpendicular to each other and corresponding anisotropy can be calculated. To help understand TA anisotropy better, we first derived the expression, adapted from commonly used fluorescence anisotropy theory, \((67, 68)\) for an anisotropic rod, which can be directly related to our CdSe and CdSe-Au NRs.

As shown in Figure S12a, there are two sets of coordinates to be considered here: the laboratory coordinates \((x, y, z)\) and the rod coordinates \((a, b, c)\). These two are related to each other through Eulerian angles \((\theta, \phi, \psi)\). Specifically, the rod coordinates can be transformed into the laboratory coordinates through the transformation matrix \(A\):

\[
A = \begin{pmatrix}
A_{aa} & A_{ab} & A_{ac} \\
A_{ba} & A_{bb} & A_{bc} \\
A_{ca} & A_{cb} & A_{cc}
\end{pmatrix}
\]  

(S18),

where:
\[ A_{xa} = \cos \theta \]
\[ A_{xb} = \sin \theta \sin \psi \]
\[ A_{xc} = \sin \theta \cos \psi \]
\[ A_{ya} = \sin \theta \sin \varphi \]
\[ A_{yb} = \cos \theta \cos \psi \sin \varphi \]
\[ A_{yc} = -\sin \psi \cos \theta \cos \psi \sin \varphi \]
\[ A_{za} = -\sin \theta \cos \varphi \]
\[ A_{zb} = \cos \psi \sin \varphi + \cos \theta \sin \psi \cos \varphi \]
\[ A_{zc} = -\sin \psi \sin \varphi + \cos \theta \cos \psi \cos \varphi \]  
(S19).

Assuming that the pump beam path is along x axis and it can be polarized along either y or z axis. The probabilities for absorption of the pump beam polarized along y and z axes are:

\[
P_{\text{pump}, y} = p_a A_{ya}^2 + p_b A_{yb}^2 + p_c A_{yc}^2 = 0.5 \cdot (1 - p_c) (A_{ya}^2 + A_{yb}^2) + p_c A_{yc}^2 \]  
(S20),

\[
P_{\text{pump}, z} = p_a A_{za}^2 + p_b A_{zb}^2 + p_c A_{zc}^2 = 0.5 \cdot (1 - p_c) (A_{za}^2 + A_{zb}^2) + p_c A_{zc}^2 \]  
(S21),

respectively. Here \( p_a, p_b, \) and \( p_c \) are the absorption components at the pump wavelength along a, b, and c directions, which are proportional to the square of absorption dipole along each axis. For an Wurtzite CdSe nanorod, we have \( p_a = p_b \) and \( p_a + p_b + p_c = 1 \). (69) Assuming that the probe beam is polarized along z axis, the absorption probability of the probe beam is:

\[
P_{\text{probe}, z} = q_a A_{za}^2 + q_b A_{zb}^2 + q_c A_{zc}^2 = 0.5 \cdot (1 - q_c) (A_{za}^2 + A_{zb}^2) + q_c A_{zc}^2 \]  
(S22),

where \( q_a, q_b, \) and \( q_c \) are the square of absorption dipole components at the probe wavelength along a, b, and c directions.

Since the nanorods are randomly oriented, the averaged transient absorption signals for different pump polarizations can be obtained by integrating over all the possible orientations:

\[
S_{zz} = \int_0^{2\pi} d\varphi \int_0^{2\pi} d\psi \int_0^{\pi} \sin \theta d\theta \int_0^{2\pi} d\theta \int_0^{2\pi} d\varphi \int_0^{\pi} \sin \theta d\theta P_{\text{pump}, y} \cdot P_{\text{probe}, z} \sin \theta d\theta \]  
(S23),

\[
S_{yz} = \int_0^{2\pi} d\varphi \int_0^{2\pi} d\psi \int_0^{\pi} \sin \theta d\theta \int_0^{2\pi} d\theta \int_0^{2\pi} d\varphi \int_0^{\pi} \sin \theta d\theta P_{\text{pump}, y} \cdot P_{\text{probe}, z} \sin \theta d\theta \]  
(S24). 

The ensemble anisotropy \( r \) is defined as:

\[
r = \frac{S_{zz} - S_{yz}}{S_{zz} + 2S_{yz}} \]  
(S25). 

The calculated anisotropy as a function of both \( p_c \) and \( q_c \) is shown in Figure 12b. It shows that the anisotropy is 0 when \( p_c \) and/or \( q_c \) is 1/3, which means that there is no detectable anisotropy once pump or probe dipole is completely isotropic.

**TA anisotropy of CdSe NRs.** For free CdSe NRs excited at the band edge (590 nm) and probed at the exciton bleach (XB), the transition dipoles for the pump and probe beams are
the same. Therefore, \( p_c = q_c \) and it corresponds to the diagonal dashed line in Figure S12b. The anisotropy shown in Figure 4A is 0.12, from which we obtain: \( p_c = 0.70 \). We also measured the anisotropy for the mid IR intraband TA signals after 590 excitation, which has negligible anisotropy (Figure S13). Since \( p_c = 0.70 \) for the pump pulse, from Figure S12b, \( q_c \) should be 1/3 for the intraband absorption. We can only probe the interband XB signal for anisotropy measurements.

**TA anisotropy of CdSe-Au NRs.** For the 800 nm excited free CdSe-Au NRs, we observed an anisotropy of 0.10 when probing the CdSe XB signal in Figure 4B. Since \( q_c = 0.70 \) for the probe pulse, we can obtain \( p_c = 0.65 \) for the pump pulse from Figure S12b. There are two possible mechanisms for this observed absorption anisotropy. First, the absorption of the damped Au plasmon is isotropic, but the plasmon damping generates hot electrons in CdSe more efficiently when excitation pulse is polarized along the rod (c axis). More specifically, the ratio of hot electron generation efficiency when exciting the CdSe-Au NRs along c, a, and b axes are 65:17.5:17.5. In the second scenario, the absorption dipole of the damped Au plasmon band is strongly polarized along c axis of CdSe NR. The angle between the plasmon absorption dipole and c axis can be calculated to be \( \sim 36.1^\circ \).

**TA anisotropy of CdS and CdS-Au NRs.** Our previous study indicates that the plasmon band in CdS-Au NRs is only weakly perturbed and charge separation in CdS-Au NRs likely follows the conventional plasmon induced hot electron transfer mechanism.(34) Therefore, we have also measured the TA anisotropy for CdS and CdS-Au NRs to compare it with CdSe-Au NRs. The UV-vis absorption spectra of CdS and CdS-Au NRs are shown in Figure S14a and a representative TEM image of the CdS-Au NRs is shown Figure S14b. In contrast to CdSe-Au NRs, the CdS-Au NRs show both excitonic and plasmonic absorption features, consistent with our previous study. (35)

The TA spectra of CdS NRs at indicated delays after 400 nm excitation are shown in Figure S15a. The kinetics of XB feature at \( \sim 450 \) nm is shown in Figure S15b. Anisotropy of XB can be calculated to be 0.11 (Figure S15b, inset), corresponding to \( p_c = 0.685 \). Note that we did not perform band edge excitation for the CdS NR because of the difficulty to obtain 450 nm pump light using our laser system. It is known that the absorption anisotropy decreases with increasing excitation photon energy. (45, 67, 68) Therefore, \( p_c \) for the band edge absorption dipole of CdS NRs is expected to be larger than 0.685.

650 nm light was used to selectively excite the plasmon band in CdS-Au NRs. An control experiment with a mixture of isolated CdS NRs and Au nanoparticles only showed typical heated Au plasmon band signals, without any noticeable CdS XB feature (Figure S16a). In contrast, the CdS-Au NRs showed a dip at \( \sim 450 \) nm that coincided with the XB feature of CdS NR (Figure S16b), which can be attributed to plasmon induced electron transfer from Au to CdS. To remove the contribution of Au to the total signal at 450 nm, the signal at \( \sim 480 \) nm (scaled by a factor C) was subtracted from that at \( \sim 450 \) nm. The scaling factor C was chosen so that the subtracted XB kinetics at \( \sim 450 \) nm agreed with the intraband mid-IR kinetics, as shown in Figure S16c. The same factor was used to extract XB kinetics for the cases where pump and probe beams are polarized either parallelly (HH) or perpendicularly (HV) to each other. As shown in Figure S16d, the signal amplitude had little
difference for HH and HV polarizations. Therefore, the calculated anisotropy is negligible. Since $p_c$ for the band edge absorption of CdS NRs is larger than 0.685, this result suggest negligible polarization dependence in the plasmon induced hot electron transfer efficiency, consistent with conventional plasmon induced hot electron transfer model.

Reduction of methyl viologens by plasmon-generated electrons

**Ligand exchange for NRs.** The original hydrophobic ligands on NRs were replaced by 11-mercaptoundecanoic acid (MUA) molecules through a reported procedure. (70,71) Typically, 40 mg of MUA and 10 mL of 0.01 M aqueous solution of KOH were added to 3 mL chloroform solution of NRs. The mixture was vigorously shaken for several minutes to transfer NRs into the aqueous phase. The upper layer was taken out and 10 mL of methanol was added to precipitate out the MUA-capped NRs. The precipitates were re-dissolved in water. In the TEM image of these MUA capped NRs (Figure S17), we found isolated nanoparticles which were most likely Au nanoparticle. We attributed this to the etching of Au tips from CdSe rods in the basic condition used in ligand exchange and have kept this process short to minimize its effect.

**Photo-driven MV$^{2+}$ reduction using CdSe-Au NRs** For the cw light driven MV$^{2+}$ reduction experiment, the concentration of aqueous CdSe-Au NRs was tuned to have an OD of 0.2 at 800 nm in a 1 cm pathlength cuvette. Into this solution (with a volume of 3 mL) 1 mg methyl viologen dichloride (MV$^{2+}$) and 1 mg sodium sulfide (Na$_2$S, as sacrificial donors) were added. The concentration of MV$^{2+}$ and Na$_2$S were kept low so that the dark reaction rate between them was slow. The reaction solution was purged with Ar for 15 min and then constantly stirred and illuminated by a red light (680±30 nm, 34.5 mW) that was produced from a Xeon lamp by applying a band pass filter. MV$^+$ radicals generated in the reaction were detected by measuring the absorption change of the solution. The amounts of MV$^+$ radicals were calculated from the difference absorbance with respect to time zero (start of illumination) using the reported extinction coefficient. (72) The experimental scheme is shown in Figure S18a.

Time-dependent differential absorption spectra of the CdSe-Au-MV$^{2+}$ system with respect to illumination time are shown in Figure S18b, which clearly shows the accumulation of MV$^+$ radicals. The accumulation kinetics is plotted in Figure S18c. In addition, we performed a series of control experiments to investigate the role of plasmonic light absorption in radical formation. As shown in Figure S18c, removing CdSe-Au NRs from the reaction solution (referred to as the blank sample) showed a much slower MV$^+$ radical formation rate, which can be attributed to slow reduction of MV$^{2+}$ (-0.446 V vs NHE) by S$^2$ (-0.450 V vs NHE) in the dark. Replacing CdSe-Au NRs by Au nanoparticles (referred to as Au sample) with the same sample absorbance at the excitation wavelength yielded similar radical generation rate as the blank sample. It implies that direct plasmon induced hot electron transfer from Au nanoparticles to MV$^{2+}$ cannot compete with the ultrafast e-e thermalization within Au. Replacing CdSe-Au NRs by CdSe NRs (of the same concentration as CdSe-Au NRs) led to a formation rate that is faster radical generation rate than the blank sample, but
still much slower than the CdSe-Au-MV$^{2+}$ system. This likely caused by imperfect filtration of lights at wavelength below the CdSe band gap.

To calculate the plasmon-induced radical generate rate $\Delta$(MV$^+$), we subtracted radical generation rate of CdSe NRs sample from that of CdSe-Au NR. Note that the reaction rate is calculated within 1 min of illumination when the radical concentration is low because the generated radicals also absorb photons around 680±30 nm, as shown in Figure S18b. Quantum efficiency (QE) for radical generation was calculated using: $\text{QE} = N_A \cdot \Delta(\text{MV}^+)/\Delta(\hbar v)$, where $N_A$ is the Avogadro constant and $\Delta(\hbar v)$ is the number of absorbed photons per minute calculated from the excitation power and sample optical density. The plasmon enhanced QE for photo-reduction of MV$^{2+}$ was calculated to be 0.75±0.10%. It should be noted that this value is likely an underestimate of the efficiency of CdSe-Au because some of the Au tips separate from the CdSe rod during the ligand exchange process (Figure S17) and absorption by these Au tips have negligible contributions to the MV$^{2+}$ photo-reduction.
Fig. S1.
TEM images of CdSe and CdSe-Au NRs. TEM images of as-prepared a) CdSe NRs (582 nm) and b) CdSe-Au NRs. HAADF STEM (c), EDX map (d), and HRTEM (e) images of CdSe-Au NRs.
Fig. S2
TEM images of CdSe QDs and CdSe QD-Au dimers. TEM images of as-prepared a) CdSe QDs and b) CdSe QD-Au dimers. The inset of b) is an amplified image showing the dimer structure. c) UV-vis absorption spectra of CdSe QDs (black solid line) and CdSe NRs (red dashed line) with similar confinement energy.
Fig. S3
TEM images of CdSe-Au NRs with the initial CdSe NRs having first excitonic peaks at 555 nm (a) and 605 nm (b), respectively.
**Fig. S4**

Transient Absorption (TA) spectra and kinetics of NR and NR-acceptor complexes. 

a) TA spectra at indicated delays after 400 nm excitation. b) TA kinetics of exciton bleach (XB) at ~580 nm (red dashed line) and its multi-exponential fit (black solid line) of CdSe NRs. c) TA spectra of CdSe NR-BQ complexes at indicated delay times after 400 nm excitation. The inset is a scheme of the complex. d) Comparison of TA kinetics of XB (red triangles) and intraband IR transition (black dashed line) in CdSe NR-BQ complexes. Also shown for comparison are kinetics of XB (blue circles) and intraband IR transition (gray solid line) in free CdSe NRs.
Fig. S5

TA spectra and kinetics of CdSe-Au NRs at 400 nm excitation. a) TA spectra of CdSe-Au NRs at indicated delays, showing exciton absorption (XA, ~600 nm) and exciton bleach (XB, ~575 nm). b) Comparison of XB kinetics in CdSe-Au NRs (red triangles) and free CdSe NRs (gray circles). The signals have been scaled to correspond to the same number of absorbed photons by the CdSe rod. c) Kinetics of XA (red dashed line) and XB (green dashed line, inverted) after subtraction of the broad absorption signal (averaged from 670 nm to 700 nm). The black solid line is a multi-exponential fit to the kinetics.
Fig. S6

TA spectra of CdSe QD-Au dimers at indicated delays after a) 400 nm and b) 800 nm excitations. c) Kinetics probed at 670-700 nm for CdSe QD-Au dimmers and CdSe-Au NRs under both 400 nm and 800 nm excitations. The black solid line is a multi-exponential fit to these kinetics.
Fig. S7
TA spectra of a mixture of isolated CdSe NRs and Au nanoparticles at indicated delays after 800 nm excitation.
Fig. S8

TA spectra and kinetics of CdSe-Au NRs after 800 nm excitation. a) TA spectra at indicated delay times after subtraction of the broad absorption feature of the Au tip. b) Kinetics of XB recovery (after subtraction of Au tip contribution) and mid-IR decay kinetics.
Electron intraband signal formation kinetics. a) Formation and decay kinetics of intraband absorption signals (probed at 3000 nm) in CdSe-Au (blue circles) within 1 ps and its fit (black solid line). Also shown for comparison is the formation kinetics of intraband absorption signals in Cd$_3$P$_2$ QDs (red triangles) under band edge resonant excitation, from which the IRF and time zero are determined. b) The fitting results with different $\tau_f$ of 10, 20, 30, 40, 60, 80, and 100 fs (with fixed IRF and time-zero). CdSe-Au data agrees best with $\tau_f$ of $20 \pm 10$ fs. c) Formation kinetics of mid-IR signals in CdSe-Au (red triangles) and CdS-Au NRs (blue circles). The black solid lines are fits to them, with corresponding formation time constants labeled.
Fig. S10
Quantification of plasmon induced charge separation quantum yields. a) Absorption spectra of Cd₃P₂ (red solid line) and PbS (black solid line) QDs. b) TA signal sizes at 3000 nm of Cd₃P₂ QDs as a function of excitation powers at 0.2-0.4 ps after excitation for 800 nm (red circles) and 400 nm (blue squares) excitations and their linear fits (black solid lines ). d) TA signal sizes at 3000 nm at 0.2-0.4 ps as a function of excitation powers for CdSe-Au NRs at 800 nm excitation (red circles) and CdSe NRs at 400 nm excitation (blue squares) and their linear fits (black solid lines ).
Scheme S1.
Schematics of energy and momentum requirements in hot electron transfer. a) Excitation of an electron into an energy level higher than the barrier ($E_b$) between Fermi level of metal and conduction band edge of semiconductor leads to hot electron transfer into semiconductor. b) Illustration of momentum conservation in hot electron transfer process using “escaping cone” in momentum space. Z direction is perpendicular to the semiconductor/metal interface. Therefore, the projection of an electron momentum on the z axis has to be larger than an onset momentum ($P_{on}$) which is determined by $E_b$. 
Fig. S11
Absorption spectra fitting for CdSe-Au. a) The absorption spectrum of isolated Au nanoparticles (gray circles) and its fit (black solid line) to a sum of a Lorentzian surface plasmon band (red dashed line) and an interband transition (blue dashed line). The absorption spectrum of b) isolated CdSe QDs and c) isolated CdSe NRs (gray circles) and their fits (black solid line) to the sum of four Gaussian excitonic bands (red dashed lines). d) The absorption spectrum of CdSe QD-Au dimers (gray circles) and its fit (black solid line) to the sum of a broadened Lorentzian surface plasmon band of Au (red dashed line), an interband transition of Au (blue dashed line), and four broadened Gaussian excitonic bands of CdSe (green dashed line). e) The absorption spectrum of CdSe-Au NRs (gray circles) and its fit (black solid line) to the sum of a broadened Lorentzian surface plasmon band of Au (red dashed line), an interband transition of Au (blue dashed line), and four broadened Gaussian excitonic bands of CdSe region near the Au tip (green dashed line), and four unperturbed Gaussian excitonic bands of CdSe region near the NR center (purple dashed line).
Fig. S12
Calculated transient absorption Anisotropy of CdSe NRs. a) A scheme of the laboratory coordinates (x, y, z) and the rod coordinates (a, b, c). Eulerian angles (θ, φ, ψ) are also labeled.
b) 2-D contour plot of the calculated anisotropy as a function of both p_c and q_c.
Fig. S13
Transient absorption anisotropy of Mid IR signals of CdSe NRs measured at 590 excitation. TA kinetics measured with parallel (red solid line) and perpendicular (blue dashed line) pump/probe polarizations. Inset: calculated anisotropy values.
Fig. S14
TEM images and absorption spectra of CdS-Au NRs. a) UV-vis absorption spectra of CdS and CdS-Au NRs. b) A representative TEM image of the CdS-Au NRs.
Fig. S15
TA spectra and kinetics of CdS NRs at 400 nm excitation. A) TA spectra at indicated delay times. b) Kinetics of XB (~450 nm) signal measured with parallel (HH, red solid line) and perpendicular (HV, green dashed line) pump/probe polarizations. Inset: calculated anisotropy values.
Fig. S16

TA spectra and kinetics of CdS-Au. A) TA spectra of a mixture of isolated CdS NRs and Au nanoparticles at indicated delays after 650 nm excitation, showing only signals due to direct excitation of Au. b) TA spectra CdS-Au NRs at indicated delays after 650 nm excitation, showing both signal due to Au plasmon band and bleach of CdS XB at 450 nm (indicated by red arrow). The sample absorbance at 650 nm and excitation power were the same for a and b. c) Kinetics of XB (red solid line) in CdS-Au obtained by subtracting the Au signal contribution at ~450 nm. The subtracted XB kinetics agrees with intraband kinetics measured at 3000 nm (green dashed line, inverted for comparison). d) XB kinetics in CdS-Au measured with parallel (HH, red solid line) and perpendicular (HV, blue dashed line) polarization. Inset: calculated anisotropy values.
Fig. S17
TEM images of MUA capped CdSe-Au NRs. Isolated Au nanoparticles are indicated by the red dashed circles.
QYs for plasmon induced steady state photoreduction of MV$^{2+}$. a) A scheme of the plasmon-induced photocatalysis experiment. A cw light is used to excite the Au tip in CdSe-Au NRs and the plasmon-induced reduction of MV$^{2+}$ into MV$^+$ radicals is monitored through static absorption spectral change. b) Difference absorption spectra of CdSe-Au NRs at indicated illumination times showing accumulation of MV$^+$ radicals. c) MV$^+$ radical concentration as a function of illumination time for CdSe-Au NRs (purple triangles), CdSe NRs (red circles), Au nanoparticles (blue squares), and blank sample (no particles, green diamonds). The black solid lines are linear fits to extract the initial rate of MV$^+$ radical generation.
Table S1.
XB recovery kinetics in free CdSe NRs and NR-BQ complexes

<table>
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<tr>
<th></th>
<th>$\tau_f$/ps</th>
<th>$\tau_1$/ns ($a_1$)</th>
<th>$\tau_2$/ns ($a_2$)</th>
<th>$\tau_3$/ns ($a_3$)</th>
<th>$\tau_{1/2}$/ns</th>
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<td>NR</td>
<td>0.31±0.15</td>
<td>0.227±0.006</td>
<td>11.0±0.2</td>
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<td></td>
<td></td>
<td>(22.9±0.2%)</td>
<td>(42.1±0.9%)</td>
<td>(35.0±0.4%)</td>
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<td>NR-BQ</td>
<td>0.31±0.15</td>
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<td></td>
<td></td>
<td>(23.7±0.4%)</td>
<td>(32.1±0.5%)</td>
<td>(44.2±1.5%)</td>
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**Table S2.**
Charge separation and recombination in CdSe-Au NRs after 400 nm excitation

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<th>$\tau_1$/fs</th>
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<td>CdSe-Au NRs</td>
<td>46±20</td>
<td>0.85±0.13</td>
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<td>(72.3±0.9%)</td>
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Table S3.
Fitting parameters for the broad-band TA absorption in CdSe QD-Au dimers

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<td>CdSe QD-Au</td>
<td>118±25</td>
<td>1.40±0.15 (73.6±1.1%)</td>
<td>20.3±0.7 (19.4±0.4%)</td>
<td>901±60 (7.0±0.1%)</td>
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Table S4.

Fitting parameters for plasmon-induced charge separation and recombination in 800 nm excited CdSe-Au NRs

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<td>CdSe-Au NRs</td>
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<td>(90.3±1.5%)</td>
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Table S5.
Fitting parameters for CdSe-Au Absorption spectra

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<th>CdSe -Au Dimers</th>
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