Nanoscale Photoinduced Charge Transfer with Individual Quantum Dots: Tunability through Synthesis, Interface Design, and Interaction with Charge Traps

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ABSTRACT: Semiconducting colloidal quantum dots (QDs) provide an excellent platform for nanoscale charge-transfer studies. Because of their size-dependent optoelectronic properties, which can be tuned via chemical synthesis and of their versatility in surface ligand exchange, QDs can be coupled with various types of acceptors to create hybrids with controlled type (electron or hole), direction, and rate of charge flow, depending on the foreseen application, either solar harvesting, light emitting, or biosensing. This perspective highlights several examples of QD-based hybrids with controllable (tunable) rate of charge transfer obtained by various approaches, including by changing the QD core size and shell thickness by colloidal synthesis, by the insertion of molecular linkers or dielectric spacers between donor and acceptor components. We also show that subjecting QDs to external factors such as electric fields and alternate optical excitation energy is another approach to bias the internal charge transfer between charges photogenerated in the QD core and QD’s surface charge traps. The perspective also provides the reader with various examples of how single nanoparticle spectroscopic studies can help in understanding and quantifying nanoscale charge transfer with QDs.

1. INTRODUCTION

Colloidal quantum dots (QDs) are an important class of semiconducting nanomaterials with exciting physical and chemical properties such as large absorption cross section, high brightness and high photostability, spectrally narrow and size- and composition-dependent emission spanning from ultraviolet to near-infrared (NIR), easiness of chemical synthesis, and surface ligand modification.1−10 QDs have been utilized in various applications in biological imaging and sensing, in optoelectronics including photovoltaics and solid-state lighting, photocatalysis, and quantum information science.2,9−10 Following the absorption of light by the QD, an electron−hole pair is generated inside its core, a neutral quasiparticle known as exciton. The electron and hole can recombine radiatively, leading to photon emission, a transition leading to a state called “on”, as it is associated with the emission of light. The QD can also undergo photocarging followed by nonradiative Auger recombination when either of the photogenerated charges is trapped outside the core. In this case, a trion is formed inside the QD’s core, either negative (hole trapping) or positive (electron trapping).20−33 The states associated with trions are either “dark (off)” or “dim (gray)”, whether the trion is positive or negative.34 Trapping of photogenerated charges outside a QD’s core has been proposed to relate to surface defects, including diffusive ones, dangling bonds, or the presence of external charge acceptors.35−39 The alternation of a QD emission between “on” and “off” or “gray” states is known as photoluminescence (PL) blinking and is therefore regulated by the so-called “internal charge traps”. When the intended utilization of QDs is to harvest light such as in photovoltaic solar cells, to generate electroluminescence like in solid-state lighting or to optically sense a biological event, colloidal QDs might be coupled with external acceptors like dyes, carbon nanomaterials, conductive polymers, metal oxides, and so on.12,38−44 In doing so, hybrid QD-based donor−acceptor systems can be fabricated by band-gap engineering of the QD and of the QD−acceptor interface.45−57 Band-gap engineering of QDs allows to obtain optimal band alignment with the acceptor component in order to promote efficient photoinduced charge transfer.39 Engineering of the donor−acceptor interface can further improve the efficiency of this process or it can allow rate tunability. This perspective discusses recent progress in our ability to impose and control nanoscale charge transfer in QD-based donor−acceptor hybrids through a variety of approaches, such as chemical synthesis, click chemistry, optically inert spacer implantation, the use of an external electric field and of varying optical excitation energy. These are straightforward approaches to tune the interfacial charge transfer in the direction one needs for a particular application, either
photovoltaics, sensing, solid-state lighting, or reversible optical switching.55–61

2. DESIGN OF QD-BASED DONOR–ACCEPTOR HYBRIDS WITH TUNABLE CHARGE-TRANSFER RATE

The kinetics of electron transfer in QD-based donor–acceptor hybrids can be described by the Marcus theory for nonadiabatic electron transfer for weakly coupled systems.62 The rate of electron transfer, \( k_{ET} \), can be expressed as a function of the driving force (\( \Delta G^0 \)), the reorganization energy (\( \lambda \)), and the electronic coupling strength (\( V \)), as shown by

\[
k_{ET} = \frac{2 \pi \cdot V^2}{\hbar} \left( \frac{1}{4 \pi \lambda k_B T} \right)^{1/2} \exp \left( -\frac{(\lambda + \Delta G^0)^2}{4 \lambda k_B T} \right)
\]

In eq 1, \( \hbar \) is the reduced Planck constant, \( k_B \) is the Boltzmann constant, and \( T \) is the temperature. In general, the driving force for electron transfer is set by the difference between the values of the lowest unoccupied molecular orbital (LUMO or conduction band, CB) energy levels of the donor and acceptor components. In addition, the electronic coupling strength, \( V \), can be expressed by an exponent-dependent decay function of the donor–acceptor interspacings, \( d \),

\[
V = V_0 \exp(-\beta d)
\]

where \( V_0 \) is a constant and \( \beta \) is a damping factor. A similar equation is used for characterizing the rate for hole transfer, except to the fact that the driving force, in this case, is set by the difference between the highest occupied molecular orbital (HOMO or valence band, VB) energy levels of the donor and acceptor components. The above molecular parameters from eq 1 governing charge transfer, in particular, the energy band difference and the separation distance between donor and acceptor components, respectively, provide a strategy to design QD donor–acceptor hybrids for the study of nanoscale interfacial charge transfer. For example, as shown herein, colloidal QD synthesis is an elegant method to tune both electron and hole transfer by varying either the core size or the shell thickness in core/shell QDs.63–65

3. TUNABILITY OF CHARGE TRANSFER VIA COLLOIDAL NANOCRYSTAL SYNTHESIS

As previously stated, the rate for charge transfer in QD-based hybrids can be controlled by band-gap engineering of QDs, precisely by varying the QD core size. This can be achieved by controlling the chemical reaction time and/or temperature and the concentrations of precursors and surfactants.65,66

3.1. Electron Transfer in Core/Shell Quantum Dot–Bridge–Fullerene Hybrids. To fabricate donor–acceptor hybrids for charge-transfer studies, we used a series of water-soluble carboxy-ended core/shell CdSe/ZnS QDs with core sizes of 2.5, 3.2, and 4.5 nm and similar ZnS shell thickness, and with corresponding emission colors peaking at 525, 565, and 605 nm, respectively (Figure 1a). We preferred the use of core/shell QDs with type I band alignment because of their enhanced chemical and physical stabilities in aqueous solution in which we assembled the hybrids.65,66 We connected each of these QDs to a water-soluble fullerene derivative, fullerene-malic acid hexaadduct (FMH), via click chemistry using an aminoaalkanethiol linker, 16-amino-1-hexadecanethiol hydrochloride; FMH, fullerene-malic acid hexaadduct. Three QDs with core sizes of 2.5, 3.2, and 4.5 nm corresponding to emission peaks of 525 nm (QD525), 565 nm (QD565), and 605 nm (QD605), respectively, were used to produce heterodimers with varying electron-transfer rate. (b) Left: absorption spectra of FMH and QDs; right: photoluminescence (PL) spectra of QD525 (green), QD565 (orange), and QD605 (red). Corresponding absorption and PL spectra have identical colors. Histograms of PL lifetimes of QDs (colored) and QD–16AHT–FMH heterodimers for (c) QD605 (red) and QD605–FMH dimer (black); (d) QD565 (orange) and QD565–FMH dimer (black); (e) QD525 (green) and QD525–FMH dimer (black). (f) Photoinduced electron-transfer rate vs QD core diameter (D) for QD–16AHT–FMH heterodimers. Reproduced with permission from ref 60.
were built (Figure 1c−e) from which mean values were extracted to compute electron-transfer rates according to

$$k_{ET} = \frac{1}{\tau_{QD-FMH}} - \frac{1}{\tau_{QD}}$$

(3)

with \(\tau_{QD-FMH}\) and \(\tau_{QD}\) mean values for the PL lifetimes of QD−16AHT−FMH dimer and QD alone, respectively, obtained from the PL histograms in Figure 1c−e. Figure 1f shows the calculated electron-transfer rate versus QDs’ core diameter with \(k_{ET}\) increasing from \(2.2 \times 10^{7}\) to \(4.9 \times 10^{8}\) s\(^{-1}\) when changing the QD core from 4.5 nm (QD605) to 2.5 nm (QDS25), thus demonstrating tunability in electron-transfer rate by band-gap engineering of donor QD.

3.2. Hole Transfer in Core/Shell Quantum Dot−Conductive Polymer Hybrids. For QD-based donor acceptor hybrids functioning on photoinduced hole transfer, the rate can also be tuned by the same approach of band-gap engineering of the QD core. In the particular example described in ref 57, we assembled negatively charged carboxyl-ended core/shell CdSe/ZnS QDs with a p-type positively charged conductive polyelectrolyte, poly(9,9′-bis(6-N,N,N-trimethylammoniumhexyl)fluorene-alt-1,4-(2,5-bis(6-N,N,N-trimethylammoniumhexyloxy))phenylene) (FHQ) by electrostatic interaction, and with FHQ functioning as a hole acceptor for QDs (Figure 2a). Using QDs of different sizes but with similar shell thickness and surface ligand (3-mercaptopropionic acid), with emission peaks at 605 nm (QD605) and 632 nm (QD632), we could change the rate for photoinduced hole transfer by tuning the valence band energy and therefore the energy gap between the VB and the HOMO of the accepting polymer FHQ (Figure 2a). This particular FHQ polymer absorbs and emits in the UV and blue regions of the spectrum, respectively (Figure 2b), and by optically pumping a QD−FHQ hybrid at 532 nm, we could solely photoexcite the QD and observe the hole transfer as a quenching of the PL emitted by the QD by the nearby FHQ polymer (Figures 2a,b and 3b). Similar to the case of electron transfer, we performed time-resolved single nanocrystal spectroscopic experiments on isolated QDs and QD−FHQ hybrids and measured PL lifetimes from such entities from which we built PL lifetime histograms, as shown in Figure 2c−f. From the mean values of the PL lifetimes estimated from Figure 2c−f and using eqs 3 and 4

$$E_{HT} = 1 - \frac{\tau_{QD-FHQ}}{\tau_{QD}}$$

(4)

we estimated an increase in hole transfer rate from \(1.1 \times 10^{7}\) to \(3.2 \times 10^{7}\) s\(^{-1}\) and in efficiency \((E_{HT})\) from 20 to 43% when decreasing the QD core size from QD632 to QD605, which demonstrates the achievement of tunability in hole transfer through QD band-gap engineering in QD−conductive polymer donor−acceptor hybrids.

As mentioned before, the surface passivation of a core-only QD by a wide band-gap semiconductor can enhance the long-term photostability of a QD and its photophysical properties such as PL quantum yield and lifetime. It does this by...
passivating surface charge traps involved in the photocarging of the core. Coating a CdSe QD with multiple ZnS shells improves both the PL quantum yield and the PL lifetime of the neutral exciton and shifts slightly the emission peak toward lower energies, as can be seen in Table 1.53 At the same time, a wide band-gap shell will act as a tunneling barrier for any charge-transfer process initiated in the core and with an external acceptor. With this in mind, we designed and assembled a series of CdSe/ZnS QD−conductive polyelectrolyte donor−acceptor hybrids (Figure 3a), where tunability in the rate for charge (hole) transfer from the CdSe core to polymer could be achieved by increasing the shell thickness, from monolayer and up (Table 1).53 As mentioned before in this paragraph, for these types of hybrids composed of negatively charged CdSe/ZnS QDs emitting at around 635 nm and a positively charged p-type conductive polyelectrolyte FHQ absorbing and emitting in the UV−blue spectral range, photoinduced hole transfer proceeds from the photoexcited CdSe core onto the p-type polymer (see Figure 3a, and energy band alignment in Figure 3b) and it can be easily monitored through the PL quenching experienced by the QD in the presence of polymer, following optical pumping at around 590 nm where only the QD absorbs.

Data characterizing the hole transfer in the QD−FHQ hybrids with varying shell thickness are shown in Figure 3c,d. We measured the hole transfer both in solution and in thin-film phases. In solution, we blended diluted QDs (200 nM) in borate buffer with FHQ polymer at different molar ratios, from 1:0 to 1:20 QD/FHQ (Figure 3c). We observed the strongest PL quenching at the highest molar ratio and for the thinnest ZnS, where we estimated an efficiency of $E_{\text{HT}} = 67\%$, which suggests efficient electrostatic binding of positively charged FHQ to the negatively charged surface of QD. With the increase in shell thickness, we start to observe the dominant role of the shell as a tunneling barrier as a decrease in PL quenching even at high molar ratios (1:20 QD/FHQ), with quenching decreasing to 40% for QD-2/FHQ, 18% for QD-3/FHQ, 11% for QD-4/FHQ, and 7% for QD-5/FHQ (Figure 3c). PL lifetime measurements of QD-X samples and QD-X/FHQ hybrids performed using a 590 nm optical pumping can be used in conjunction with eq 3 to compute hole transfer rates versus ZnS shell thickness for QD-X/FHQ hybrids in solution (QD/FHQ molar ratio of 1:20) to reveal the shell thickness dependency of the hole transfer and the increased tunneling character at thicker shell (Figure 3d, black-colored data), with the strongest rate $k_{\text{HT}}$ of about $2.0 \times 10^8$ s$^{-1}$ observed for QD-1/FHQ hybrid, i.e., the QD with the thinnest shell. For the thickest shell, hole transfer does not proceed at all since there is no observable quenching. According to eq 1, changes in hole transfer rate in these hybrids are expected mainly from changes in the electronic coupling strength, $V = V_0 \exp(-\beta d)$, since they bear QDs with same size cores such that parameters like the driving force ($\Delta G^0$) and the reorganization energy ($\lambda$) do not change. As such, the hole transfer rate $k_{\text{HT}}$ for QD-X/FHQ hybrids will be sensitive only to changes in donor−acceptor separation distance, e.g., ZnS shell thickness, $t_s$, and will be given by $k_{\text{HT}} = k_0 \exp(-\beta t_s)$. A fit of $k_{\text{HT}}$ versus ZnS shell thickness is shown in Figure 3d, black line, with a $\beta \sim 0.2$ Å$^{-1}$, and it confirms our ability to tune the hole transfer rate through shell engineering. If the solution of QD-X/FHQ is spin-cast on a solid support, an increase in hole transfer rate is observed when compared to the solution case (Figure 3d, red-colored data), with the strongest rate $k_{\text{HT}}(\text{QD-1/FHQ}) \approx 4.6 \times 10^8$ s$^{-1}$ observed for the QD-1/FHQ, the hybrid with the thinnest shell. Similarly, the hybrid with the thickest shell does not experience any quenching, suggesting that the tunneling of the photogenerated hole through the shell and onto the polymer is not possible anymore at such shell thickness (4.2 nm). The increase in hole transfer rate from solution to solid thin films was attributed to a denser packing of the FHQ polymer chains on the QD surface, leading to increased electronic coupling between the donor and acceptor in thin film versus solution.

Table 1. Structural and Photophysical Parameters of Core/Shell QDs with Increased Shell Thickness

| CdSe/ZnS | shell thickness (nm) | QY (%) | PL peak (nm) | $\tau_{\text{QD}}$ (ns) |
|----------|----------------------|--------|--------------|------------------|
| QD-1     | 1.2                  | 7.2    | 634          | 9                |
| QD-2     | 1.7                  | 9.4    | 635          | 12               |
| QD-3     | 2.2                  | 16.0   | 636          | 21               |
| QD-4     | 2.7                  | 22.0   | 637          | 32               |
| QD-5     | 4.2                  | 25.0   | 638          | 32               |

4. TUNABILITY OF ELECTRON TRANSFER VIA OPTICALLY INERT SPACERS

Click chemistry is a popular tool to couple various motifs to biological specimens like proteins and enzymes and has become popular in the material science field when functionalizing colloidal nanoparticles for various studies.72 With the help of click chemistry, we developed a surface-based stepwise assembly method to create inorganic−bridge−organic heterodimers composed of colloidal quantum dots as donors and fullerene as acceptors. Details on the method have been provided in a preceding paragraph and can also be found in refs 59 and 60 (Figure 1a). Here, we discuss a specific class of these hybrids, where the bridge, an aminosilanethiolated linker, is used to change the separation distance between the donor and acceptor components to achieve distance-dependent, tunable electron transfer.59,60 We used linkers of varying lengths to connect a CdSe/ZnS QD emitting at 605 nm with a water-soluble fullerene (FMH, Figure 4), namely, 6-amino-1-hexanethiol hydrochloride (6AHT), 11-amino-1-undecanethiol hydrochloride (11AUT), and 16-amino-1-hexadecanethiol hydrochloride (16AHT). By controlling the density of hybrids linked to a glass support, we could achieve concentrations optimal for performing single nanoparticle spectroscopic studies of distance-dependent electron transfer. We measured PL lifetimes from individual QD605 nanocrystals on glass support and from QD605−bridge−FMH hybrids of different bridge lengths and constructed PL lifetime histograms shown in Figure 4a−d, and they show progressive advance of both the mean value and the full width at half-maximum toward smaller values when going from isolated QDs (Figure 4a) to QD−FMH hybrids, with the observed values becoming smaller for shorter linker (Figure 4b−d correspond to 16AHT, 11AUT, and 6AHT linkers, respectively): 20 ns (standard deviation $\sigma \approx 6.5$ ns) for isolated QDs, 5 ns ($\sigma \approx 6.7$ ns) for QD−16AHT−FMH, 3 ns ($\sigma \approx 5.9$ ns) for QD−11AUT−FMH, and 1 ns ($\sigma \approx 4.4$ ns) for QD−6AHT−FMH. Computing electron-transfer rates according to eq 3 leads to Figure 4f, which clearly shows exponential-dependent electron transfer versus donor−acceptor distance, $k_{\text{ET}} = k_0 \exp(-\beta d)$, with an attenuation coefficient $\beta \sim 0.1$ Å$^{-1}$. Furthermore, it is observed that with stronger electron transfer (shorter linker), the standard deviation for PL
Figure 4. Fullerene FMH, aminoalkanethiol linkers with different lengths, and CdSe/ZnS QDs as components for the electron-transfer hybrid. (a–e) Histograms of PL lifetimes of (a) isolated QDs, (b) QD−16AHT−FMH, (c) QD−11AUT−FMH, (d) QD−6AHT−FMH, and (e) QDs deposited on a monolayer of FMH without a linker. (f) Electron-transfer rate vs linker length (R) for QD−linker−FMH hybrids. (g, h) PL intensity trajectories of single QD measurements for (g) isolated QD and (h) QD−11AUT−FMH. Also shown are histograms of PL intensity counts. (i, j) Probability distributions of (i) \( P(t_{on}) \) and (j) \( P(t_{off}) \) for isolated QD (black squares) and heterodimer, QD−16AHT−FMH (red circles), QD−11AU−FMH (green triangles), and QD−6AHT−FMH (blue rhombus). Reproduced with permission from refs 59 and 60.

lifetime histograms in Figure 4b–d decreases, although each of the lifetimes contributing to these histograms was calculated in such a way as to account for similar error (standard deviation). In the absence of the linker (Figure 4e), which is for isolated QDs deposited on a monolayer of FMH molecules, the PL lifetime histogram is broad, with a mean value close to that of isolated QDs on glass support. This demonstrates the important function of the aminoalkanethiol linkers in promoting and controlling the electron transfer in these hybrids.

Electron transfer of a photoexcited QD with a strong external acceptor like fullerene (bare fullerene can accept up to six electrons) affects its PL blinking by competing with the QD’s internal charge traps. In the case of this series of QD−linker−FMH hybrids, we investigated how electron transfer affects the PL blinking of isolated QDs when part of the hybrid. Isolated QDs on glass support feature PL blinking in the form of a quasi-two-state level (Figure 4g) with a clear distinction between the on- and off-levels. QD−linker−FMH hybrids blink differently, featuring a multistate on/off-blinking behavior with no clear distinction between the on- and off-states (Figure 4h). Associated PL intensity histograms built from such PL intensity traces show clear differences between the two types of blinking, two-state (Figure 4g) and multistate (Figure 4h). Using a so-called intensity threshold method, traces like those shown in Figure 4g,h can be analyzed with respect to the times a QD spends in the on-state (probability of occurrence of on-times, \( P(t_{on}) \)) and off-state (probability of occurrence of off-times \( P(t_{off}) \)). For isolated QDs on a glass support, both \( P(t_{on}) \) and \( P(t_{off}) \) follow an inverse power-law distribution, which can be modeled by a power-law model

\[
P(t_i) = b \times t^{-m_i} \quad (i = on, \ off)
\]

(5)

where \( b \) is a constant, and \( m_{on} \) and \( m_{off} \) are the power-law exponents for the on- and off-states, respectively. Fitting parameters are shown in Table 2. For QD−linker−FMH hybrids, \( P(t_{on}) \) distributions for hybrids also display power-law dependency but only at short times. At longer times, they become exponential such that a more complex model with a truncated power-law model must be used to model these data for hybrids

\[
P(t_{on}) = b \times t^{-m_{on}} \exp\left(-\frac{t}{\tau_{on}}\right)
\]

(6)

where \( \tau \) is a crossover time from the power-law to exponential dependency. In addition, \( P(t_{off}) \) distributions of QD−linker−FMH hybrids also show deviations from a power-law dependency at longer times, but these can only be modeled by a stretched exponential bending tail at long times and next to the power law model for short times

\[
P(t_{off}) = b \times t^{-m_{off}} \exp\left(-\left(\frac{t}{\tau_{off}}\right)^{\alpha}\right)
\]

(7)

From isolated QDs to QD−linker−FMH hybrids, there is an increase in blinking activity, seen here by an increase in the value of \( m_{on} \) (shorter on-times), and, at the same time, among the three hybrids, an increase in \( m_{off} \) with increased strength in electron transfer, i.e., shorter linker (Table 2). An opposite trend is observed for the off-times, that is, smaller values for \( m_{off} \) (longer off-times) with stronger electron transfer and smaller than those observed for isolated QDs. These trends clearly reflect the competition introduced by the electron transfer with external acceptors to the blinking of the QD which involves internal charge traps.

One other hybrid system involving QDs and external acceptors we recently designed and assembled is based on near-infrared (NIR) absorbing/emitting core/shell PbS/CdS QDs and TiO₂ thin film (Figure 5a). The energy band alignment between PbS core and TiO₂ favors photoinduced electron transfer from PbS QDs into TiO₂. This is true, as long as there is no overlap between the absorption of TiO₂ and the emission of PbS QD so that a competing energy transfer is excluded (Figure 5b). Similar to the case of core/shell CdSe/ZnS QDs, the wide bandgap CdS shell in the case of core/shell PbS/CdS QDs serves the purpose of a tunneling barrier for the electron transferring from the PbS core onto TiO₂, thus making possible to probe the electron transfer via PL quenching (the lack of a wide band-gap shell will make the transfer superefficient, leaving no PL to be detected in the

Table 2. Fitting Parameters Derived from Probabilities Shown in Figure 4i,j and by Using Equations 5–7

| molecule | \( m_{on} \) | \( \tau_{on} \) (ms) | \( m_{off} \) | \( \tau_{off} \) (ms) |
|----------|---------|----------------|--------|----------------|
| isolated QD | 1.35 | 1.55 | | |
| QD−16AHT−FMH | 1.45 | 770 | 1.45 | 910 |
| QD−11AUT−FMH | 1.46 | 430 | 1.4 | 830 |
| QD−6AHT−FMH | 1.55 | 250 | 1.3 | 770 |

P(0.5)
QD−acceptor hybrid). To demonstrate tunability by an optically inactive spacer, we introduced a dielectric layer of Al₂O₃ of 1 nm between the QD and acceptor. From isolated QDs on glass support to QDs deposited on TiO₂ thin film, we observed substantial quenching, as shown by the PL lifetime histograms of single nanocrystal lifetimes in Figure 5c,d, on average, 2.24 μs on glass and 1.06 μs on TiO₂, which corresponds to a rate for the electron transfer of \( k_{\text{ET}} \) (QD−TiO₂) ≈ 4.9 × 10⁵ s⁻¹. The insertion of 1 nm Al₂O₃ between the QD and TiO₂ slowed down the quenching, with the PL lifetime recovering back to 1.5 μs (Figure 5e), which corresponds to a rate for electron transfer of \( k_{\text{ET}} \) (QD−Al₂O₃/TiO₂) ≈ 2.15 × 10⁵ s⁻¹. As such, tunability in the rate for electron transfer can be easily demonstrated by the use of donor−acceptor spacers.

5. CHARGE TRANSFER WITH INTERNAL TRAPS: TUNABILITY OF ELECTRON TRANSFER BY EXTERNAL FACTORS

As mentioned at the beginning of this perspective, an isolated QD can undergo photocharging followed by efficient non-radiative Auger recombination when either of the photo-generated charges is trapped outside the core, by surface defects and/or dangling bonds acting as traps. We call this charge transfer with internal traps. This charge transfer followed by charge recombination with the remaining charge in the core induces an alternation between emissive and nonemissive states populated by the QD, which, in turn, leads to PL blinking. In this paragraph, we discuss two examples on how charge transfer can be reversibly manipulated by external factors affecting internal charge traps: (i) through the use of an external electric field reversibly manipulating the energy of the internal trap and (ii) through the use of low- and high-energy...
optical pumping, which access different types of charge traps leading to different dynamics in the emission of a QD.\textsuperscript{56,61}

5.1. Internal Charge-Transfer Tunability via an External Electric Field. The influence of an external electric field $E$ on the PL emitted by isolated QDs has been related to the quantum-confined Stark effect and promised as a way to directly control the optical switching behavior of these nanoparticles beyond blinking.\textsuperscript{52-54} To demonstrate our ability to reversibly tune internal charge transfer in CdSe/ZnS QDs, we incorporated highly diluted QDs in a capacitor-like architecture with the QDs sandwiched between two insulating layers of SiO$_2$ and poly(methyl methacrylate) (PMMA), with the material further sandwiched between two electrodes, one of indium tin oxide (ITO) and one of aluminum (Figure 6a) so that an $E$ oriented perpendicular to the electrodes would be present when bias is applied to the device.

We applied a modulated (triangular) external electric field $E$ to the device and observed that the PL intensity and PL lifetime from an isolated QD also become modulated, with the two molecular parameters strongly correlated. In fact, we observed two types of behavior under modulated external $E$ : isolated QDs that emit with a PL intensity/lifetime signal following synchronously the modulation (Figure 6c) and isolated QDs that show opposite or asynchronous response in emitted PL intensity/lifetime (Figure 6d). We next measured PL intensities and PL lifetimes from isolated QDs under constant bias ($E \neq 0$) while maintaining the direction of the external $E$, and without bias ($E = 0$). We found that about 55% of the probed isolated QDs exhibited a decrease in PL lifetime following applied bias, on average from 24.3 ns ($E = 0$) to 20.6 ns ($E \neq 0$), and this was accompanied by a decrease in PL intensity, and we categorized this population as QD(A). The remaining 45% of isolated QDs exhibited an increase in the PL lifetime, on average from 24.7 ns ($E = 0$) to 27.8 ns ($E \neq 0$), which was accompanied by an increase in PL intensity, and we categorized this population as QD(B). PL lifetime histograms of these two QD populations under $E = 0$ and $E \neq 0$ are shown in Figure 6e,f. We investigated how the PL blinking dynamics of these two groups is affected by external bias (Figure 6g–i). We constructed probability distributions $P(t_{\text{on}})$ and $P(t_{\text{off}})$ using the previously described threshold method and fit each probability with a power-law model (eq 5). We observed that the two groups responded differently to the external $E$ : group QD(A) exhibited a decrease in on-time with applied external $E$ ($m_{\text{on}}$ changes from 1.36 at $E = 0$ to 1.53 at $E \neq 0$), while group QD(B) shows an increase in on-time with applied external $E$ ($m_{\text{on}}$ changes from 1.56 at $E = 0$ to 1.29 at $E \neq 0$). To explain these different behaviors of the two groups with applied bias, we refer the reader to the cartoon in Figure 6k. We know that QDs have an intrinsic permanent dipole moment (about 70 D) developed along the nanocrystal’s $c$ axis of the wurtzite crystal structure,\textsuperscript{85} this dipole moment can generate an internal electric field ($E_{\text{int}}$) with a direction along this same $c$ axis. This $E_{\text{int}}$ can bias the energy depth of the internal trap states associated with blinking, making traps oriented parallel to the direction of the permanent dipole moment to become energetically favorable. When applying an external $E_{\text{ext}}$ to a QD, this can either increase or decrease the strength of the local field $E_{\text{int}}$ experienced by the charge carriers in the trap states. If the QD has a permanent dipole moment (projection in the $x$ axis) aligned antiparallel to the $E_{\text{ext}}$, an electron will be trapped easily (increased internal charge-transfer rate) and it will be retained longer in the trap state (deep trap), a manifestation seen as a decrease in the on-time probability (increase of $m_{\text{on}}$), such as observed in group QD(A), whereas group QD(B)
includes QDs with a permanent dipole moment (projection in the x axis) aligned parallel with the \( \vec{E}_{\text{ext}} \) and exhibits an increase in on-time blinking (decrease in \( m_{\text{on}} \)), as we saw in Figure 6f. In consequence, we demonstrate the ability to reversibly control the PL emitted by a QD with an external electric field, which biases the internal charge-transfer process associated with blinking.

5.2. Internal Charge-Transfer Tunability via Optical Excitation. One approach to reversibly alter the internal charge-transfer process of a QD with its surface traps is to change the photon excitation energy. Near-infrared absorbing and emitting PbS/CdS QDs blink differently under different optical excitation energies, whether cold or hot excitons (electron–hole pairs) are produced following a particular optical excitation. For example, 633 nm is a low energy optical excitation, just above the band-gap edge of the QD, thus producing cold excitons, while 488 nm is a high energy optical excitation producing hot excitons.61 In Figure 7a–c, we show that the PL blinking of an isolated PbS/CdS QD emitting at around 900 nm switches reversibly from a classic telegraph-like blinking under 633 nm excitation (low energy) to a multistate blinking under 488 nm excitation (high energy).60 Changing the excitation back to 633 nm (low energy) restores the two-state telegraph-like blinking behavior. This effect can be captured also by analyzing the probabilities \( P(t_{\text{on}}) \) and \( P(t_{\text{off}}) \) of isolated QDs obtained with 633 and 488 nm optical excitations, respectively (Figure 7d,e). For \( P(t_{\text{on}}) \), power-law fits with eq 5 reveal that \( m_{\text{on}} \) increased from 1.62 at 633 nm excitation to 1.86 at 488 nm excitation. Such an increase points toward an increase in blinking activity, which accounts for a decrease in on-time. For \( P(t_{\text{off}}) \), fits according to eq 6, a modified power-law model, including an exponential tail-off, reveals power-law exponents and crossover times \( \tau = 2.4 \) s for 488 nm excitation. This suggests an increase in the off-time from 633 to 488 nm excitation. These changes in blinking dynamics are similar to those observed for the CdSe/ZnS–FMH hybrid, where a QD is connected with an external electron acceptor (see section 4).

Figure 7f,g provides a mechanistic explanation for the reversible changes observed with alternating low-energy (633 nm) and high-energy (488 nm) optical excitations.61,66–70 In Figure 7f, a cold exciton is formed following excitation above the band-gap edge, which can recombine radiatively to emit from the band-gap edge state or it can connect nonradiatively with QD’s surface traps, leading to two-state on/off blinking (Figure 7a). In Figure 7g, high-excitation energy produces hot excitons, which can either cool down to the band-gap edge state, where they can recombine and emit photons or they can cross over through a transition state and populate defect states from which radiative recombination can occur and additional trap states can be accessed (Figure 7g, the right part depicted in blue). This crossover leads to an increase in blinking activity and results in multistate emission. Therefore, by changing the optical excitation energy, we can tune internal charge transfer with different defect states within an isolated QD.

6. CONCLUSIONS AND OUTLOOK

In this perspective, we presented a variety of synthetic and experimental approaches to control the nanoscale charge transfer in colloidal quantum dot hybrids, most of them originating from modifications of molecular parameters defining the rate of the process in the well-known theory of Marcus for nonadiabatic electron transfer for weakly coupled systems. We have shown that colloidal nanocrystal synthesis, in particular, both core and shell engineering, can provide elegant ways to control the driving force and the electronic coupling strength for either electron or hole transfer. We have shown that optically inactive donor–acceptor spacers such as alkane-based linkers and dielectric nanomaterials can be used to tune the rate of charge transfer. Besides charge transfer with external acceptors, we have provided two examples where we could reversibly tune internal charge transfer between QD’s core and surface traps with the help of external electric fields and alternating optical excitation energy. The progress gained from these QD hybrids functioning on charge transfer can provide useful information for the design of active materials for next-generation high-efficient optoelectronics, sensors, and quantum materials. One can envision combining QDs with semiconducting nanowires in creating QD–1D hybrids such as QDs with TiO₂ and with ZnO nanowires for photocatalytic activities or QDs with 2D materials like graphene or transition-metal dichalcogenides for improved solar cell, solid-state lighting, and energy storage applications. The replacement of “toxic” colloidal QDs with more environmentally friendly InP and CuInS₂ QDs can produce hybrids for the large market of biological and medical sensing which function on nanoscale charge transfer. We believe that the progress gained from our charge-transfer studies of QD-hybrid systems can provide useful insights into the design, control, and optimization of novel QD-based hybrids and related devices.

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quantum dot light-emitting diodes with simultaneous high brightness and efficiency. *Nat. Photonics* 2019, 13, 192–197.

21. Kodiamati, M. S.; Lian, S.; Schatz, G. C.; Weiss, E. A. Energy transfer-enhanced photocatalytic reduction of protons within quantum dot light-harvesting–catalyst assemblies. *Proc. Natl. Acad. Sci. U.S.A.* 2018, 115, 8290.

22. Huang, C.; Li, X.-B.; Tung, C.-H.; Wu, L.-Z. Photocatalysis with Quantum Dots and Visible Light for Effective Organic Synthesis. *Chem. – Eur. J.* 2018, 24, 11530–11534.

23. Srinivasa, V.; Nowack, K. C.; Shahei, M.; Vandersypen, L. M. K.; Taylor, J. M. Simultaneous Spin-Charge Relaxation in Double Quantum Dots. *Phys. Rev. Lett.* 2013, 110, No. 196803.

24. Weinstein, Y. S.; Hellberg, C. S.; Levy, J. Quantum-dot cluster-state computing with encoded qubits. *Phys. Rev. A* 2005, 72, 020304.

25. Sanchez, M. L. K.; Wu, C.-H.; Adams, M. W. W.; Dyer, R. B. Optimizing electron transfer from CdSe QDs to hydrogenase for photofugal H₂ production. *Chem. Commun.* 2019, 5579–5582.

26. Lv, X.; Hu, C.; Shang, J.; Sit, P. H. L.; Lam, F. L. Y.; Teo, W. Y. Enhanced photovoltaic charge transfer on Mn-doped CdS/TiO₂ nanotube arrays: The roles of organic substrates. *Catal. Today* 2019, DOI: 10.1016/j.cattod.2019.02.012.

27. Liang, Z.-Y.; Huang, M.-H.; Guo, S.-Y.; Yu, Y.; Chen, W.; Xiao, F.-X. Nanoporous 2D semiconductors encapsulated by quantum-sized graphene carbon nitride: tuning directional photoinduced charge transfer via nano-architecture modulation. *Catal. Sci. Technol.* 2019, 9, 672–687.

28. Feng, J.; Li, F.; Li, X.; Ren, X.; Fan, D.; Wu, D.; Ma, H.; Du, B.; Zhang, N.; Wei, Q. An amplification label of core–shell CdSe@CdS QD sensitized GO for a signal-on photoelectrochemical immuno-sensor for amyloid β-protein. *J. Mater. Chem. B* 2019, 7, 1142–1148.

29. Samadi-Maybodi, A.; Shariati, M. R. Enhanced photocatalytic activity in the reverse type-I QD through the shell-oriented cascaded charge transfer. *J. Photochem. Photobiol., A* 2018, 365, 169–177.

30. Efros, A. L.; Rosen, M. Random Telegraph Signal in the Photoluminescence Intensity of a Single Quantum Dot. *Phys. Rev. Lett.* 1997, 78, 1110–1113.

31. Galland, C.; Ghosh, Y.; Steinbruck, A.; Sykora, M.; Hollingsworth, J. A.; Klimov, V. I.; Htoon, H. Two types of luminescence blinking revealed by spectroelectrochemistry of single quantum dots. *Nature* 2011, 479, 203–207.

32. Gómez, D. E.; van Embden, J.; Mulvaney, P.; Ferné, M. J.; Rubini, S.; Din-Dunlop, H. Exciton–Trion Transitions in Single CdSe–CdS Core–Shell Nanocrystals. *ACS Nano* 2009, 3, 2281–2287.

33. Qin, W.; Guyot-Sionnest, P. Evidence for the Role of Holes in Blinking: Negative and Oxidized CdSe/Cds Dots. *ACS Nano* 2012, 6, 9125–9132.

34. Jha, P. P.; Guyot-Sionnest, P. Trion Decay in Colloidal Quantum Dots. *Nano Lett.* 2009, 9, 1011–1015.

35. Wang, X.; Qu, L.; Zhang, J.; Peng, X.; Xiao, M. Surface-Related Emission in Highly Luminescent CdSe Quantum Dots. *Nano Lett.* 2003, 3, 1103–1106.

36. Jones, M. Z.; Lo, S. S.; Scholes, G. D. Signatures of Exciton Dynamics and Carrier Trapping in the Time-Resolved Photoluminescence of Colloidal CdSe Nanocrystals. *J. Phys. Chem. C* 2009, 113, 18632–18642.

37. Tang, J.; Marcus, R. A. Mechanisms of fluorescence blinking in semiconductor nanocrystal quantum dots. *J. Chem. Phys.* 2005, 123, No. 054704.

38. Jin, S.; Lian, T. Electron Transfer Dynamics from Single CdSe/ZnS Quantum Dots to TiO₂ Nanoparticles. *Nano Lett.* 2009, 9, 2448–2454.

39. Tsvrdy, K.; Frantsuzov, P. A.; Kamat, P. V. Photoinduced electron transfer from semiconductor quantum dots to metal oxide nanoparticles. *Proc. Natl. Acad. Sci. U.S.A.* 2011, 108, 29–34.

40. Greenham, N. C.; Peng, X.; Alivisatos, A. P. Charge separation and transport in conjugated-polymer/semiconductor-nanocrystal composites studied by photoluminescence quenching and photoconductivity. *Phys. Rev. B: Condens. Matter Mater. Phys.* 1996, 54, 17628–17637.
(41) Liu, D.; Wu, W.; Qiu, Y.; Lu, J.; Yang, S. Chemical Conjugation of Fullerene C60 to CdSe Nanocrystals via Dithiocarbamate Ligands. J. Phys. Chem. C 2007, 111, 17713–17719.
(42) Sun, B.; Marx, E.; Greenham, N. C. Photovoltaic Devices Using Blends of Conjugated CdSe Nanoparticles and Conjugated Polymers. Nano Lett. 2003, 3, 961–963.
(43) Huyhn, W. U.; Dittmer, J. J.; Libby, W. C.; Whiting, G. L.; Alivisatos, A. P. Controlling the Morphology of Nanocrystal–Polymer Composites for Solar Cells. Adv. Funct. Mater. 2003, 13, 73–79.
(44) Maiti, S.; Dana, J.; Ghosh, H. N. Correlating Charge-Carrier Dynamics with Efficiency in Quantum-Dot Solar Cells: Can Excitonics Lead to Highly Efficient Devices? Chem. – Eur. J. 2019, 25, 692–702.
(45) Mandal, S.; George, L.; Tkachenko, N. V. Charge transfer dynamics in CuPbBr3 perovskite quantum dots–anthraquinone– fullerene (C60) hybrids. Nanoscale 2019, 11, 862–869.
(46) Moroz, P.; Jin, Z.; Sugiyama, Y.; Lara, D. A.; Rzagoniaeva, N.; Yang, M.; Kholmicheva, N.; Khan, D.; Mattoussi, H.; Zamkov, M. Competition of Charge and Energy Transfer Processes in Donor–Acceptor Fluorescence Pairs: Calibrating the Spectroscopic Ruler. ACS Nano 2018, 12, 5657–5665.
(47) Ding, C.; Zhang, Y.; Liu, F.; Kitabayake, Y.; Hayase, S.; Toyoda, T.; Wang, R.; Yoshino, K.; Minemoto, T.; Shen, Q. Understanding charge transfer and recombination by interface engineering for improving the efficiency of PbS quantum dot solar cells. Nanoscale Horiz. 2018, 3, 417–429.
(48) Cao, S.; Wang, J.; Ma, F.; Sun, M. Charge-transfer channel in quantum dot–graphene hybrid materials. Nanotechnology 2018, 29, No. 145202.
(49) Bloom, B. P.; Liu, R.; Zhang, P.; Ghosh, S.; Naaman, R.; Beratan, D. N.; Waldeck, D. H.; Zhang, P.; Beratan, D. N. Controlling the Electron-Transfer Kinetics of Quantum-Dot Assemblies. J. Phys. Chem. C 2017, 121, 14401–14412.
(50) Graff, B. M.; Bloom, B. P.; Wierzbinski, E.; Waldeck, D. H. Electron Transfer in Nanoparticle Dyeassembled on a Colloidal Template. J. Am. Chem. Soc. 2016, 138, 13260–13270.
(51) Zhu, H.; Yang, Y.; Hyeon-Deuk, K.; Califano, M.; Song, N.; Wang, Y.; Zhang, W.; Prezhdo, O. V.; Lian, T. Auger-Assisted Electron Transfer from Photoexcited Semiconductor Quantum Dots to Molecular Species: Evidence for Trap-Mediated Transfer. ACS Nano 2017, 11, 8346–8355.
(52) Liu, R.; Bloom, B. P.; Waldeck, D. H.; Zhang, P.; Beratan, D. N. Controlling the Electron-Transfer Kinetics of Quantum-Dot Assemblies. J. Phys. Chem. C 2017, 121, 14401–14412.
(54) Chen, J.-S.; Doane, T. L.; Li, M.; Zang, H.; Maye, M. M.; Cotlet, M. 0D–2D and 1D–2D Semiconductor Hybrid Composites for Solar Cells. Nano Lett. 2014, 14, 1263–1269.
(55) Xu, Z.; Hine, C. R.; Maye, M. M.; Meng, Q.; Cotlet, M. Shell Thickness Dependence Photoinduced Electron Transfer in Hybrid Conjugated Polymer/Quantum Dot Nanocomposites: From Ensemble to Single Hybrid Level. ACS Nano 2012, 6, 4984–4992.
(56) Zang, H.; Routh, P. K.; Meng, Q.; Cotlet, M. Electron transfer dynamics from single near infrared emitting lead sulphide-cadmium sulfide nanocrystals to titanium dioxide. Nanoscale 2017, 9, 14664–14671.
(57) Zang, H.; Routh, P. K.; Alam, R.; Maye, M. M.; Cotlet, M. Core size dependent hole transfer from a photoexcited CdSe/ZnS quantum dot to a conductive polymer. Chem. Commun. 2014, 50, 5958–5960.
(58) Zang, H.; Cristina, M.; Shen, X.; Liu, M.; Camino, F.; Cotlet, M. Charge trapping and de-trapping in isolated CdSe/ZnS nanocrystals under an external electric field: indirect evidence for a permanent dipole moment. Nanoscale 2015, 7, 14897–14905.
(59) Xu, Z.; Cotlet, M. Photoluminescence blinking dynamics of colloidal quantum dots in the presence of controlled external electron traps. Small 2012, 8, 253–258.
heterojunction of PbS quantum dots and a low-bandgap polymer. J. Mater. Chem. A 2014, 2, 3978–3985.
(80) Li, C.-Y.; Wen, T.-C.; Lee, T.-H.; Guo, T.-F.; Huang, J.-C.-A.; Lin, Y.-C.; Hsu, Y.-J. An inverted polymer photovoltaic cell with increased air stability obtained by employing novel hole/electron collecting layers. J. Mater. Chem. 2009, 19, 1643–1647.
(81) Zhao, H.; Liang, H.; Gonfa, B. A.; Chaker, M.; Ozaki, T.; Tijssen, P.; Vidal, F.; Ma, D. Investigating photoinduced charge transfer in double- and single-emission PbS@CdS core@shell quantum dots. Nanoscale 2014, 6, 215–225.
(82) Park, K.; Deutsch, Z.; Li, J. J.; Oron, D.; Weiss, S. Single Molecule Quantum-Confined Stark Effect Measurements of Semiconductor Nanoparticles at Room Temperature. ACS Nano 2012, 6, 10013–10023.
(83) Empedocles, S. A.; Bawendi, M. G. Quantum-Confined Stark Effect in Single CdSe Nanocrystallite Quantum Dots. Science 1997, 278, 2114.
(84) Park, S.-J.; Link, S.; Miller, W. L.; Gesquiere, A.; Barbara, P. F. Effect of electric field on the photoluminescence intensity of single CdSe nanocrystals. Chem. Phys. 2007, 341, 169–174.
(85) Shim, M.; Guyot-Sionnest, P. Permanent dipole moment and charges in colloidal semiconductor quantum dots. J. Chem. Phys. 1999, 111, 6955–6964.
(86) Trinh, M. T.; Seir, M. Y.; Choi, J. J.; Owen, J. S.; Zhu, X. A Hot Electron–Hole Pair Breaks the Symmetry of a Semiconductor Quantum Dot. Nano Lett. 2013, 13, 6091–6097.
(87) Pelton, M.; Smith, G.; Scherer, N. F.; Marcus, R. A. Evidence for a diffusion-controlled mechanism for fluorescence blinking of colloidal quantum dots. Proc. Natl. Acad. Sci. U.S.A. 2007, 104, 14249.
(88) Frantsuzov, P. A.; Marcus, R. A. Explanation of quantum dot blinking without the long-lived trap hypothesis. Phys. Rev. B: Condens. Matter Mater. Phys. 2005, 72, No. 155321.
(89) Hwang, G. W.; Kim, D.; Cordero, J. M.; Wilson, M. W. B.; Chuang, C.-H. M.; Grossman, J. C.; Bawendi, M. G. Identifying and Eliminating Emissive Sub-bandgap States in Thin Films of PbS Nanocrystals. Adv. Mater. 2015, 27, 4481–4486.
(90) Gao, J.; Johnson, J. C. Charge trapping in bright and dark states of coupled PbS quantum dot films. ACS Nano 2012, 6, 3292–3303.