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Introduction

Radiative and nonradiative energy transfers (ETs) are important tools for manipulating nanoscale materials.^{1–8} Quantum cutting is an attractive optical phenomenon where a material absorbs a high-energy photon and emits multiple photons with lower energy, similar to that in singlet fission.^{9–16,33} In a solar cell, these lower-energy photons are absorbed by the photovoltaic

Förster and nanometal surface-energy transfer in CsPbCl₃/Yb³⁺ quantum-cutting multilayer structures

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Recently, in nanophotonics, thin metal films owing to the plasmon modes they support and their perovskite nanostructures exhibit novel optical properties, which have attracted considerable interest. Both the Förster resonant energy transfer (FRET) of the dopant-induced right-angled Yb³⁺–V_{Pb}–Yb³⁺ defect state and a pair of Yb³⁺ ions in all-inorganic perovskite nanocrystal (PeNC) CsPbCl₃:Yb³⁺ quantum-cutting (QC) materials and the nanometal surface-energy transfer (NSET) of the excitons of PeNC–Ag nanoparticles (NPs) were investigated experimentally in CsPbCl₃:Yb³⁺/PMMA/Ag/Si (CY_{*i*}, *i* = 1, 2, 3, 4, 5, 6), CsPbCl₃:Yb³⁺/PMMA/Si (CY_{*i*}), and CsPbCl₃/PMMA/Ag/Si (CA_{*i*}), representing three species of multilayer structures. It was found that due to the mediation of the Ag film and an increase in the interaction volume of donors–acceptors, FRET efficiencies increased from 26% to 66% as the spacer (or wave-guiding layer) thicknesses decreased from 63.7 to 17.8 nm. The energy-transfer efficiencies of CA_{*i*} in the NSET in the surface–surface scheme followed a $d^{-1.6}$ -distance dependence. This distance dependence approached the d^{-2} -distance dependence expected of a point-to-surface or 0D–2D energy transfer (ET). The ET in quantum cutting (QC) modulated by plasmons undoubtedly paves a way for improving the FRET and NSET performances of materials.

layer below, together with transmitted photons, thus improving the spectral coverage of the solar cell. Recently, the Yb³⁺-doped lead halide perovskite (CsPbCl₃:Yb³⁺) has attracted immense interest17,18 owing to its photoluminescence quantum yield (PLQY) approaching 200%^{19,20} as well as other novel optical characteristics. Through a combination of techniques including synthesis, variable-temperature PL spectroscopy, and transientabsorption and time-resolved PL spectroscopy, the results showed that the formation of shallow Yb³⁺-induced defects plays a critical role in facilitating a nonradiative energy-transfer process that de-excites the photoexcited nanocrystal and simultaneously excites two Yb^{3+} dopant ions, which is the quantum cutting (QC) phenomenon. Further, quantum-cutting Yb-doped perovskite thin films with PLQY over 190% have been reported.18,19 A key distinction between this material and all previous quantumcutting materials is its strong broadband absorption at energies relevant for quantum cutting. This feature allows a much greater harvesting of solar photons by CsPbCl₃:Yb³⁺ than by alllanthanide quantum cutters. Moreover, the composition tunability of the CsPbCl₃ absorber material allows the absorption threshold to be tailored to minimize thermalization losses, and quantum-cutting energy efficiencies over 90% have been demonstrated for converting absorbed blue photons to near-infrared (NIR) emitted photons.²¹⁻²⁴ The nonradiative energy transfer



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between donors and acceptors in the QC process has been poorly explored in the literature to date. Furthermore, reports on the modulation of metal nanoparticles (MNPs) on the plane for the QC process are scarcer. Here, the observed ET from the excitons of PeNPs to Yb³⁺ and Ag NPs has been found to be involved in both FRET and NSET processes. These two most common resonant energy transfers have been extensively used to account for the ET for various donor-acceptor pairs.^{25–27}

In this study, we introduced plasmon modulation in the ET of CsPbCl₃:Yb³⁺ QC to control the performance of materials. An enhancement in the ET efficiency was observed in the CsPbCl₃:Yb³⁺/PMMA/Ag/Si (CYA_i, i = 1, 2, 3, 4, 5, 6) films. FRET efficiencies increased from 26% to 66% as the spacer thicknesses decreased from 63.7 to 17.8 nm. However, when Ag layers were absent, other conditions remained the same; the ET efficiencies for the CsPbCl₃:Yb³⁺/PMMA/Si (CY_i) sample series fluctuated around 50%. It was evident that the variations in the transfer efficiencies for the serial samples, CYAi, were due to the modification in the plasmons of the Ag film. The ET process of PeNC excitons on the Ag NP plane are governed by the NSET mechanism in CsPbCl₃/ PMMA/Ag/Si (CA_i) films. The nonradiative energy-transfer efficiency for PeNCs interacting with Ag NP acceptors on a plane within the NSET showed a $d^{-1.6}$ -separation dependence as opposed to the d^{-4} dependence for the FRET to a plane of acceptors.²⁸

Results and discussion

In the CsPbCl₃:Yb³⁺ QC process, the donor is a dopant-induced right-angled Yb³⁺–V_{Pb}–Yb³⁺ defect state and the acceptor is a pair of Yb³⁺ ions that are both coupled to this defect state.^{30,31} Both FRET and NSET mechanisms have been used to describe ET processes, as shown in Fig. 1. Here, the quenching of the emission of colloidal quantum dots in proximity to a monolayer of Ag nanoparticles is observed. The PMMA spacer layers of different thicknesses were sandwiched between CsPbCl₃:Yb³⁺ (~20 nm) and Ag films (~30 nm), building up the three structures, namely CsPbCl₃:Yb³⁺/PMMA/Ag/Si (CYA_i *i* = 1, 2, 3,



Fig. 1 Scheme of FRET (donor is the right-angled $Yb^{3+}-V_{Pb}-Yb^{3+}$ defect state, and the acceptor is a pair of Yb^{3+} ions) and NSET(donors are the excitons of PeNCs and acceptors are Ag NCs). Ag films were spin-coated (thickness 17.8–63.7 nm) with a colloidal synthesis solution.

4, 5, 6), CsPbCl₃:Yb³⁺/PMMA/Si (CY_{*i*}), and CsPbCl₃/PMMA/Ag/Si (CA_{*i*}).

The transmission electron microscopy (TEM) images and corresponding histograms of CsPbCl₃:Yb³⁺ PeNCs and Ag NPs are presented in Fig. 2(a)–(d), respectively. The diameters of CsPbCl₃:Yb³⁺ PeNCs and Ag NPs were about 8 and 7 nm, respectively. Fig. 3 shows the decay curves of (a) CsPbCl₃:Yb³⁺/ PMMA/Ag/Si (CYA_i *i* = 1, 2, 3, 4, 5, 6), (b) CsPbCl₃:Yb³⁺/PMMA/Si (CY_{*i*}), and (c) CsPbCl₃/PMMA/Ag/Si (CA_{*i*}), respectively. The PL emission spectra of CsPbCl₃:Yb³⁺ PeNCs under the excitation of 375 nm are shown in Fig. 2(e). The emission peaks are located at 412 and 990 nm, respectively, with the latter peak being stronger than the former, as most of the excitation energy is used in QC processes.

The PL spectrum (black) of CsPbCl₃:Yb³⁺ PeNCs and Ag NP absorption spectrum (red) remarkably overlapped (Fig. 2(f)), which was not expected for the NSET mechanism but is used to calculate the Förster radius R_0 . The colloidal CsPbCl₃:Yb³⁺ (radius $r_{PeNCs} = 4$ nm) and Ag NPs ($r_{AgNP} = 3.5$ nm) were deposited on Si substrates *via* the spin-coating method. Spacers with various thicknesses were sandwiched between them.

The PL lifetimes of donors in three configurations were measured (Fig. 3(a–c)) under excitation at 375 nm and monitored at 412 nm. The FRET transfer (quenching) efficiencies were calculated by the equation $\eta_{\text{FRET}} = 1 - \tau_{\text{DA}}/\tau_{\text{D}}$, where τ_{DA} and τ_{D} are the PL lifetimes of excitons measured in the presence and absence of acceptors^{32–35} (listed in Table 1). These decay curves were fitted by $I = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) + I_0$ and the mean value $\tau_a = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2)$. This is believed to be more accurate compared to that of Yb³⁺–V_{Pb}– Yb³⁺ (defect state) and the acceptor (a pair of Yb³⁺ions) practical distance *d*, and the transfer efficiencies could be described by eqn (1) (point-surface) or by the relation $\eta_{\text{FRET}} \sim d$,

$$\eta_{\text{FRET}} = \frac{1}{1 + \frac{2d^n}{C_{Ag}\pi R_0^6}}.$$
 (1)

The concentration of Ag NPs (C_{Ag}) is $3 \times 10^{14} \text{ m}^{-2}$ and the Förster radius R_0 , which is the characteristic distance at which the energy transfer efficiency, is 50% and is given by^{29,30}

$$R_0 = 0.0211 \left[\frac{\kappa^2 Q Y}{\varepsilon^4} J \right] \tag{2}$$

where κ^2 is the orientation factor of the dipoles and has a value of 2/3 for randomly oriented dipoles in this study. QY is the PL quantum yield of NPs, ε is the refractive index of the surrounding medium, and $J = \int I_{PeNP} \times \varepsilon_{AgNP}(\lambda) \lambda^4 d\lambda$ is the normalized spectral overlap of the donor PeNC emission spectrum (I_{PeNC} (λ)) and the acceptor Yb³⁺ (or Ag NP) extinction spectrum (ε_{Yb} (λ) or $\varepsilon_{AgNP}(\lambda)$). This indicates that the fitting parameter n = 1.0617 (surface–surface) or the relation $\eta_{FRET} \sim d^5$ process²⁷ is similar to the FRET point-line³¹ $\sim d^5$. Notably, this process included both the FRET (a defect state-Yb³⁺ions) and NSET (PeNP-Ag).

By moving the Ag film away or eliminating the PeNC–Ag process, the experiment performed on CY_i samples resulted in



Fig. 2 (a) and (c) TEM images of CsPbCl₃:Yb³⁺ PeNCs and Ag NPs and (b) and (d) corresponding histograms. (e) Emission spectrum of CsPbCl₃:Yb³⁺ PeNCs. (f) Emission (absorption) spectra of CsPbCl₃:Yb³⁺ PeNCs (black-line) and Ag NPs (red-line).

nearly invariable transfer-efficiency values (blue spheres), as seen in Fig. 4 (dashed line for guiding the eye). It was expected that the distance between the donor-acceptor (D–A) would be constant in CsPbCl:Yb³⁺ molecules. Therefore, the transfer efficiencies only fluctuated around 50%. Consequently, it could be deduced that the variation in the transfer efficiencies for the serial CYA_{*i*} samples came mainly from the modification of the Ag film plasmon. The ET was governed by the NSET mechanism in the CsPbCl₃/PMMA/Ag/Si system (CA_{*i*}). The energy-transfer efficiencies between PeNC-Ag NPs cannot be obtained by equation $\eta_{\text{FRET}} = 1 - \tau_{\text{DA}}/\tau_{\text{D}}$ but instead by the general energy-transfer efficiency:^{32–34}

$$\eta_{\rm ET}^{\rm gen} = \frac{1}{1 + \left(\frac{d}{d_0^{\rm gen}}\right)^n} \tag{3}$$

where

$$d_0^{\text{gen}} = \left(\frac{0.225\phi_{\rm D}c^3}{\omega_{\rm D}^2\omega_{\rm F}k_{\rm F}}\right)^{1/4} \tag{4}$$

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Table 1 Experimental data and parameters, (a) CsPbCl₃:Yb³⁺/PMMA/Ag/Si $(CYA_i i = 1, 2, 3, 4, 5, 6)$, (b) of CsPbCl₃:Yb³⁺/PMMA/Si (CY_i) and (c) of CsPbCl₃/PMMA/Ag/Si (CA_i)

| | τ_1 (ns) | τ_2 (ns) | A_1 | A_2 | χ^2 | τ_{a} (ns) | η | <i>d</i> (nm) |
|------|---------------|---------------|-------|-------|----------|-----------------|----------------------|---------------|
| C0 | 0.72 | 3.30 | 0.151 | 0.007 | 0.907 | 1.1721 | | |
| CYA1 | 1.05 | 2.82 | 0.123 | 0.002 | 1.062 | 0.3959 | 0.6622 | 17.8 |
| CYA2 | 0.50 | 10.00 | 0.211 | 0 | 1.3 | 0.5 | 0.59 | 25.2 |
| CYA3 | 0.50 | 3.45 | 0.206 | 0.003 | 0.769 | 0.7694 | 0.52 | 27.4 |
| CYA4 | 0.53 | 0.89 | 0.163 | 0.022 | 0.947 | 0.5965 | 0.4911 | 29.2 |
| CYA5 | 0.77 | 20.00 | 0.153 | 0 | 0.792 | 0.77 | 0.3431 | 48 |
| CYA6 | 0.86 | 0 | 0.190 | 0 | 1.00 | 0.86 | 0.2663 | 63.7 |
| CY1 | 0.55 | 19.8 | 0.197 | 0 | 0.730 | 0.55 | 0.5308 | 17.8 |
| CY2 | 0.57 | 20.00 | 0.185 | 0 | 0.643 | 0.57 | 0.5137 | 25.2 |
| CY3 | 0.52 | 17.44 | 0.203 | 0 | 0.653 | 0.52 | 0.5564 | 27.4 |
| CY4 | 0.51 | 19.22 | 0.207 | 0 | 0.638 | 0.51 | 0.5649 | 29.2 |
| CY5 | 0.56 | 20.00 | 0.119 | 0 | 0.907 | 1.01 | 0.5220 | 48 |
| CY6 | 0.51 | 20.00 | 0.124 | 0 | 0.928 | 0.99 | 0.5100 | 63.7 |
| CA1 | 0.51 | 2.26 | 0.191 | 0.005 | 0.815 | 0.6919 | 0.0175 | 17.8 |
| CA2 | 0.05 | 1.19 | 1.441 | 0.005 | 1.676 | 0.1370 | 0.0044 | 25.2 |
| CA3 | 0.60 | 1.44 | 0.173 | 0.004 | 1.049 | 0.6442 | 0.0032 | 27.4 |
| CA4 | 0.59 | 2.82 | 0.173 | 0.014 | 0.839 | 0.4986 | 0.0024 | 29.2 |
| CA5 | 0.55 | 18.67 | 0.188 | 0 | 0.714 | 0.55 | 3.36 $	imes$ $^{-4}$ | 48 |
| CA6 | 0.80 | 2.70 | 0.134 | 0.004 | 0.761 | 0.9739 | 1.08 $	imes$ $^{-4}$ | 63.7 |

where $\Phi_{\rm D}$ is the quantum yield of the donor, *c* is the velocity of light, $\omega_{\rm D}$ is the angular frequency of the donor electronic transition, $\omega_{\rm F}$ is the Fermi frequency, and k_F is the Fermi wave vector of the metal. In this case, the $d_0^{\rm gen}$ value is calculated using $\Phi_{\rm D}$ = 0.086, c = 3 \times 10^{10} cm s⁻¹, $\omega_{\rm D}$ = 3.8 × 10^{15} s⁻¹, $\omega_{\rm F}$ = 8.3 × 10^{15} s⁻¹, and $k_{\rm F}$ = 1.2 × 10^8 cm^{-1} (ref. 32). The calculated d_0^{gen} for this system is 4.0 nm. The relationship between the CsPbCl3 PeNC-Ag NP transfer efficiencies of the serial samples CA_i and the distance *d* is given by^{35–38}

$$\eta_{\text{NSET}} = \frac{1}{1 + \frac{3(d - r_{\text{AgNP}})^n}{C_{\text{Ag}}\pi d_0^4 (3d - r_{\text{AgNP}})}}$$
(5)



Fig. 4 The experimental data and curve fitted by eqn (1) (black solid squares and solid line) of CsPbCl₃:Yb³⁺/PMMA/Ag/Si (CYA; i = 1, 2, 3, 4, 5, 6), the blue spheres, dashed line for guiding the eye for $CsPbCl_3:Yb^{3+}/$ PMMA/Si (CY_i), the pink inverted triangle and curve fitted by eqn (5) of CsPbCl₃/PMMA/Ag/Si (CA_i), which were amplified 40 times for comparing in the same figure, were presented, respectively.

where $d_0 = d_0^{\text{gen}}$ and d are the same as in eqn (1). The practical distance of the donor PeNC excitons and the acceptor Ag NPs (surface-surface) is denoted as d. Consequently, the experimental data (pink inverted triangles) and curve fitted by eqn (5) (pink line) are shown in Fig. 4. The fitting parameter n = 2.6 (surface–surface) or $\eta_{\rm NSET} \sim d^{-1.6}$ approached the d^{-2} -distance dependence (point-tosurface NSET).³⁰⁻⁴⁰ It is well known that the FRET efficiency highly depends on a number of factors, such as spectral overlap, distance, and orientation.37 Moreover the spectral overlap, namely energy matching, is indispensable for resonance energy transfer. However, for NSET, there were no clear requirements in the spectral overlap. The spectral overlap between the donor PeNC excitons and acceptor

Conclusions

In this study, Yb³⁺-doped CsPbCl₃ PeNCs were synthesized through a modified hot-injection method and Ag NPs were synthesized following a previously reported method by Peng et al.³⁰ Three types of different components, CsPbCl₃:Yb³⁺/ PMMA/Ag/Si (CYA_i i = 1, 2, 3, 4, 5, 6), CsPbCl₃:Yb³⁺/PMMA/Si (CY_i), and CsPbCl₃/PMMA/Ag/Si (CA_i), were deposited by the spin-coating method. Both Förster resonant energy transfer (FRET) and nanometal surface-energy transfer (NSET) mechanisms were involved in the quantum cutting (QC) processes of CYA_i. It was indicated that FRET (the donor defect state-the acceptor Yb³⁺ state) were modified by NSET (the donor excitons of CsPbCl₃PeNCs-the acceptor Ag NPs). The NSET of CA_i was weaker than the FRET in CYA_i with the ET efficiency being smaller by two orders of magnitude. The performance could be improved but for d (17.8–63.7 nm) being beyond the range of \sim 22 nm.³⁸ A coupled surface plasmon was shown to mediate the ET from the donor to acceptor. Applying wave-guiding structures (PMMA-Ag interfaces) for ET should allow a directional control over the flow of excitation energy. The suitably designed metallic nanostructures could allow subwavelength-scale manipulation of light and provide an interface to the outside world.

Experimental

Materials and methods

PbCl₂ (99.999%, Sigma-Aldrich), PbBr₂ (99.999%, Alfa), Cs₂CO₃(99.9%, Beijing Chemical Work), octadecene (ODE, 90%, Beijing Chemical Work), acetone (99.7%, Beijing Chemical Work), *n*-hexane (97%, Beijing Chemical Work), YbCl₃·6H₂O (99.99%, Beijing Chemical Work), oleic acid (OA, 90%, Beijing Chemical Work), oleylamine (OAm, 80–90%, Beijing Chemical Work), and toluene (99.5%, Beijing Chemical Work) were used directly without further purification.

Synthesis of CsPbCl₃PeNCs

The all-inorganic CsPbCl₃PeNC and Yb³⁺ ion doped (concentration 9%) CsPbCl₃ were synthesized through a modified hotinjected method²⁷ but this was met with some difficulties associated with the poor precursor solubility (particularly YbCl₃·6H₂O).

Synthesis of Cs-oleate

First, 0.8 g of Cs_2CO_3 was loaded into a mixture of 30 mL of octadecene and 2.5 mL of oleic acid and then heated to 200 °C until the white powder was completely dissolved. Then, the mixture was kept at 150 °C for 1 h under vacuum. Notably, during the synthesis of PeNCs, the temperature of the Cs-oleate mixture should be kept at 120 °C at least to avoid precipitation. ODE (50 mL), oleylamine (OAm, 6 mL), OA (6 mL), and PbCl₂ (0.52 g) were loaded into a 250 mL three-neck flask, heated to

120 °C, evacuated, and refilled with N₂ followed by heating the solution to 120 °C for 1 h. After the complete solubilization of the PbCl₂ salt, the temperature was raised to 200 °C. In addition, OAm (6 mL) and OA (6 mL) were subsequently injected to solubilize the solution at 200 °C. Then, the Cs-oleate solution (5 mL, 0.125 M in the ODE, prepared as described above and preheated before injection) was quickly injected and after 1 min the reaction mixture was cooled by an ice-water bath. After centrifugation at 8000 rpm for 10 min, the supernatant was discarded and the particles were redispersed in *n*-hexane. Then, the NCs were precipitated with acetone and centrifuged again.

Synthesis of CsPbCl₃:Yb³⁺ PeNCs. ODE (50 mL), oleylamine (OAm, 8 mL), OA (8 mL), PbCl₂ (261.4 mg), and YbCl₃·6H₂O (364.3 mg) were loaded into a 100 mL three-neck flask, heated to 120 °C, evacuated, and refilled with N₂, followed by heating the solution to 120 °C for 1 h. After the complete solubilization of PbCl₂ salt, the temperature was raised to 200 °C. Further, OAm (8 mL) and OA (8 mL) were subsequently injected to solubilize the solution at 200 °C. Then the Cs-oleate solution (5 mL, 0.125 M in the ODE, prepared as described above and preheated before injection) was quickly injected, and, 1 min later, the reaction mixture was cooled by ice-water bath. After centrifugation at 8000 rpm for 10 min, the supernatant was discarded and the particles redispersed in n-hexane. Then, the NCs were precipitated with acetone and centrifuged again.

Preparation of Ag nanocrystal (NC). Ag nanoparticles (NPs) were synthesized following a previously reported method by Peng.²⁸ AgNO₃ (0.17 g) was mixed with OLAM (20 mL) in a 50 mL 3-necked round-bottom flask, heated up to 60 °C and maintained at this temperature until the complete dissolution of the AgNO₃ powder. The temperature was then increased up to 180 °C with a ramp of ≥ 10 °C min⁻¹. The reaction was kept for 1 h before it was cooled down to room temperature. The resulting dark-brown solution was washed with anhydrous acetone, centrifuged at 9000 rpm for 6 min, and redispersed in hexane. The washing procedure was repeated two times and the final NC precipitate was redispersed in equal volumes of anhydrous hexane and octane (0.5 mL of each). Further dilutions were performed in accordance with the film-preparation process.

Characterization

Transmission electron microscopy (TEM) images were obtained by a transmission electron microscope (JEM-2000EX) operating at an acceleration voltage of 200 kV. The PL spectra were recorded with a spectrophotometer (Edinburgh FSL-920) and pumped with an optical parametric oscillator (OPO) tuned to 980 nm as an excitation source. Time-resolved PL decay spectra were measured using an FLS-920 spectrometer, which directly gave the fitting PL lifetimes.

Author contributions

Chunxu Liu: Propose experimental plan, formal analysis, investigation visualization validation, writing – original draft. Jisen Zhang: Material prepare and synthesis. Yongyi Chen: methodology, software, formal analysis. Lijie Wang: spin-coating, analysis and control of films. Yue Song: measurement and analysis of time-resolved potoluminescent spectra. Lijun wang: supervision, funding acquisition, project administration.

Conflicts of interest

Paper

There are no conflicts to declare.

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