Review article

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Prospects and applications of plasmon-exciton interactions in the near-field regime

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Abstract: Plasmonics is a rapidly developing field at the boundary of fundamental sciences and device engineering, which exploits the ability of metal nanostructures to concentrate electromagnetic radiation. The principal challenge lies in achieving an efficient conversion of the plasmon-concentrated field into some form of useful energy. To date, a substantial progress has been made within the scientific community in identifying the major pathways of the plasmon energy conversion. Strategies based on the hot electron injection and the near-field energy transfer have already shown promise in a number of proof-of-principle plasmonic architectures. Nevertheless, there are several fundamental questions that need to be addressed in the future to facilitate the transition of plasmonics to a variety of applications in both light amplification and optical detection. Of particular interest is a plasmon-induced resonance energy transfer (PIRET) process that couples the plasmon evanescent field to a semiconductor absorber via dipole-dipole interaction. This relatively unexplored mechanism has emerged as a promising light conversion strategy in the areas of photovoltaics and photocatalysis and represents the main focus of the present minireview. Along these lines, we highlight the key advances in this area and review some of the challenges associated with applications of the PIRET mechanism in nanostructured systems.

Keywords: PIRET; plasmon; plasmon-exciton; plasmonics.

1 Introduction

Plasmon resonances near metal surfaces allow concentrating the incident radiation far beyond the limits of the geometrical optics [1, 2]. The local enhancement of the electromagnetic (EM) field is particularly prominent in the case of noble metal colloids, the optical extinction coefficients of which surpass those of similar-sized semiconductor or organic counterparts by several orders of magnitude (see Figure 1A) [3–8, 10, 11]. The benefits of superior extinction characteristics of metals can be used through several strategies that couple the EM field of surface plasmons to semiconductor or molecular absorbers [12, 13]. The ensuing near-field interaction can lead to the transfer of metal energy to the semiconductor material in the form of either hot electrons or excitons. Both mechanisms have potential implications as a strategy for increasing the optical absorption in photovoltaic (PV) and photocatalytic devices [12–17] or enhancing the photoluminescence (PL) intensity of metal-coupled fluorophores [18–20]. Other promising applications of plasmon energy conversion include surface-enhanced Raman scattering (SERS), where plasmons enable a nearly single-molecule detection level [21], or SP lasers, where non-localized plasmons (surface plasmon polaritons) allow a more compact storage of the optical energy deployable for laser miniaturization [22]. To date, however, the observed experimental benefits of the plasmonic energy conversion are still below their predicted potential. In PV devices, for example, the plasmon enhancement of the optical absorption is often limited to the effect of geometric light scattering [23], whereas in plasmon-enhanced fluorescence applications the enhancement mechanism is subject to the competition with coexisting quenching processes [24]. The experimental gap between the predicted and observed effects of plasmonics is believed to arise from the complex nature of plasmon-exciton interactions [25]. Even in the weak coupling regime, factors such as a random orientation of a semiconductor dipole or a rapid decoherence of collective electron oscillations can readily obscure the underlying enhancement mechanisms.

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Figure 1: The excitation and decay of localized plasmons in metal nanoparticles.

(A) Extinction cross-sections of common nanoscale sensitizers divided by the NP volume. The comparison highlights superior light-harvesting characteristics of metal NPs relative to semiconductor QDs and organic polymers (P3HT) [3–8]. Adapted with permission from Ref. [9]. Copyright 2014 American Chemical Society. (B) Timescale of the surface plasmon evolution in noble metal NPs, including stages of plasmon dephasing and light scattering (10–20 fs), hot carrier redistribution (200 fs–1 ps) via electron-electron decay, and electron-phonon cooling (1–10 ps).

The energy stored in localized surface plasmons of metal nanoparticles (NPs) can be transferred to a semiconductor absorber via several coupling mechanisms. These are generally categorized as a far-field scattering [26–29], a near-field energy transfer [30, 31], and a hot electron transfer [32–34] (see Figure 1B). The far-field scattering of EM radiation represents a geometrical reflection of light by metal NPs. Due to its diffusive action, it can be used to increase the optical path inside the semiconductor film more efficiently than a back reflector. For instance, in comparison to planar mirrors, where the absorption enhancement due to reflection F is limited to 2, an optimized photonic arrangement of metal NPs can lead to a $F=4n^2$ enhancement in the film absorption (where n is the refractive index of the film) [35], making this strategy more robust than a reflective coating on the back electrode (Figure 2). The far-field scattering strategy has been therefore proven fairly successful in plasmonic PV schemes and currently represents one of the most practical designs for converting the plasmon energy into the device photocurrent [37, 38].

The plasmon energy conversion mediated by hot electrons [39–41] relies on the photoinduced transfer of free high-energy electrons that emerge as a result of plasmon dephasing. If an electron's energy exceeds the metal-semiconductor Schottky barrier, it could be transferred to the conduction band of a nearby semiconductor and quickly thermalized to its band edge. The same potential barrier will then prevent conduction-band electrons in a semiconductor from transferring back into the metal. Harvesting hot electrons of metal NPs toward potential applications in PV and photocatalysis has been the subject of several recent reviews [24, 42, 43]. One potential drawback of the plasmon-induced electron transfer concerns a relatively

Figure 2: Comparison of absorption enhancement strategies for PV devices.

The theoretical enhancement factor F is equal to 2 for a plan mirror, $4n^2$ for an optimized plasmonic array based on far-field scattering (geometrical optics limit), and is the greatest for the case of strongly confined EM fields of localized plasmons (near-field) [36], where $F < 60n^2$. The inset graph shows the ratio of scattering (far-field) to absorption (near-field) cross-section in Au NPs versus the NP size.

Figure 3: Comparison between far-field (scatter), near-field (PIRET), and hot electron-based plasmon energy conversion processes through theoretical estimates of the relative enhancement in semiconductor excitations.

(A) Relative enhancement versus the plasmon's dephasing stage and the semiconductor bandgap with the plasmon energy fixed at 1.8 eV. (B) Cut-out of the 3D plot in (A) at a semiconductor bandgap of 1.8 eV. The semiconductor dephasing time is shown for comparison. The dashed line in (A) shows the approximate position of the cut in (B). Adapted from Ref. [47] with permission from the PCCP Owner Societies.

small fraction of hot electrons, which can overcome the Schottky barrier. Theoretically, it is estimated that no more than 1% of the surface plasmon energy can be harvested this way [24].

The near-field resonant energy transfer from a metal NP to a semiconductor absorber represents another possibility for extracting the photoinduced energy of localized surface plasmons. In this case, the transfer of excitations occurs before plasmon dephasing, making a significant fraction of the metal localized energy available for a transfer to a semiconductor. The strong distance dependence of the energy exchange in the near field was initially evidenced through the use of variable thickness oxide spacers in plasmon-semiconductor assemblies [44, 45]. This process was later attributed to the coupling of electrical dipoles in metal and semiconductor components analogous to the Förster resonance energy transfer (FRET) in semiconductor systems [46]. The underlying energy exchange, referred to as the plasmon-induced resonance energy transfer (PIRET) mechanism, was different from FRET in a sense that it represented a coherent energy exchange with both metal and semiconductor components capable of transferring the photoinduced energy to their respective energy partners. Employing PIRET mechanism for light energy conversion in light-harvesting or light-emitting devices represents a fast emerging field of plasmonics, which offers the possibility of surpassing the $4n^2$ geometrical optic limit of absorption/emission enhancement (see Figures 2 and 3) [36, 48]. Along these lines, we will highlight the basic principles of PIRET in metal-semiconductor systems and describe how PIRET is currently used by PV and light-emitting schemes. In addition, we will highlight some recent advances in the development of spectroscopic tools for quantifying the

plasmon-exciton energy transfer quantum efficiency in plasmonic systems and provide an outlook of the emerging concepts for the application of PIRET processes in light conversion applications.

2 Surface plasmon relaxation

Free electron oscillations in metal NPs remain coherent only for as long as they are coupled to the incident radiation, which causes surface plasmons to dephase in less than 20 fs. During this stage, the plasmon electric dipole moment decreases due to Landau damping [49] and the evanescent EM field surrounding a metal NP subsides. Once electron coherence vanishes, the excited-state distribution of an NP evolves from a resonant behavior to that of independent electron-hole pairs in bulk metals, which are described by a high-temperature Fermi distribution. The resulting hot carrier population subsequently decays back to the Fermi level through electron-electron interactions in 0.1–1.0 ps followed by the thermal decay of secondary electron-hole excitations via electron-phonon interactions in 1–10 ps [50–52] (Figure 1B). At this stage, most of the plasmon energy has transformed into heat. The characteristic time constants associated with different stages of the plasmon evolution depend on the dielectric environment, size, and shape of a metal NP. Furthermore, the proportions of the plasmon energy that are being released either optically through far-field scattering or thermally via near-field relaxation are functions of NP size (see Figure 2, inset). Whereas the plasmon-induced heat generation has potential applications in the biomedical fields, such as photothermal therapy for cancer treatment or targeted drug delivery [53, 54], thermal relaxation

of plasmons is generally not desirable for PV or photocatalytic applications.

3 PIRET

PIRET between a metal and a semiconductor is mediated by the evanescent EM field of a metal NP. This type of energy exchange can be described within the FRET framework as the interaction of metal and semiconductor electric dipole moments. In contrast to FRET, however, the PIRET process is considered to be coherent. Namely, the thermal relaxation of donor molecules that give rise to Stokes shifts in the FRET process is not observed during PIRET, such that the latter type of energy transfer proceeds without excitation energy loss [46]. This leads to an important difference between FRET, where the acceptor energy cannot be transferred back to a donor, and PIRET, where the energy transferred from a metal surface to a semiconductor is coherent and thus could proceed in either direction. The ability to harvest the plasmon energy through PIRET therefore requires a detailed understanding of the factors that determine the direction and the rate of the coherent energy transfer between metal and semiconductor NPs.

In deriving the rate equation for the PIRET process, we assume that, before plasmon dephasing, its energy is stored in the form of the electric field polarization. The concentration of photoinduced energy at this stage can be several orders of magnitude larger than the incident EM field. Such an enhancement of the near-field surrounding a metal NP is routinely employed by SERS applications [55], where vibrational features of molecules near metal surfaces are enhanced by more than 10^6 . In the case of the PIRET process, such near-field enhancement of the semiconductor (fluorophore) absorption is expected to be linear with the field enhancement ($\sim 10^3$). The increase in the exciton population of the semiconductor moiety associated with the PIRET process, ΔN_{PIRET} , can be estimated using the dipole-dipole approximation for two NPs as a function of the metal-semiconductor distance [46, 56]:

$$\Delta N_{\text{PIRET}} = 1 + E_{\text{PIRET}} = 1 + \frac{\alpha_{\text{SP}}(\omega)}{\alpha_{\text{semi}}(\omega)} \left(\frac{1}{1 + (R/R_0^{\text{PIRET}})^n} \right) \quad (1)$$

where $n=4-6$ depending on whether the dipoles are considered as surface or point like, α is the absorbance coefficient, E_{PIRET} is the exciton transfer efficiency, and R_0 is the donor-acceptor distance corresponding to a 50% efficiency. Notably, radius R_0 is a function of the donor

and acceptor dipole frequencies, orientation, dielectric constant, and semiconductor absorption cross-section. A more rigorous description of the coherent energy transfer formalism for the PIRET process is given in Ref. [46], which employs a frequency-dependent absorption distribution of R_0 in Eq. (1). To this end, both a plasmon donor and a semiconductor acceptor were approximated with two-level transitions, resulting in a coupled four-level system [9]. The plasmon was then treated statistically in the density matrix, whereas the semiconductor was represented by the sum of two-level interband transitions weighted by the joint density of states [57].

4 Application of PIRET in PV

The utilization of PIRET in PV devices has received an increased amount of attention in recent years [58–61]. One of the first advances in introducing this mechanism to PV devices was realized by incorporating Au NPs within organic polymer solar cells [9]. To facilitate plasmon-exciton coupling in the near-field regime, organically coated Au NPs were introduced directly into the polymer blend. With the relatively small size of Au nanostructures (~ 20 nm), far-field scattering effects were assumed to be negligible. Furthermore, the possibility of hot electron contribution into photocurrent was also considered to be minimal due to the presence of polyethylene glycol change-insulating coating of metal surfaces. As shown in Figure 4, the presence of metallic NPs caused an apparent enhancement in the absorption of the polymer layer by up to 100% at the resonance, which led to a corresponding 32% increase in the device power conversion efficiency (PCE; see Figure 4A). Another pioneering work [59] has reported similar results for bulk-heterojunction polymer solar cells doped with 20 nm Au NPs. In this case, Au nanostructures were fixed onto indium tin oxide-coated glass, allowing the near field to affect a portion of the absorber layer. Owing to long diffusion lengths of excitons in polymer films, the photoinduced energy was assumed to be efficiently transferred away from a metal layer toward the organic heterojunction, which was corroborated by a 14% increase in the PCE of Au-doped films. Interestingly, the employment of 75 nm Au nanocubes within the same polymer heterojunction has resulted in a 12% drop in the PCE compared to the control sample.

The effect of plasmon-induced energy transfer on the PCE of PV devices has also been investigated in a quantum dot (QD) solar cell device architecture [60]. To this end, CdS-coated Au NPs were mixed with PbS/CdS core/shell semiconductor nanocrystals (NCs) in solution and

Figure 4: The plasmon-induced energy transfer in photovoltaic devices.

(A) Current-voltage characteristics of the representative polymer solar cell containing different concentrations of 20 nm Au NPs. (B) Experimental and theoretical (inset) absorbance enhancement factors of the active polymer layer containing different concentrations of Au NPs. (C) Theoretical near-field distribution around an Au NP in the active layer. Adapted from Ref. [58] with permission from the Royal Society of Chemistry.

Figure 5: Current-voltage characteristics of plasmonic (Au, PbS) and control (PbS-only) QD solar cells featuring organic interlinking (A) and matrix encapsulation (B) of Au and PbS NP blends.

The low photocurrent of the organic-linked devices in (A) was attributed to charge scattering on Au, which was significantly suppressed in matrix-encapsulated NP films. The relatively low photovoltage of matrix-encapsulated solar cells was believed to be caused by Au-induced Fermi-level pinning. (C) Scanning electron microscopy image of a matrix-encapsulated (PbS, Au) film. (D) Schematic of the depleted heterojunction PV cell doped with Au NPs. Adapted with permission from Ref. [60]. Copyright 2014 American Chemical Society.

subsequently processed onto TiO₂ to form a depleted heterojunction (see Figure 5D). The thermal impact of residual heating in Au NPs was mitigated through the use of an all-inorganic film design featuring a crystalline matrix

encapsulating an array of Au and PbS NPs [62–64]. In this geometry, the far-field scattering of surface plasmons was negligible due to the relatively small size of Au nanostructures (<10 nm). The overall benefit of the near-field

Figure 6: Plasmon enhanced photocurrent in dye-sensitized solar cells.

(A) Illustration of the two mechanisms contributing to the plasmon energy conversion in metal@TiO₂ core/shell NPs. (B) Characteristic transmission electron microscopy (TEM) image of an Ag@SiO₂ NP. (C) In the case of Ag@TiO₂ colloids, contact and spectral overlap exist between metal and semiconductor, such that both PIRET and hot electron injection processes are mutually detected. (D) Addition of an SiO₂ barrier to Ag@TiO₂ eliminates hot electron injection. (E) Switching the metal core to Au eliminates spectral overlap and PIRET. (F) Inserting a SiO₂ barrier in Au@TiO₂ eliminates both hot electron injection and PIRET despite strong light absorption by the plasmonic Au. Adapted with permission from Ref. [65]. Copyright 2015 American Chemical Society.

absorption enhancement strategy was evidenced through a moderate improvement of the solar cell efficiency (Figure 5B). For instance, the incorporation of 0.3% of Au NPs (by particle volume) has enhanced the average PCE from 4.0% to 4.2%, with the best-performing device exhibiting 4.5% of PCE (Figure 5B). The increased short circuit current (a gain of $41 \pm 3\%$) was the primary factor contributing to the enhanced PCE, whose effect was somewhat reduced owing to a small drop in the open circuit voltage.

Another study has explored the near-field plasmonic enhancement of the photocurrent generation within the framework of dye-sensitized solar cells (DSSC) [61]. In this work, silica-coated nanocubes (Au@SiO₂ nanocubes) were embedded into the photoanodes of DSSCs resulting in a PCE of 7.8% relative to 5.8% for the reference (TiO₂ only) device. The 34% gain in the DSSC performance was attributed to the near-field effect, which was supported by finite-difference time-domain simulations. Ultimately, the study was able to conclude that high-intensity fields at hot spots of nanocube structures increase the plasmonic molecular coupling, amplifying both exciton and carrier generation in a semiconductor.

Transient absorption spectroscopy was also employed as a strategy for differentiating between plasmon-induced charge and energy transfer mechanisms in metal@TiO₂ core/shell NPs [65]. To this end, an SiO₂ intermediate layer was introduced at the interface of metal and TiO₂ domains using a metal@SiO₂@TiO₂ geometry (Figure 6B). It was observed that, for Ag@SiO₂@TiO₂ NPs, the localized surface plasmon resonance of Ag overlapped the absorption band edge of TiO₂, enabling PIRET, whereas the SiO₂ barrier suppressed hot electron transfer (see Figure 6D). For Au@TiO₂, hot electron injection occurred due to the absence of the SiO₂ barrier, but the lack of a spectral overlap between Au and TiO₂ disabled PIRET (Figure 6E). In Ag@TiO₂, both hot electron transfer and PIRET took place (Figure 6C). In Au@SiO₂@TiO₂, there was no enhancement caused by the plasmon resonance for any photoconversion type in TiO₂ despite strong light absorption by Au (Figure 6F). The results of this study clearly demonstrated the existence of different plasmonic enhancement mechanisms in the near-field regime.

In summary, we would like to stress that a plasmonic enhancement of PV characteristics offers a great

opportunity for allowing low-cost thin-film materials to reach single-crystalline performance levels. In this regard, the employment of the PIRET scheme that couples localized surface plasmons to molecular or nanostructured semiconductor absorbers can potentially enable a high-yield photoinduced energy conversion but requires further investigation. The areas of particular interest include the characterization of the ultrafast dynamics of the plasmon-enhanced EM field and the development of strategies for harvesting its localized energy through a coherent coupling of plasmon and exciton electrical dipoles.

5 Application of the plasmon near field in PL enhancement

Early studies of the metal-enhanced fluorescence (MEF) [20, 66–74] have identified the existence of several competing processes that contribute to the energy exchange between a metal NP and a semiconducting fluorophore. In particular, the strong field of metal NPs can enable both forward (PIRET) and backward (FRET) directions of the energy flow. Such bilateral energy exchange makes it difficult to unravel the interplay of fluorescence enhancement (ΔFL_{PIRET}) and quenching (ΔFL_{FRET}) factors into the emission of the metal-anchored fluorophore. Under these conditions, the cumulative effect of both processes can be expressed through the absolute change of the fluorophore emission due to a proximal surface plasmon dipole:

$$\begin{aligned} \Delta FL_{\text{energy transfer}} &= \frac{FL_{\text{plasmon}}}{FL_0} = \Delta FL_{\text{PIRET}} \times \Delta FL_{\text{FRET}} \\ &= (1 + E_{\text{PIRET}}) \times (1 - E_{\text{FRET}}) \\ &= \left(1 + \frac{\alpha_{\text{plasmon}}}{\alpha_{\text{semi}}} \times \frac{1}{1 + (R/R_0^{\text{PIRET}})^n} \right) \\ &\quad \times \left(1 - \frac{1}{1 + (R/R_0^{\text{FRET}})^n} \right) \end{aligned} \quad (2)$$

where $n=4-6$ depending on whether the dipoles are considered as surface or point like, α is the wavelength-dependent absorbance coefficient, and R_0 is the donor-acceptor distance corresponding to a 50% efficiency.

In addition to PIRET and FRET energy transfer mechanisms, the fluorescence of a semiconductor in the vicinity of a metal surface could diminish due to the exothermic transfer of photoinduced charges back to metal. This process is particularly pronounced in systems lacking an insulating spacer or a Schottky barrier at the metal-semiconductor interface. The metal-induced transfer of photoinduced electrons causes a nonradiative dissociation

of semiconductor excitons and therefore leads to fluorescence quenching. If we assume that such backward charge transfer occurs with an average rate of Γ_{PET} , then its effect on the plasmon-induced fluorescence enhancement could be expressed through the corresponding reduction of the fluorophore emission quantum yield (QY) as follows:

$$\Delta FL_{\text{QY}}(\text{PET}) = QY_{\text{PET}} / QY_0 = (\Gamma_{\text{rad}} + \Gamma_{\text{non-rad}}) / (\Gamma_{\text{rad}} + \Gamma_{\text{non-rad}} + \Gamma_{\text{PET}}) \quad (3)$$

where QY_0 represents the QY of an isolated fluorophore.

The modification of the fluorophore radiative rate due to an interaction with surface plasmons represents another potential contribution into the emission changes of metal-anchored molecules. When dyes exhibit a high fluorescence QY, the field-induced modification of the emission rate does not usually produce significant changes in the emission intensity [75]. This is because the time interval associated with a plasmon-induced modification of the semiconductor radiative rate is limited to the plasmon dephasing time, which is relatively short. As the plasmon electrical dipole ceases to exist approximately 10–20 fs after excitation, its stimulated emission contribution into the semiconductor exciton decay vanishes as well. Considering that the spontaneous emission time constant for isolated emitters (e.g. NCs and organic dyes) lies in the picosecond to nanosecond range, the plasmon-induced modification of the total emission intensity would only be significant if its near-field effect increases the overall radiative rate by a factor of a thousand or more. This scenario is only possible for an ideal alignment of the two electric dipoles and precise hot-spot placement of a molecule, which is difficult to control under realistic conditions. However, in the case of weakly emitting molecules, the plasmon-induced rate modification could become a significant factor contributing to the fluorescence enhancement. Indeed, for these dyes, the emission QY [$QY = \Gamma_{\text{rad}} / (\Gamma_{\text{rad}} + \Gamma_{\text{nonrad}})$] becomes particularly sensitive to changes of the radiative rate and has been shown to result in up to ninefold fluorescence enhancement in the presence of the plasmon near field [20]. The effect of plasmon stimulated emission (SE) on the fluorescence enhancement could be expressed through the corresponding increase in the emission QY:

$$\Delta FL_{\text{QY}}(\text{SE}) = QY_{\text{SE}} / QY_0 = \frac{\Gamma_{\text{SE}}(t)}{\Gamma_{\text{rad}}} \times \frac{\Gamma_{\text{rad}} + \Gamma_{\text{non-rad}}}{\Gamma_{\text{SE}}(t) + \Gamma_{\text{non-rad}}} \quad (4)$$

where QY_0 is the QY of isolated fluorophores and $\Gamma_{\text{SE}}(t)$ is a time-dependent radiative rate enhanced by the SE in the presence of the plasmon near-field, which returns to Γ_{rad} after plasmon dephasing.

Figure 7: Metal-enhanced fluorescence in assemblies of Au nanorods and dye molecules.

(A) Calculated near-field intensity map for an Au nanorod ($\lambda_{\text{plasmon}} = 629$ nm) measuring 47 nm in length and 25 nm in width. The excitation wavelength was set to 633 nm. (B) Fluorescence enhancement factors (ξ) versus the spectral position of the surface plasmon resonance. Excitation wavelengths were 594 nm (blue) and 633 nm (red). The distance between the molecule and the nanorod's tip was 5 nm. (C) Simplified scheme of the experiment. (D) Typical one-photon PL image of individual Au nanorods. The excitation was at $\lambda = 633$ nm. Reprinted with permission from Ref. [20]. Copyright 2014 American Chemical Society.

Many of the literature reports on plasmon-enhanced fluorescence have actually demonstrated quenching of the emission, $\Delta\text{FL}_{\text{plasmon}} < 1$, particularly when the size of a metal NP was less than 20 nm [76–80]. In this size regime, quenching can occur via exciton-to-plasmon energy transfer (FRET), according to Eq. (2), or through a photoinduced charge transfer back to the metal (Eq. 3). Both processes could potentially overwhelm the effect of PIRET-based enhancement, resulting in the overall fluorescence quenching. This scenario was illustrated in a recent work [81], where silica-coated Au NPs were used to modify the emission intensity of surface-anchored dyes. By tuning the thickness of the silica shell, the team was able to study the effect of Au-dye distance on the efficiency of the quenching process. It was observed that the fluorescence of four different dyes was quenched in a distance-dependent manner that agreed with predictions based on the dipole-dipole plasmon-exciton energy exchange model (FRET process). In another work [75], the quenching of dye emission due to

near-field interactions with a proximal Au NP was observed to follow $1/[1 + (d/d_0)^4]$ scaling, where d_0 was the Förster radius. By varying the Au-dye separation using duplex DNA spacers with specific chemical modifications, the team was able to show that the FRET distance dependence was best described as a result of coupling of the surface and point dipoles, which gave a characteristic fourth power dependence. From an application standpoint, such quenching of fluorescence near metal surfaces has been fairly successful in biosensing applications [77, 81], where the emission reduction was used to indicate docking of an analyte to a metal-anchored receptor.

Experimental observations of plasmon-enhanced fluorescence ($\Delta\text{FL}_{\text{plasmon}} > 1$) have been almost exclusively limited to systems featuring large-diameter metal NPs often exceeding 30 nm in size [20, 66, 82–85]. The corresponding fluorescence enhancement factors appeared to be particularly large in the case of metal nanorods, where slower dephasing surface plasmons [86–88] exhibited a greater

probability of interacting with semiconductor excitons through the PIRET mechanism. In the case of weak emitters, the fluorescence enhancement arising from the plasmon-exciton energy transfer was augmented even further by the plasmon-induced modification of the exciton radiative rate. The latter process was particularly relevant in the case of near-infrared (NIR) dyes exhibiting a generally low emission QY. An example of plasmon-induced fluorescence enhancement due to rate modification is illustrated in Ref. [83], where the emission of the LS288 NIR dye was increased up to three orders of magnitude. The largest enhancement factor was observed when a dye was separated from the surface of Au nanorods by 4 nm using the polyelectrolyte dielectric spacer. Increasing the dye-nanorod spacing resulted in the decay of plasmon-enhanced fluorescence in a manner that closely followed the decay of the electric field intensity from the surface of Au nanostructures, suggesting both PIRET and rate modification enhancement mechanisms.

In another example of MEF, a three-order magnitude fluorescence gain was reported for a dye-nanorod system [20] (see Figure 7). This study was able to distinguish between process-specific enhancement factors corresponding to the plasmon-induced energy transfer (ΔFL_{PIRET}) and the rate increase (ΔFL_{QY}), such that, for the observed total enhancement of $\Delta FL = 1100$, the growth of the exciton populations due to PIRET was estimated to be $\Delta FL_{PIRET} \sim 130$ with the rate modification contributing a $\Delta FL_{QY} \sim 9$ -fold emission gain. An interplay of PIRET-based and rate modification-based enhancements (ΔFL_{PIRET} and ΔFL_{SE}) has also been investigated in the work of Ayala-Orozco et al. [89], where several types of dyes were coupled to Au nanomaterials.

Taken all together, the plasmon-induced enhancement of the fluorophore emission could be expressed as a product of four factors (see Figure 8), which correspond to processes of (1) plasmon-exciton energy transfer via PIRET ($\Delta FL_{PIRET} > 1$), (2) exciton-to-plasmon fluorescence quenching via FRET ($\Delta FL_{FRET} < 1$), (3) enhancement of dye QY due to plasmon-induced rate modification (for weakly emitting dyes; $\Delta FL_{QY} > 1$), and (4) reduction in fluorescence QY due to the photoinduced charge transfer back to metal ($\Delta FL_{PET} < 1$). Accordingly, the expression for the plasmon-enhanced fluorescence can be given as

$$\Delta FL_{tot} = \frac{FL_{plasmon}}{FL_0} = \Delta FL_{PIRET} \times \Delta FL_{FRET} \times (\Delta FL_{QY} \times \Delta FL_{PET})$$

$$= \left(1 + \frac{\alpha_{met}}{\alpha_{semi}} \times \frac{1}{1 + (R/R_0^{PIRET})^n} \right) \times \left(1 - \frac{1}{1 + (R/R_0^{FRET})^n} \right)$$

$$\times \frac{\Gamma_{SE}(t)(\Gamma_{rad} + \Gamma_{non-rad})}{\Gamma_{rad}(\Gamma_{SE}(t) + \Gamma_{non-rad} + \Gamma_{PET})} \quad (5)$$

Figure 8: Diagram illustrating possible fluorescence enhancement and quenching mechanisms in a metal-semiconductor system. The near-field energy exchange between electrical dipoles of the plasmon and semiconductor permits both forward (PIRET) and backward (FRET) direction of the energy transfer. The fluorescence of the semiconductor dye is also affected by plasmon-induced changes in the fluorescence QY. These include both the QY enhancement due to the plasmon-induced increase in the radiative decay rate Γ_{SE} (SE) and the QY reduction due to the backward transfer of photoinduced charges to metal (Γ_{PET}).

where $n = 4-6$ depending on whether metal and semiconductor dipoles are considered to be surface or point like, α is the wavelength-dependent absorbance coefficient, R_0 is the donor-acceptor distance corresponding to a 50% efficiency, $\Gamma_{SE}(t)$ is the time-dependent radiative rate enhancement by the SE in the presence of the plasmon near-field, and Γ_{PET} is the rate of the photoinduced backward charge transfer from semiconductor to metal.

6 Application of the plasmon near-field enhancement in catalysis

The employment of surface plasmon resonances in catalytic reactions [90–94] has been explored through several different schemes. The most straightforward approach relied on the employment of far-field scattering by metal NPs toward increasing the optical extinction of photoelectrochemical electrodes [94, 95]. The plasmon near-field regime has also been explored through the utilization of both electron and energy transfer mechanisms in catalytic reactions. For instance, the transfer of hot electrons to a semiconductor has been demonstrated to reduce molecules or to create high-energy carriers in the external electrodes that were capable of catalyzing chemical reactions [96–99]. Similarly, the transfer of the plasmon energy by the PIRET process was shown to increase the

Figure 9: Schematic illustration of the plasmon-enhanced CO oxidation catalysis using Ag@SiO₂/Pt core/shell/shell NPs. The optimal performance is observed in the intermediate Ag size regime (25–50 nm) associated with the suppressed far-field scattering and enhanced near-field energy transfer (PIRET). Adapted with permission from Ref. [60]. Copyright 2017 American Chemical Society.

exciton population in a semiconductor component, thus contributing to its catalytic activity [89, 100–103].

In the case of PIRET, photocatalytic enhancement is expected when transferred excitons dissociate into energized electrons and holes (see Figure 9). These charges carry a portion of the plasmon photoinduced energy and can potentially contribute to reductive and oxidative photocatalytic processes, respectively. Conversely, the direct excitation of the semiconductor component can result

in the exciton loss due to the proximity of a metal NP. As mentioned above, the FRET process can remove an exciton from a semiconductor before it dissociates. Due to the interplay of forward and backward energy transfer mechanisms, the corresponding plasmon effect on the photocatalytic activity of semiconductors has varied between negligible [90] and clearly detectable [104].

Cushing et al. [104] have shown that the generation of electron-hole pairs in a semiconductor via the PIRET process can enhance the visible-light photocatalytic activity compared to the semiconductor alone (see Figure 10). This was achieved using an Au@SiO₂@Cu₂O core/shell/shell NP geometry optimized for the photoinduced energy transfer from an Au to a Cu₂O domain. The intermediate shell of SiO₂ was introduced as a barrier to photoinduced charges designed to suppress the electron transfer processes between the Au and Cu₂O components. Furthermore, the size of the plasmonic core in metal@SiO₂@Cu₂O nanostructures was sufficiently small ($d \approx 20$ nm) to suppress carrier generation due to far-field scattering [105]. The resulting photocatalytic activity, measured through the photodegradation of methyl orange, was shown to increase in the following order: Au < Cu₂O < Au@Cu₂O < Au@SiO₂@Cu₂O.

A nonmonotonic dependence of the plasmon photocatalytic efficiency on the metal particle size was observed in a recent study employing core@shell/satellite (Ag@SiO₂/Pt) antenna (Ag)-reactor (Pt) complexes (Figure 9)

Figure 10: Plasmon-enhanced photocatalytic activity of Cu₂O.

(A) Discrete dipole approximation simulation of the local EM field induced by the Au plasmonic core and extending into the surrounding Cu₂O shell for input radiation along the x-axis, with (B) cross-sectional slices showing the EM field as a function of distance from the center of the Au core. (C) High-resolution TEM image of the Au@SiO₂@Cu₂O interface regions. Adapted with permission from Ref. [104]. Copyright 2012 American Chemical Society.

[106]. By varying the diameter of Ag NPs in photocatalytic CO oxidation reactions, the team observed a detectable enhancement of the photocatalytic activity only when the Ag NP size was in the intermediate range (25 and 50 nm), with larger or smaller species yielding no enhancement due to Ag plasmons. Such resonant behavior was explained as due to the balance between maximized local field enhancements at the catalytically active Pt surface and minimized collective scattering of photons out of the catalyst bed by the complexes. In particular, the study concluded that the near-field enhancement at the Pt-CO interface facilitated direct interfacial electronic transitions, enabling the plasmon-induced photocatalytic enhancement of up to 40%.

7 Measuring PIRET efficiency

The development of plasmonic applications using the PIRET mechanism is still in its early stages. Although many works have demonstrated the potential feasibility of this phenomenon in PV, solid-state lighting, and photocatalysis, the ultrafast timescale and nanometer-scale range of this interaction made it difficult to control the energy transfer process in a predictive manner. Along these lines, an important challenge lies in the experimental determination of PIRET efficiency independent of other energy exchange processes. Conventional methods often infer the plasmon-exciton transfer efficiency from the corresponding enhancement of the semiconductor emissive, PV, or photocatalytic figures-of-merit, which is aided by tracking distance-dependent signatures of these characteristics. The problem is that the obscure nature of the plasmon enhancement distance dependence, resulting from a complex spatial distribution of the plasmon electric field, does not always allow distinguishing PIRET contribution (ΔFL_{PIRET}) from competing PET and FRET mechanisms.

As an alternative to distance dependence-based methods, PIRET quantum efficiency can be measured directly using a recently developed sample-transmitted excitation PL (STEP) spectroscopy [107]. This method was originally designed for measuring the energy transfer efficiency in systems with nonemissive donors and, as such, is uniquely suited for characterizing plasmonic materials. In particular, the STEP technique distinguishes the metal-to-semiconductor energy transfer contribution from metal-induced quenching processes, such as the charge transfer, enabling accurate estimates of the plasmon-exciton energy conversion efficiency.

The STEP measurements of PIRET quantum efficiency rely on correlating the changes in the acceptor (semiconductor) emission with the spectral modulation of the excitation light. Such modulation is performed using a variable optical density (OD) excitation filter, which is designed to attenuate the spectral band corresponding to the donor absorption. If the plasmon-induced energy transfer is present, the suppression of donor excitations should lead to the proportional suppression of the acceptor emission. Quantitatively, this approach allows calculating the percentage of photons absorbed by the donor (e.g. a metal NP), the energy of which is transferred to the acceptor moiety exclusively via the energy transfer mechanism. In cases where the “backward” semiconductor-to-metal FRET is also significant, the STEP measurements give the combined efficiency of the two processes:

$$E_{STEP} = E_{PIRET} - E_{FRET}$$

The details of the STEP spectroscopy for measuring the energy transfer efficiency in donor-acceptor assemblies have been described in the recent literature (see Refs. [107–109]). The method is based on the assumption that the number of photons emitted by an acceptor N_A^{PL} depends linearly on the number of excited acceptor (A) and donor (D) molecules, N_A and N_D , respectively:

$$N_A^{PL} = QY_A(N_A + E_{D \rightarrow A}N_D) \quad (6)$$

where $E_{D \rightarrow A}$ is the quantum efficiency for the $D \rightarrow A$ energy transfer and QY_A is the emission QY of fluorophore A in the presence of fluorophore D (as measured in the donor-acceptor assembly). To determine $E_{D \rightarrow A}$, a donor-acceptor sample is excited using a broadband light source to induce the emission of the acceptor dye N_A^{PL} . The excitation light is then spectrally shaped using donor-like or acceptor-like filters (Figure 11A) designed to suppress the excitation of donor or acceptor species in the investigated sample ($N_D \ll N_A$ or $N_A \ll N_D$, respectively). If the spectral profile of the excitation light $n(\lambda)$ and the OD of the excitation filter are known, one can predict the change in the acceptor emission as a function of a single parameter, $E_{D \rightarrow A}$.

Figure 11A (inset) illustrates the STEP approach for extracting the energy transfer efficiencies using an example of Au (donor) and CdSe (acceptor) NP mixture. To this end, a normalized acceptor emission $f_D = N_A^{PL}/N_A$ was plotted as a function of the filter OD as shown in the inset. The measured parameters M_1 and M_2 were then used to calculate the energy transfer efficiency as follows: $E_{D \rightarrow A} = (M_1/M_2) \times (N_A^0/N_D^0)$, where (N_A^0/N_D^0) represents the ratio of acceptor to donor excitations in the sample before the application of the excitation filter as determined from

Figure 11: Measurements of the PIRET efficiency by means of STEP spectroscopy.

(A) Diagram illustrating the STEP spectroscopy concept for a blend of Au NPs and CdSe NCs. The excitation filter attenuates the spectral band of the excitation light that matches the absorption range of energy-donating Au NPs. The predicted reduction in the number of photoexcited donor species (Au NPs) is compared to the corresponding reduction in the emission of energy-accepting CdSe NCs to obtain the donor-acceptor energy transfer efficiency, E_{PIRET} (inset). (B) Electric field intensity amplification calculated for 21 and 9.1 nm Au NPs. The electric field response of spherical NPs was calculated classically by the T matrix linking the outgoing (Hankel) fields with the incident (Bessel) fields [110]. The dielectric field of Au was assumed to be $\epsilon = -8.4953 + 1.6239i$. (C) PIRET from 9.1 nm Au NPs to a surrounding matrix of CdSe NCs. Evolution of the scaled CdSe emission (f -ratio) versus the OD of the donor-type excitation filter (Cy3.5) is shown by blue circles. The experimental data for Au-CdSe assemblies are compared to two parametric model curves, corresponding to $E_{Au \rightarrow CdSe} = 1\%$ and 2% . The f -ratio measured for the acceptor-only control sample (red circles, CdSe NC film) reveals no dependence on the donor-filter OD, consistent with the absence of the energy transfer in this case. (D) PIRET from 21.0 nm Au NPs to a surrounding matrix of CdSe NCs. The evolution of the scaled CdSe emission (f -ratio) versus the OD of the donor-type excitation filter (Cy3.5) is shown by blue circles. The experimental data for Au-CdSe assemblies were fitted with a set of model parametric curves, indicating that $E_{Au \rightarrow CdSe} = 29\text{--}30\%$. The f -ratio measured for the acceptor-only control sample (red circles, CdSe NC film) is independent of the donor-filter OD, consistent with the absence of the energy transfer in this case.

the known excitation and absorption profiles. Alternatively, one can fit the experimentally measured f_d with a model parametric curve f_{theor} , featuring a single fitting parameter, $E_{D \rightarrow A}$. To obtain $f_{theor}(E) = N_A^{PL}(E)/N_A$, $N_A^{PL}(E)$ is determined using Eq. (6) as a parametric function of the energy transfer efficiency E .

The application of the excitation filter in STEP spectroscopy differs from how it is conventionally applied in optical techniques considering that it does not block the excitation of a particular component but rather attenuates its photon absorption by a predetermined fraction. For instance, as described in Ref. [108], an excitation filter using a solution of Cy3.5 molecules can selectively

attenuate the excitation of 9.1 nm Au nanostructures, thus reducing the Au-to-CdSe energy transfer rate in a blend of Au and CdSe NPs. The resulting reduction in the CdSe acceptor PL due to the absence of the near-field contribution from Au is then converted to the Au-to-CdSe energy transfer efficiency, $E_{Au \rightarrow CdSe}$. As shown in Figure 11C, the scaled acceptor PL (f -ratio) is first measured for a control sample containing only CdSe NCs. The evolution of $f_{CdSe-only}$ with the increasing excitation filter (Cy3.5) OD exhibited an expected zero-slope trend (red circles), confirming the absence of the energy transfer in nonplasmonic films. When plasmonic Au + CdSe films were used, the $f_{Au-CdSe}$ (blue circles) revealed a characteristic OD dependence,

corresponding to $E_{\text{Au} \rightarrow \text{CdSe}}$ of 1%–2%. Therefore, between 1% and 2% of photons absorbed by 9.1 nm Au NPs shared the photoinduced energy with CdSe. Conversely, the assembly of 21.0 nm Au and CdS-capped CdSe NPs showed a considerable decline of the f -ratio with increasing excitation filter OD. The comparison of the experimental data to model calculations (Eq. 6) was used to estimate the energy transfer efficiency of $E_{\text{Au} \rightarrow \text{CdSe}} = 29.5\%$. Therefore, in the case of the larger-diameter Au nanostructures, 29%–30% of photons absorbed/scattered by the plasmonic effect were transferred to the CdSe sublattice excitons.

To address the possible correlation between the spatial dimensions of the near-field enhancement region in Au NPs and $E_{\text{Au} \rightarrow \text{CdSe}}$, we have calculated the electric field intensity of about 9.1 and 21 nm Au NPs (Figure 11B). To this end, a classical approach using the T matrix linking the outgoing and incident fields was employed [110]. The resulting field enhancement, $\log_{10}(|E/E_0|^2)$, was graphically superimposed onto a matrix of CdSe/CdS NCs placed at minimum expected distances from the surfaces of metal NPs. The qualitative comparison of the electric field ranges in the two cases confirmed the premise that larger Au NPs induce a stronger electric field in neighboring CdSe/CdS NCs, which explains a comparatively greater PIRET efficiency for this system.

8 Prospective strategies for using PIRET in optoelectronic devices

The plasmonic effect of metal nanostructures allows concentrating light beyond the limits of geometrical optics. This characteristic is potentially deployable in many areas of science and engineering, including light harvesting, sensing, detection, and Raman scattering. The fundamental challenge faced by the majority of these applications lies in the ability to convert the energy of localized surface plasmons to bandgap excitations of a proximal semiconductor. The conversion process should be fast enough to outpace the competing thermal decay of electrons in metals, which depletes the plasmon energy in a few picoseconds.

To increase the efficiency of plasmon energy conversion, the general understanding of the ultrafast energy flow in plasmonic systems should be improved. To date, substantial progress has been made by the scientific community in identifying the major pathways of the plasmon-exciton energy exchange. For instance, strategies based on hot electron injection and resonant near-field energy transfer have shown promise for light conversion. These experiments, backed by the progress in the theoretical description of localized plasmon resonances, have led to

the general understanding of plasmon-exciton coupling in a weak field regime (no carrier wave-function overlap). Nevertheless, several fundamental questions remain to be unanswered and need to be addressed in the future to facilitate the transition of plasmonics to a variety of applications in light conversion and optical detection.

One of the future research directions toward the development of plasmonic materials should target the fundamental understanding of ultrafast localized fields both experimentally through new characterization tools and nanoscale architectures and theoretically via the development of fully quantum mechanical approaches. Of particular interest is a PIRET process that remains relatively unexplored. In contrast to threshold-limited hot electron transfer, the PIRET mechanism can be used to extract a significant portion of the plasmon energy, making it particularly appealing in areas of PV and photocatalysis. The ultrafast nature of this process and the competition with the backward FRET, however, were shown to significantly limit the ability to extract the plasmon energy in realistic systems. This calls for further research of the plasmon-exciton interaction in a short-range (1–10 nm) regime.

The future progress in plasmonics will also depend on the successful development of imaging strategies for probing and controlling the plasmon near-field and ensuing plasmon-exciton interactions with subnanometer spatial sensitivity. In this regard, near-field scanning optical microscopy offering deep-subwavelength resolution appears to be particularly promising [111, 112]. When equipped with time-resolving capabilities [113], the ultrafast nanoscopy of plasmonic structures can reveal the spatial dynamics of the evanescent field around metal nanostructures. The near-field scanning methods can be combined with the STEP spectroscopy for estimating the net flow of energy in plasmon-semiconductor assemblies.

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