Sizing Up Excitons in Core-Shell Quantum Dots *via* Shell-Dependent Photoluminescence Blinking

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ABSTRACT

Semiconductor nanocrystals or quantum dots (QDs) are now widely used across solar cell, display and bioimaging technologies. While advances in multi-shell, alloyed and multinary core-shell QD structures have led to improved light-harvesting and photoluminescence (PL) properties of these nanomaterials, the effects that QD-capping have on the exciton-dynamics that govern PL-instabilities such as blinking in single-QDs, is not well understood. We report experimental measurements of shell-size dependent absorption and PL-intermittency in CdSe-CdS QDs that are consistent with a modified charge-tunnelling, self-trapping (CTST) description of the exciton-dynamics in these nanocrystals. By introducing an effective, core-exciton size that accounts for delocalization of charge-carriers across the QD-core and shell, we show that the CTST models both the shell-depth dependent red-shift of the QD band-gap and changes in the on/off-state switching statistics that we observe in single-QD PL-intensity trajectories. Further analysis of

CdSe-ZnS QDs, shows how differences in shell-structure and integrity affect the QD band-gap and PL-blinking within the CTST framework.

KEYWORDS

semiconductor quantum dots; core-shell nanocrystals; photoluminescence intermittency; single molecule spectroscopy; charge transfer; stochastic simulation

Exciton-dynamics play a key role in the photovoltaic and photoluminescence properties of nanomaterials, effecting their performance in a range of technologies, from solar cells and catalysis to lighting, displays and bioimaging.[1] For nanomaterials with dimensions smaller than the Bohr exciton radius and archetypically 0-dimensional, semiconductor quantum dots (QDs), quantum confinement gives rise to size-dependent properties.[2-4] In addition to size-tunable emission,[5] properties including reactivity,[6] photoluminescence (PL) stability[7] and charge-transfer[8] all depend strongly on the location of the exciton electron and hole in the QD. At sub-Bohr dimensions, mobile charge-carriers will frequently sample the QD-surface and core, as well as the host-medium surrounding the QD. As such, interfacial-states arising from unterminated bonds[9, 10] and the QD-host dielectric mismatch,[11, 12] along with trap-states on ligands[13, 14] and in the host,[15, 16] will all influence charge-carrier transport and recombination at the nanoscale.

At the single-QD level, exciton-dynamics manifest as intermittency or blinking between radiative, on-states and quenched, off-states in the temporal evolution of the PL intensity trajectory. Since the first observations of PL intermittency in QDs,[17] blinking has been the subject of extensive experimental and theoretical study and review.[18] Along with observations of intermediate grey-state emission,[19] PL enhancement,[20] fluorescence lifetime correlations[21] and memory effects,[22] the complex dynamics observed in single-QD emission provides a critical test

for any comprehensive description of exciton-dynamics in these nanomaterials. A number of models have been successful in accounting for PL blinking in QDs, from early charging-tunnelling models of Verberk *et al*.[23] and Kuno *et al*.,[24] through diffusion-controlled electron transfer (DCET) models and non-trapping hypotheses of Marcus *et al.*,[25, 26] to more recent charging and multiple-recombination center (MRC) descriptions of grey-state emission.[27-30]

Recent efforts focused on the suppression of blinking and increased tunability of QD properties have revealed additional roles that capping, charging and surface-states play in charge-carrier delocalization, trapping and recombination in QDs. Investigations of PL intermittency in CdSe nanorods have reinforced the actions of surface-states and the particle nanoenvironment in trapping both long-lived bright and quenched-states of the QD.[31] Studies on band-engineered, type-I core-shell (CdSe-ZnS) and type-II QDs (CdSe-ZnTe, CdTe-CdSe) have highlighted the effects of core-confined exciton charge-carriers in the former, and in the latter, electron-hole separation into core and shell structures, on the spectral tuning of QD emission across visible (type I) and infrared (type II) frequencies.[32] More recently, it has been shown that softening the core-shell potential in graded-shell QDs (CdSe-$Cd_xZn_{x-1}S$, CdSe-$CdSe_xS_{1-x}$-CdS), leads to enhanced exciton-delocalization,[33, 34] decreased electron-hole wavefunction overlap, suppressed Auger relaxation rates and reduced PL-quenching.[35] Time-resolved studies on single-QDs under the electrochemical control of charge on the nanocrystal, have not only revealed distinct flavours of PL-intermittency, so-called A-type and B-type blinking,[21] but also a number of exciton-states with different levels of PL-quenching.[29, 36] Most notable in the case of CdSe-CdS, is assignment of the off-state and a deeply quenched "grey-state" to positive (X^+) and negative (X^-) trion-states of the QD, respectively, where delocalization of the electron-wavefunction in the latter makes radiative recombination competitive with a suppressed Auger-quenching.

We recently advanced a charge-tunnelling and self-trapping (CTST) description of exciton-dynamics in QDs that models, not only the dielectric-host dependent blinking observed in core-shell nanocrystals and long-lived grey-states, but also PL enhancement and decay through QD-shell and core degradation.[37] In the CTST model, PL blinking was assigned to transitions between a dark, Auger-quenched, ionised, core-charged exciton-state (CX^+) and emissive, neutral core-exciton (NX^0) and ionised surface-charged (SX^+) states of the QD *via* exciton-electron (e_x) tunnelling. Intermediate grey-states and PL enhancement observed in single, core-shell CdSe-ZnS QDs were attributed to exciton-hole (h_x) tunnelling between radiative-core and dark-surface states. PL modulation was then found to be strongly dependent on the charge-state of the QD and location of the excess-hole (h^+), the band-offset of the capping material and the cap-depth.

Importantly, the kinetics of CTST (Figure 1) has been formulated explicitly in terms of macroscopic properties of the QD-host system, namely QD-size and the electrostatics of the QD-interface and the surrounding medium. More specifically, expressions for excitation, emission and Auger quenching rate constants, k_x, k_r and k_A have been derived from empirically measured QD size and band-gap relationships.[38-40] In CTST, on-off blinking is governed by the forward (+) and back (-) e_x-tunnelling rate constants, k_{ion}^{+} , k_{on}^{-} and k_{off}^{-} connecting the neutral NX^0-state and ionized states, SX^+ and CX^+, while h_x-tunnelling rate constants, k_h^+ and k_h^-, determine the equilibrium between bright, core-h_x and dark, surface-h_x fractions that further modulates PL intensities in the emissive NX^0 and SX^+-states. We note that charge-carriers in CTST are interchangeable in that e_x-tunneling between the QD-core and surface can also modulate PL-intensities in the case of hole-ejection from the QD and formation of the negative trion state. The tunnelling rate constants are defined by size-dependent, QD and charge-carrier capture cross-sections and tunnelling probabilities that are sensitive to the different barrier-lengths and heights

along the separate e_x and h_x-tunnelling coordinates. Mean tunnelling barrier-potentials are determined by valence-band (VB) and conduction band (CB) energies of the QD and offsets of the shell and surface and host-trap energies (Note S1 and Figure S1 in SI). In the CTST model, the tunnelling-electron is stabilized by the reaction-field (self-energy) it generates in the polarizable dielectric matrix (or ligands) surrounding the QD, while the excess-hole self-traps at the surface due to the reaction field produced through the dielectric mismatch at the QD-host interface.

In this article, we report experimentally measured PL intermittency in core-shell CdSe-CdS QDs, which display shell-depth dependent blinking statistics, as characterised by the on-time and off-time probability density distributions (PDDs) extracted from single QD PL-intensity trajectories. We show that a simple modification of the CTST model describing an effective QD-core "exciton radius", not only accounts for the red-shift in the first-exciton absorption with shell-thickness, but also changes in the on and off-time blinking statistics.

RESULTS AND DISCUSSION

We fabricated core-shell CdSe-CdS nanocrystals with a fixed CdSe core-size and carefully-controlled CdS capping-layer thickness, through standard colloidal synthesis routes.[41] Successive ionic layer adsorption and reaction (SILAR) was used to control epitaxial growth and number of CdS monolayers (ML) deposited on the CdSe-core.[42] For a typical series of QDs with shells ranging 0 to 4 CdS ML, the QDs exhibited clear size dependent absorption and PL emission spectra with increasing ML number (Figure 2 a). Further analysis of transmission electron micrographs (Figure 2 b) revealed size distributions (Figure 2 c) with a core-diameter 3.4 ± 0.2 nm and shell diameters of 4.1 ± 0.3, 4.9 ± 0.3 and 5.9 ± 0.2 nm. We found these sizes consistent with the 0, 1, 2 and 3 cycles of CdS ML growth on the CdSe-core, when a CdS lattice spacing[43] of 0.36 nm

(Figure S2 in SI) is used to determine ML numbers 0, 0.9, 2.1, 3.5 ML from the core and shell diameters.

Red-shift of the first-exciton with increasing shell thickness is accounted for by leakage (exponential decay) of the e_x and h_x-wavefunctions into the shell, which will depend on the conduction-band (CB) and valence-band (VB) offsets of the capping-medium relative to the core-material. In particular, for CdSe-CdS the CB-offset is of the order 0.3 eV allowing e_x-delocalisation beyond the QD-core into the shell, with the larger exciton-radius giving rise to a lower QD band-gap. For core-only QDs the band-gap scales quadratically with the inverse of the QD-core radius, R_c, due to quantum confinement of the exciton.[4] On this basis, for core-shell CdSe-CdS QDs, we define an effective radius of confinement, the "exciton-radius" R_x, using a simple relationship between QD diameter and the first-exciton wavelength.[39] In this case, the effective radius (Figure 2 d) is derived from the empirical fit $E_{QD} = 1.74 + 0.45/R_x^2 + 0.5/R_x$,[37] (Figure S3 in SI), where $E_{QD} = hc/\lambda$ and λ is the wavelength of the first-exciton absorption peak, which we found to scale near-linearly at low CdS ML number (Figure 2 d inset). For our CdSe-CdS QDs, the dependency of the band-gap on R_x gives a simple functional relationship between the effective, exciton-radius and CdS ML number (Figure 2 e).

PL intensity trajectories of single-QDs were recorded for our CdSe-CdS nanocrystals with varying shell-thickness over the range 0 to 3.5 ML. Trajectories were observed to shift from largely PL-off to mostly PL-on with increasing cap-depth (Figure 3 a), a feature captured in the intensity histograms (Figure 3 b) of over 10^4 data points (>1000 s at 80 ms per PL integration). Trajectories were analysed for switching between bright, PL-on and dark, off-states using a 2σ threshold above the dark-state mean intensity and on- and off-time PDDs constructed from over 50000 events from 25-30 QDs. We note that long intensity trajectories (>20 min), with minimal

PL enhancement or decay are essential for an effective analysis of blinking statistics.[44, 45] Furthermore, while some variation in the PL-on state intensity is evident in the QD-trajectories analysed, intermediate, grey-state emission was not observed at sufficiently discrete and distinct levels to permit a separate analysis from on-off state blinking statistics. Significantly, we observed measurable differences between on- and off-time PDDs over the 0, 0.9, 2.1 and 3.5 CdS ML range (Figure 3 c). PDDs were fitted with the ubiquitous truncated power-law (TPL), $P(t) = At^{-\alpha}e^{-t/\tau_c}$, used to describe the decay (α) and cut-off (t_c) in on/off blinking events in single-QDs, organic-dyes and fluorescent proteins.

Qualitatively, off-time PDDs were seen to change little over the sample range, while on-times exhibit increased truncation of the PDD and a decrease in the power-law decay with shell thickness. The latter trend is more evident in the accumulated histograms of exponents extracted from fitting the TPL to the PDDs from individual QDs, which shift markedly to lower α_{on} and more weakly to higher α_{off} with increasing CdS ML number (Figure 3 d and Table 1). On the simplest level, observed trends in the intensity trajectories and power-law exponents are consistent with a model of exciton charge-carrier tunnelling through a CdS shell-barrier of increasing length, where QD charging and hence PL quenching is increasingly less likely and longer on-times increasingly more likely. On a more complex level, on-time PDDs exhibit decreasing truncation times, τ_c, with increasing cap-depth (Table 1), a trend that appeals to a more detailed examination of the exciton-dynamics for explanation.

We used the modified CTST model in a standard stochastic simulation algorithm (SSA) to generate single-QD intensity trajectories from which on/off-time PDDs were extracted and analysed using the TPL. In the modified-CTST, all former core-size dependent parameters such as the rate constants, k_x, k_r and k_A and tunnelling constants k_{ion}^{+} , k_{on}^{-}, k_{off}^{-} and k_h^{+} and k_h^{-}, are made

dependent on R_x (Note S1 in SI). The exciton-radius, R_x itself is derived from the first exciton absorption (Figure 2 a) for each 0 to 3.5 ML CdS capped QD, as outlined above. In CTST, following ionisation of the QD *via* e_x-tunnelling, the branching ratio between CX^+ and SX^+-states is determined by the probability of h^+-trapping on the QD-surface. This was made dependent on the surface to volume atom fraction to reflect the scaling of trap densities on a per atom basis. Here, we retain the general form, $p_s = 4a\,R_s^2/R_c^3$, where $R_s = D/2$ is the shell-radius derived from the TEM-PSD (Figure 2 c), R_c is the core-radius (R_s at 0 ML) and a is an atomic radius, assumed here to approximate half the CdSe bond-length (~ 0.26 nm).[37] Core-CdSe and CdS-shell band-energies were taken from literature values[46] and all other parameters are matched closely to experimental conditions; notably the excitation wavelength 473 nm and intensity 0.1 $kWcm^{-2}$ ultimately determine the excitation rate through an R_x dependent cross-section.[39] Given the limits of stochastic uncertainty, on- and off-time PDDs produced within the CTST-framework show good qualitative agreement with experiment (Figure 3 e).

Further analysis of the PDDs with the TPL showed strong correlations between experimental exponents and (on-time) cut-off times and those obtained from CTST simulations (Figure 4 a-c and Table 1). In particular, α_{on}, shows the same decrease with increasing CdS ML number, while α_{off} was found near-constant over the shell-thickness range. Most significant is the trend in the cut-off times, τ_c where both the model value and the TPL value obtained from stochastic simulation compared-well with experiment. In CTST the on-time cut-off is given by $\tau_c = \Gamma_{on}^{-1}$, where Γ_{on} is the truncation rate[37]

$$\Gamma_{on} = k_{xx}|F|^2 \left(\frac{r_h}{R_x}\right)^3 e^{-E_a/kT} \quad (1)$$

Here $k_{xx} = k_x f_c$ is biexciton formation rate, where f_c is the core-exciton fraction (Note S1 in SI) and $F = 3\varepsilon_s/(2\varepsilon_s + \varepsilon_{QD})$, is the local-field factor for a QD of dielectric constant ε_{QD} in a surrounding medium of permittivity ε_s. The cubic term defines a reduce probability of electron recombination at the surface-localised h^+-trap of radius, r_h, compared with the core-exciton and the Arrhenius term accounts for a weak temperature dependence.[25, 47] The expression is consistent with intensity dependent studies of cut-off times that identified a role for the biexciton in QD blinking.[48] In the CTST-model, quenching of the surface-localized h^+ occurs *via* "hot" electron recombination that competes with radiative recombination with a residual core-h_x, where the delocalized-electron is produced from fast Auger relaxation of the biexciton-state SXX^+ (Figure 1d and Figure S4 in SI). We note that a negative, core trion-state fraction can be formed in the SXX^+ state, with both h^+-trapped and h_x-sampling the surface. In this case we assume, radiative recombination competes favourably with the Auger-excitation of the excess-electron, due to delocalization of the electron wavefunction and a reduced electron-electron-hole overlap.[36] The probability for h^+-quenching is then determined by the ratio of e_x -h^+ and e_x-h_x "overlap" volumes $(r_h/R_x)^3$. In simulations, the cut-off rate is evaluated using a QD-size dependent dielectric constant,[49] ε_{QD}, with the dielectric constant of the QD-surround matched to that of the organic capping layer (octadecylamine), $\varepsilon_s = 2$. For the experiments performed under air the organic-ligand is assumed largely collapsed and dominates QD-surface coverage, such that the QD-ligand dielectric mismatch dictates the self-energy of the surface-hole, rather than QD interactions with the glass substrate or air. To restrict modification of the CTST-model to a single change in definition of the QD-core radius, we maintain the hole-trap radius defining the localization of h^+ at the QD-surface at $r_h = 0.3$, as per previous studies.[37] However, it should be recognized that the cut-off rate constant defined by Equation 1 will be sensitive to exact values of the h^+-trap size and

the dielectric constant at the QD-host interface. For example, increasing the dielectric constant at the QD-surface to that of the glass substrate, $\varepsilon_s = 3.8$, requires a 1/3 reduction in the trap radius to obtained cut-off times within 50% of those obtained for $\varepsilon_s = 2$ and $r_h = 0.3$ nm (Table 1), although the trend to shorter times with increasing shell-thickness remains consistent. We reiterate that for simulations presented here, substitution of the effective exciton-radius, R_x, in all QD-core radius dependent rate constants represents the only modification to the CTST model. For our experimental conditions, the modified-CTST model gives excitation, emission and Auger rate constants with orders of magnitude, $k_x \sim 10^5$ s^{-1}, $k_r \sim 10^7$ s^{-1} and $k_A \sim 10^{10}$ s^{-1}, respectively, a forward e_x-tunnelling constant of order, $k_{ion}^{+} \sim 10^6$ s^{-1} and back-tunnelling constants, $k_{on}^{-} \sim 10$ s^{-1} and $k_{off}^{+} \sim 100$ s^{-1} (for a fixed tunneling length of 1 nm) and an exciton-hole tunnelling-equilibrium constant varying as $k_h^{+}/k_h^{-} \sim 1$ to 100 (in the SX^+-state) with increasing shell thickness (Table S1 in SI).

To understand the trends observed in our experimental TPL exponents, $\alpha_{on/off}$, we compared average on and off-times with switching rates between the bright, SX^+ and dark, CX^+ states of the QD. For a non-stationary, on-off blinking process, the power-law component of on- and off-time distributions is strictly invariant with a mean dependent on the range of times analysed. To compare PDD decays across all shell-thicknesses, we calculated mean on(off) durations between a minimum time, t_{min}, defined by the photon integration time (80 ms) and a maximum, t_{max}, defined by the shortest cut-off time across all cap-depths (1.9 s for on-times and 69s for off-times), where the mean is given by $\langle\tau\rangle = (1-\alpha)/(2-\alpha) \cdot (t_{max}^{2-\alpha} - t_{min}^{2-\alpha})/(t_{max}^{1-\alpha} - t_{min}^{1-\alpha})$. Thus, for fixed t_{min} and t_{max}, the mean residence time increases as $(\alpha-1)/(2-\alpha)$ with decreasing α, for $1 \leq \alpha \leq 2$. We found the trends in both mean on- and off-times, $\langle\tau_{on}\rangle$ and $\langle\tau_{off}\rangle$, matched closely the expected trend in mean residence times of the SX^+-state and CX^+-state derived from the CTST-

model (Figure 4 d-e). The mean residence time then derives from the probability, p_s, of h^+-trapping on the ionised QD-surface and the mean electron-recombination rate in each charged-state. Specifically, for switching between SX^+ and CX^+ it can be shown (Note S2 in SI) that $\langle\tau_{on}\rangle^{-1} = (1-p_s)\langle k_{on}^-\rangle$ and $\langle\tau_{off}\rangle^{-1} = p_s\langle k_{off}^-\rangle$, where $\langle k_{on}^-\rangle$ and $\langle k_{off}^-\rangle$ are mean tunnelling rates constants from the host-trap to the charged-QD derived from[37]

$$k = A\frac{\sigma}{4\pi R_0^2}e^{\left(-l\sqrt{8m\beta}/\hbar\right)} \tag{2}$$

Here, the tunnelling probability is dependent only on the tunnelling length, l, and mean barrier height β, while the attempt-to-escape frequency, A, capture cross-section, σ, and electron-trap to QD-hole, centre-to-centre distance, R_0, are all sensitive to the size of the QD-core or h^+-trap. In particular, for the localize surface-h^+ in SX^+, $\sigma = \pi r_h^2$, while for the core-h^+ in CX^+, $\sigma = \pi R_x^2$.

For electron-return in the on-state, SX^+, it can be shown that the increase in mean on-time $\langle\tau_{on}\rangle$ with increasing R_x (Figure 4 d) derives from the increase in the surface h^+-trapping probability, p_s, with shell thickness and surface-to-core atom number ratio. The effect is compounded by a back-tunnelling constant, $\langle k_{on}^-\rangle$, that decreases with increasing exciton size as the confinement energy lowers. In the case of electron-return in the off-state, CX^+, the increase in p_s with the shell radius now results in a strong decrease in the mean off-time $\langle\tau_{off}\rangle$ with increasing R_x (Figure 4 e). In this case the decrease is moderated by an e_x-tunnelling constant, $\langle k_{off}^-\rangle$, that increases with R_x through the QD capture cross-section. We note that the origin of the power-law exponent in CTST differs from existing charge-tunnelling models that have shown that, for switching between neutral-on and charged-off states of the QD, $\alpha = 1 + \sqrt{\phi_f/\phi_b}$, where ϕ_f and ϕ_b are forward and back e_x-tunnelling barriers, to and from the host-trap, respectively.[23, 24] Our results show α_{on} and α_{off} in

CTST derive largely from switching between the dark-CX^+ and bright-SX^+ states with the neutral NX^0-state, a transient intermediate. Since electron recombination occurs from an external trap in both charged on and off-states, both on and off-times will be power-law distributed, due to the range of back-tunnelling rates that result from a random distribution of electron-trap distances from the QD.

In a final analysis of TPL cut-off times for on-time PDDs, we found the increasing truncation rate observed experimentally to be strongly dependent on biexciton formation within the CTST mechanism for SX^+-state quenching (Figure S4 in SI).[37] Here, k_{xx} approximates an $R_x^{6.3}$ dependence (Figure 4 f) through a QD-volume and band-gap dependent absorption cross-section, a weak inverse size-dependence of the radiative rate and a reduced core-exciton fraction due to h_x-tunnelling (Figure S5 in SI). The biexciton rate and h^+-quenching probability, $(r_h/R_x)^3$, combine to give a truncation rate scaling as $\Gamma_{on} \propto R_x^{3.3}$, which maps to the decrease in τ_c with increasing shell thickness (Figure 4 c) through the dependence of R_x on CdS ML number (Figure 1e). We find predicted values of the cut-off times match-closely experimental values (within error) across the range of CdS MLs analysed. We note that cut-off times obtained from PDDs derived from simulations show divergence at the bare, core-only QD (0 ML), with a larger than predicted cut-off time. A subtle interplay between slow electron recombination in both SX^+ and CX^+ states and equally slow h^+-quenching in SX^+, tends to broaden the distribution of truncation rates and lengthen mean cut-off times across individual simulations. We further recognise that the small sampling of truncation events at long times, leads to large fitting errors of the TPL to PDDs from both simulation and experiment. However, model values (Equation 1) show good quantitative agreement with experiment and the trend of decreasing cut-off times with increasing CdS ML number is consistent between experiment and simulation. Interestingly, the size-dependency of the

bright, SX^+-state cut-off here compares well with other measures of PL-quenching reported elsewhere. For example, Early *et al.* have related on-time power-law truncation in CdS-ZnS QDs to a biexciton driven process, with an ionisation probability from the radiative neutral-state that scales as $R^{-3.5}$ and correlates with the decreased electron-hole wavefunction overlap in the ZnS shell with increasing QD-core radius.[50] Blaudeck *et al.* have shown that the PL-quenching rate in bulk, colloidal CdSe-ZnS QDs in toluene (at a fixed optical density, *i.e.* fixed excitation rate, k_x) decreases with a similar dependence on QD-core diameter, approximately $(2R)^{-2.8}$, in the presence of a pyridyl-functionalised porphyrin surfactant molecule.[51] In this case, the molecule acted as a charge-carrier trap and probe of exciton-wavefunction leakage at the QD-surface, with the probability density of electron-wavefunction overlap at the probe displaying the same QD-core size dependency as the PL-quenching rate. Despite, the similar trends in on-time truncation and PL quenching with QD-size, the origin of the size-dependency differs from CTST in that cut-off is generally attributed solely to ionisation of the neutral, radiative-state to an Auger-quenched, core-charged state rather than a quenching of the bright, surface-charged state. It may be that both mechanisms play some role in power-law truncation, along with the cut-off that will arise from a limited set of trap-states in a MRC description blinking.

To conclude we compare our results with previous studies on shell-dependent QD blinking.[52-54] Wang *et al.*[52] have examined blinking in multilayered CdSe/CdS/$Zn_xCd_{1-x}S$/ZnS QDs, reporting shell-thickness dependencies of the power-law exponents that align-well with our measurements. In particular over the same range 0 to 3.5 ML shells, α_{on} was found to decrease (1.35 to 1.0) and α_{off} increase (1.4 to 2) with increasing cap-depth. Furthermore, measurement of the power dependence of truncation rates in the on-time PDDs of these QDs, showed a trend to higher rates and shorter cut-off times with increasing shell-thickness, consistent with observations report here.

Most recently, Gao *et al.*[53] have examined shell-dependent transitions between on, grey and off-states in the PL emission from CdSe-CdS QDs. Although the study focused on the resolution of different exciton-states through the correlation of PL lifetimes with bright, intermediate and dark-state emission intensities, on and off-time blinking statistics are presented that show similarities with our data. Notably, on-time and off-time (log-log) PDDs trend to lower and higher gradients, respectively, with increasing shell-thickness (0-4 CdS ML), although no explicit analysis of the TPL parameters was performed and trends in the truncation-times are less easy to discern in the data. We also note that the diffraction-limited, pulsed-laser excitation intensities (1-10 μW) used in these experiments were some 5-50 times larger than the CW laser power-densities used in our experiments. Significantly, the authors develop a model to account for multi-level emission observed at these moderate to high excitation rates, which we discuss in relation to CTST in our concluding remarks.

In earlier studies, Heyes *et al*.[54] reported TPL parameters from the analysis of blinking in ZnS capped CdSe QDs in the range 0 and 7 ML. On and off-time exponents, as well as the on-time cut-off, were found to vary ($\alpha_{\mathrm{on}} = 1.9 \pm 0.1$, $\alpha_{\mathrm{off}} = 1.6 \pm 0.1$ and $\tau_{\mathrm{c}} = 5.5 \pm 1.4$ s), with little or no obvious correlation with shell-thickness. Here, we note that ZnS shells tend to lack the integrity that CdS shells offer due to lattice mismatch and lead to less reliable blinking statistics. Interestingly, in experiments we have performed on CdSe-ZnS QDs, we observed a first-absorption band-shift with QD-size (Figure 5 a-b), as well as blinking statistics (Figure 5 c-e) that display similar trends to CdSe-CdS QDs, but with different shell-thickness dependencies. For example, the red-shift in QD band-gap with shell-radius, $R_{\mathrm{s}} = D/2$, is smaller in ZnS than CdS (Figure 6 a), which would appear consistent with a larger CB-offset that constrains leakage of the electron-wavefunction into the ZnS-shell and the lowering of the exciton-energy. On the other

hand, on-time PDDs show a shortening of cut-off times, τ_c, with increasing shell thickness that is more consistent with a reduced shell-radius and effective ZnS ML number that matches closely that of CdS (Figure 6 b). We find through simulation, that parameterizing the CTST model with ZnS shell-thicknesses derived from ZnS deposition cycles in the synthesis and TEM-PSDs, along with the correct CdSe to ZnS, CB and VB-offsets (1.4 eV and -0.6 eV) from the literature,[55] does not reproduce our experimental TPL parameters well. Most significant, is a large, over-estimation of the cut-off times with large ZnS ML number (Figure 6 b inset). On closer inspection of the EM images, we observed a significant loss of structure in the ZnS shell compared to CdS (Figure 6 c and 6d and Figure S6 in SI). The former displays a largely irregular and anisotropic surface in contrast to the well-ordered surface of the latter, which can been attributed to differences in the core-shell lattice mismatch.[56] Given the evident loss of "complete" monolayers in the ZnS shell, we propose an effective shell-thickness to account for cut-off times close to those observed for CdS. For simplicity, we use the shell radius dependence of the first-exciton wavelength in "closed-shell" CdSe-CdS QDs (Figure 6 a) to derive the effective R_s and hence ZnS ML number in the CdSe-ZnS QDs. Impressively, by using the reduced number of ZnS MLs and shell-thickness, predicted cut-off times were found to align closely with experiment, trending correctly to shorter times with increasing ZnS ML number (Figure 6 b).

Within the CTST mechanism for SX^+-state quenching, biexciton formation depends strongly on the core exciton-fraction. In the case of a reduced-shell radius, the effective core-exciton radius increases rapidly with ZnS ML (Figure 6 e) such that k_{xx} scales strongly with R_x (Figure 6 f), as per CdS capped-QDs. Here, h_x-tunnelling between the QD-core and surface has little influence on the core-exciton fraction due to small tunnelling lengths, $d = R_s - R_x$, between the effective-core and shell-surface. For "over-sized" shells, the reverse is true; R_x increases slowly with ZnS ML

number and the h_x-tunnelling length rises steeply with shell-thickness. The core-exciton fraction is now significantly reduced due to a shift in the h_x-equilibrium towards the QD-surface. The shift arises from the mismatch in tunnelling barriers to and from the surface, where h_x-h^+ repulsion lowers the barrier-height to forward-tunnelling and raises the barrier to back-tunnelling from the surface. The net effect is significantly reduced biexciton formation rates with increasing R_x (Figure 6 f) and consequently decreased h^+-quenching rates with shell-thickness. This same mechanism of core-exciton modulation forms the origin of grey-states and PL enhancement in CTST.[37] We note that even for a reduced, effective ZnS shell or indeed "complete" CdS-shells that the red-shift of the first exciton will saturate at some maximum wavelength for large shell thicknesses (~620 nm for 19 CdS ML),[57] beyond which R_x will remain constant as R_s grows and the tunneling-length, d will increase linearly with shell-depth. Again the core-exciton fraction, the biexciton formation rate and ultimately the on-time truncation rate are all lowered as for the "over-sized" ZnS shells. The effect here is that the truncation of on-times will peak at some saturating cap-depth and decline at "giant" shell-thicknesses. Such an effect explains our observations of increasing truncation at small CdS ML numbers and may account for previous observations of little or no-truncation at long on-times (as per off-times) in so-called "giant" QDs with large (>16) CdS ML numbers.[58]

CONCLUSIONS

In sum we have performed a systematic study on shell-thickness dependent PL intermittency in core-shell QDs, the results of which are described well within a modified CTST framework of exciton-dynamics. The red-shift in the first exciton absorption with increasing shell-thickness is associated with e_x-delocalization into the QD-shell and motivates the introduction of an effective exciton-radius, R_x in the CTST-model that falls between core and shell radii and naturally accounts

for the QD size-dependent band-gap. The effective radius was also found to adequately describe the size-dependent rate-constants in our stochastic simulations of single QD intensity trajectories that reproduce the shell-dependent blinking statistics we observe in both CdSe-CdS and CdSe-ZnS QDs. Analysis of the distributions of PL-on and off-state dwell-times in both experimental and simulated QD trajectories using the ubiquitous truncated power-law, revealed distinct trends in the TPL parameters, α_{on}, α_{off} and τ_{on} that were readily accounted for in the context of the CTST model. The observed trends to longer on-times and shorter off-times with shell thickness are attributed to the decrease in the rate of transition out of the bright, SX^+-state, $\langle\tau_{\mathrm{on}}\rangle^{-1}$ and increased rate out of the dark, CX^+-state, $\langle\tau_{\mathrm{off}}\rangle^{-1}$, that follow closely the increased probability of excess h^+-trapping at the QD-surface with an increase in surface-area. The increasing truncation observed in the power-law distribution of on-times is rationalized in the CTST-model by quenching of long dwell-times associated with the surface-charged, PL-on state, by hot-electron recombination with the excess, surface-hole. The Auger-mediated process provides an alternative mechanism for power-law truncation, but supports a QD-size dependency (R_{x}^{-3}) in the cut-off rate (at fixed biexciton formation rate), that closely matches that of the QD-ionisation probability and PL quenching rates measured elsewhere.[50, 51] Ultimately on-time truncation in CTST is controlled by the exciton charge-carrier equilibrium constant, $k_{\mathrm{h}}^{+}/k_{\mathrm{h}}^{-}$ between the QD-core and surface that determines the core-exciton and biexciton fractions. The dependence of this equilibrium constant on shell-thickness can be loosely compared to that defined by charge separation (or electron transfer, ET) and recombination (or hole transfer, HT) rates derived from PL-lifetimes by Zhu *et al.*[59] in core-shell-acceptor (CdSe-ZnS-anthraquinone) systems. Both ET and HT rates were found to decrease as $k(d) = k_0 e^{-\beta d}$ with increasing shell thickness d, but with different transmission coefficients $\beta = 0.35$ and $\beta = 0.91$, respectively. In this case, the equilibrium between charge

separation and recombination scales, as $k_{\mathrm{ET}}/k_{\mathrm{HT}} \propto e^{0.56d}$, and will thus be pushed toward the charge-separated state with increasing shell thickness. The dependence is analogous to the exponential growth in $k_{\mathrm{h}}^{+}/k_{\mathrm{h}}^{-}$ with shell-thickness that we find in CTST (Supplementary Table S1).[37] Finally, we note that the modified-CTST model presented here, does not formerly differentiate between the different degrees of confinement of the electron and hole in CdSe-CdS QDs. The effective exciton-radius, R_{x}, then provides only a measure of exciton-delocalization beyond the QD-core (R_{c}) but within the QD-shell (R_{s}) radii that is consistent with our observations of a first-exciton red-shift *and* increased on-time power-law truncation with shell-thickness. Recasting the CTST-model to include explicit e_x-tunnelling between core and surface states of the QD, with suppressed h_x-tunnelling to reflect greater hole-confinement, may provide greater physical insight into individual charge-carrier dynamics as well as the flexibility to model more complex PL-phenomena in different QD-morphologies and heterostructures. For example, in the recent shell-dependent PL studies by Gao *et al.*,[53] a compelling scheme has been proposed to account for bright, grey and off-states that include; dark, biexciton and charge-separated states; intermediate, charged-surface, core-trion states; the neutral, PL-on state and an additional, bright surface-charged, neutral-core QD-state. The bright-state was associated with the measurement of a short PL-lifetime (< 1 ns), along with neutral-state (~20 ns), during transient periods of strong emission in the QD PL-intensity trajectory. The reduced radiative-lifetime was attributed to increased overlap of the e_x and h_x-wavefunctions in the core, due to an enhanced confinement of the exciton-electron induced by the repulsive-field of a surface-trapped electron. Interestingly, theory on core-only QDs, suggests e_x and h_x-wavefunctions are rather polarized in the presence of a charge trapped externally to the QD, with reduced overlap and emission from the NX^0-state.[49] In addition, both positive, CX^+ and negative CX^- trion-states have been shown to exhibit reduced

radiative recombination probabilities compared to NX^0, due to charge-carrier correlations; in the former, due to hole-hole repulsion and in the latter, due to a weaker but still effective, electron-electron correlation.[60] While it is evident that charge-carrier interactions play an important role in QD exciton-dynamics, effects of carrier-localization (*via* trapping) and delocalization (*via* tunnelling) on the polarization and separation, or conversely, enhanced confinement of charge-carrier wavefunctions in core-shell QDs are less well understood. Incorporating these effects in the CTST-model, along with additional ultra-fast carrier relaxation processes that have been identified in recent time-resolved transient absorption experiments,[61] will ultimately provide a more complete description of exciton-dynamics in QDs and other nanomaterials.

MATERIALS AND METHODS

Chemicals. Cadmium oxide (CdO) 99.5% trace metals basis, stearic acid (SA) 95% reagent grade, 1-octadecene (ODE) 90% technical grade, octadecylamine (ODA) 90% technical grade, trioctylphosphine (TOP) 90% technical grade, sulfur 99.5%, oleic acid (OA) 90% technical grade, zinc oxide (ZnO) 99% ACS reagent were sourced from Sigma Aldrich. Selenium 99.999% 200 mesh was sourced from Alfar Aesar. Ethanol, chloroform and *n*-hexane were sourced from VWR. Chemical were used without further purification.

CdSe core synthesis. CdSe QDs were synthesised according to a modified literature procedure.[41] A trioctylphosphine-selenide (TOP-Se) stock solution was first prepared by dissolving Se shot (0.157 g) in TOP (2 ml) in a round-bottom flask (RBF) at room temperature under rapid stirring. A three neck RBF (25 mL), equipped with condenser, stir bar, rubber septa and thermocouple (Eurotherm 2116) was charged with CdO (25 mg), SA (0.22 g) and ODE (3

mL). The flask was evacuated on a schlenk line, heated to 80 ºC for 20 minutes stirring at 800 rpm, placed under argon and heated further to 250 ºC. The formation of cadmium stearate was indicated by the mixture becoming clear and colourless. The solution was cooled to room temperature, followed by the addition of ODA (1.60 g) and ODE (5 mL). The mixture was again heated to 80 ºC under vacuum for 20 minutes, placed under argon and heated to a higher 270 ºC. The temperature was allowed to stabilise before the TOP-Se stock solution (2 mL) was rapidly injected. The reaction was allowed to proceed at 250 ºC for 2 minutes before passively cooling to room temperature. The deep orange/red viscose mixture was dissolved in chloroform before adding ethanol to precipitate the nanocrystals. The cloudy suspension was centrifuged at 3700 rpm for 20 minutes (Heraeus Multifuge 3S) and the supernatant decanted. The remaining QD pellet was washed with ethanol before dissolving the QD product *n*-hexane.

CdS shell synthesis. Epitaxial shell growth was performed according successive ion layer adsorption reaction (SILAR) methods described elsewhere in the literature.[42] A two neck RBF (50 mL) was charged with CdO (93 mg), OA (2.3 mL) and ODE (7 mL). The system was equipped with a condenser, stir bar, rubber septa and thermocouple and filled with argon before heating to 250 ºC under rapid stirring. After the solution turned clear and colourless it was allowed to cool to 100 ºC and kept under argon until required. To a single neck RBF, sulfur (20 mg) and ODE (6 mL) was added, the mixture placed under argon and heated to 165 ºC with continuous stirring until the solution went clear and colourless. The flask was then cooled to room temperature and kept under argon until required. Finally ODA (1.0 g), ODE (4 mL) and CdSe cores in n-hexane (3 mL) were loaded into a three neck RBF and the flask evacuated at room temperature to remove low boiling point solvents. The temperature was gradually increased up to 100 ºC and left under

vacuum for 30 minutes before an argon atmosphere was restored. The temperature was increased to 235 ºC for precurssor injection. Shell growth was calculated according to the methodology of Li *et al*.[42] The initial CdSe concentration may be estimated from the Beer-Lambert law and an empirical fitting function.[39] Successive cadmium and sulfur precursor injections were added at intervals of 20 minutes until the desired shell thickness had been achieved. The mixture was cooled to room temperature and dissolved in chloroform before adding ethanol to precipitate the core-shell CdSe-CdS QDs. The suspension was centrifuged at 3700 rpm for 20 minutes, the supernatant decanted and the recovered solid washed with ethanol before re-dispersing in *n*-hexane.

ZnS shell synthesis. ZnO (80 mg), OA (2.5 mL) and ODE (7.5 mL) were added to a two neck RBF (50 mL), equipped with a condenser, stir bar, rubber septa and thermocouple. Under argon the flask was heated to 300 ºC with rapid stirring and kept at temperature until a clear colourless solution was formed. The flask was then cooled to 100 ºC and kept under argon until required. The addition of ZnS capping layers *via* injections of the zinc and sulfur precursors followed the same procedure for the CdS capping described above.

Single molecule measurements. Fluorescence measurements were carried out using a modified inverted microscope (Nikon, Eclipse TE2000–U, Japan) operating in objective-type total internal reflection (TIRF) mode. A 473 nm CW laser (Scitec Instruments, UK) was coupled through the objective lens (Nikon, Plan Apo, 60_, NA 1.45, Japan) to the sample *via* a dichroic beamsplitter (Semrock, FF509-Di01, USA). The excitation beam was passed through a $\lambda/4$ Fresnel rhomb and made to internally reflect at the sample using a 200 mm plano-convex TIRF lens that focused the laser off-axis at the back focal-plane of the objective lens. For PL intermittency experiments the

TIRF lens was adjusted to obtain an excitation footprint approximately 50 μm in diameter with an intensity of 100 Wcm^2, accounting for near-field enhancement. QD fluorescence collected by the objective was passed through the dichroic filter and a second bandpass filter (Semrock, Brightline 609/54, USA) before detection on a watercooled ICCD camera (Princeton Instruments, PI-Max 512 GenIII). Image-stacks were recorded (μManager, USA) with 80 ms integration per frame (12.5 fps) for up to 20-30 minutes providing typically 15000-22500 frames per movie of QD blinking. Prior to QD deposition the QD concentrations were adjusted to achieve surface densities of approximately 0.1 QD/μm^2 to ensure good spatial separation of single-QDs. Coverslips (Menzel Glaser, 22×40, #1.5, EU) were ozonated for 30 minutes (Novascan, PSD Series, USA) to remove residual fluorescence prior to QD deposition. Samples were prepared by spin-coating the dilute solutions onto a coverslip at 3000 rpm. Focus drift during acquisition was minimised using an active feedback loop.[37] The return TIR beam was projected onto a CMOS camera (Thorlabs, DCC1645C, UK) and the xy-displacement of the beam image correlated with the z-focus of the objective lens. Focus was maintained using a motorized focus drive (Prior Scientific, PS3H122, UK) and an automated macro (ImageJ, USA).

Image processing and analysis. Image-stacks of QD movies were processed (ImageJ, USA) to extract single-QD PL intensity trajectories PL-on and off-time using standard procedures.[37] A threshold was set equal at 2σ above the dark-state mean, typically corresponding to the minima in the intensity histogram of bright and dark states. The on and off-times were extracted for between 25-30 individual QDs for each shell-thickness. The on and off-time probability density distribution (PDD) for each QD was calculated according to $P(t_i) = 2N_i/[(t_{i+1} - t_i) + (t_i - t_{i-1})]$, where N_i is the number of occurrences of a given on/off event of duration t_i , while t_{i+1} and t_{i-1} are

durations of the proceeding and preceding events respectively. Each recorded PL-trace covered 20-30 minutes, providing 1000-3000 on/off switching events, although we note thick-shells typically showed numbers of blinking events at the low end. On and off-time PDDs for individual QDs were fitted with the truncated power (TPL), $P(t) = At^{-\alpha}e^{-t/\tau_c}$, by varying parameters A, α and τ_c using a Levenberg-Marquardt algorithm for non-linear least-squares minimisation (Origin 8, OriginLab Corp., USA).

UV-Vis absorption, PL emission. UV-Vis data was collected on a ThermoSpectronic UV-Vis 300 at a scan speed of 240 nm/min. PL information was obtained using a PerkinElmer LS 45 fluorescence spectrometer at a scan speed of 500 nm/min exciting at 470 nm. The photomultiplier tube was set to 650 V and the excitation and emission slits were set at 10.0 nm.

TEM, SAED, HRTEM, HAADF and STEM-EDX. A solution of the QDs for each core-shell composition studied was drop-cast onto a carbon-coated copper TEM grids (Agar Scientific, Formvar/Carbon on 400 Mesh Copper). Low resolution size distribution TEM was conducted using a Hitachi-7100 operating at an accelerating voltage of 100 kV using a LaB6 electron gun. The microscope was coupled to an axially-mounted Gatan Ultrascan 1000 CCD camera. SAED patterns were captured using a JEOL JEM-1400Plus at 120 kV and collected on a Gatan Orius SC1000 CCD camera. High-angle annular dark field (HAADF)-STEM, high-resolution TEM (HRTEM) and EDX data were acquired using a FEI Osiris TEM equipped with a Schottky X-FEG gun and a Super-X EDX system. Spectrum images (SIs) were acquired using a focused electron probe scanned across selected regions of interest. SIs provided both structural information from electron scatter on the high HAADF detector and composition from X-rays emitted in the local

electron beam volume. The resulting EDX SI comprised a three-dimensional data set, with *xy* locating the probe position and *z* corresponding to the X-ray energy. SIs were acquired with a probe current of 0.7 nA and acceleration voltage of 200 kV. Spatial sampling was between 0.5 and 1 nm/pixel, with a dwell time of 200 ms/pixel. Data acquisition and elemental mapping was perform using Tecnai imaging analysis (TIA) software.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at http://pubs.acs.org.

Additional information includes a details of the CTST model, rate equations, steady-state solutions and definitions of the rate constants, analysis of mean residence times in on- and off-state. Supplementary figures show reaction coordinates used in the CTST model, HR-TEM data, the size-dependent QD band-gap, absorption cross-sections, excitation rates and exciton-fractions defined in the CTST model, HAADF and EDX data for CdSe-CdS and CdSe-ZnS nanocrystals.

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Author Contributions

M. Osborne conceived the research, developed the stochastic simulation algorithm and CTST-model, conducted simulations and contributed to the writing of the manuscript. A. Fisher conducted all synthetic procedures and characterisation of QDs including electron microscopy, single molecule microscopy and PL intermittency analysis. A. Fisher contributed experimental data and details of methods in the manuscript.

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REFERENCES

(1) Kovalenko, M. V.; Manna, L.; Cabot, A.; Hens, Z.; Talapin, D. V.; Kagan, C. R.; Klimov, V. I.; Rogach, A. L.; Reiss, P.; Milliron, D. J.; Guyot-Sionnnest, P.; Konstantatos, G.; Parak, W. J.; Hyeon, T.; Korgel, B. A.; Murray, C. B.; Heiss, W., Prospects of Nanoscience with Nanocrystals. *ACS Nano* **2015,** *9,* 1012-1057.

(2) Efros, A. L.; Efros, A. L., Interband Absorption of Light in a Semiconductor Sphere. *Sov. Phys. Semicond.* **1982,** *16,* 772-775.

(3) Ekimov, A. I.; Onushchenko, A. A., Quantum Size Effect in the Optical-Spectra of Semiconductor Micro-Crystals. *Sov. Phys. Semicond.* **1982,** *16,* 775-778.

(4) Brus, L. E., A Simple-Model for the Ionization-Potential, Electron-Affinity, and Aqueous Redox Potentials of Small Semiconductor Crystallites. *J. Chem. Phys.* **1983,** *79,* 5566-5571.

(5) Murray, C. B.; Norris, D. J.; Bawendi, M. G., Synthesis and Characterization of Nearly Monodisperse CdE (E = S, Se, Te) Semiconductor Nanocrystallites. *J. Am. Chem. Soc.* **1993,** *115,* 8706-8715.

(6) Boles, M. A.; Ling, D.; Hyeon, T.; Talapin, D. V., The Surface Science of Nanocrystals. *Nat. Mater.* **2016,** *15,* 141-153.

(7) Lee, S. F.; Osborne, M. A., Brightening, Blinking, Bluing and Bleaching in the Life of a Quantum Dot: Friend or Foe? *ChemPhysChem* **2009,** *10,* 2174-2191.

(8) Zhu, H. M.; Yang, Y.; Wu, K. F.; Lian, T. Q., Charge Transfer Dynamics from Photoexcited Semiconductor Quantum Dots. *Annu. Rev. Phys. Chem.* **2016,** *67,* 259-281.

(9) Gomez-Campos, F. M.; Califano, M., Hole Surface Trapping in CdSe Nanocrystals: Dynamics, Rate Fluctuations, and Implications for Blinking. *Nano Lett.* **2012,** *12,* 4508-4517.

(10) Brawand, N. P.; Voros, M.; Galli, G., Surface Dangling Bonds Are a Cause of B-Type Blinking in Si Nanoparticles. *Nanoscale* **2015,** *7,* 3737-3744.

(11) Banyai, L.; Gilliot, P.; Hu, Y. Z.; Koch, S. W., Surface-Polarization Instabilities of Electron-Hole Pairs in Semiconductor Quantum Dots. *Phys. Rev. B* **1992,** *45,* 14136-14142.

(12) Orlandi, A.; Goldoni, G.; Manghi, F.; Molinari, E., The Effect of Dielectric Polarization-Induced Surface States on Many-Body Configurations in a Quantum Dot. *Semicond. Sci. Technol.* **2002,** *17,* 1302-1311.

(13) Chon, B.; Lim, S. J.; Kim, W.; Seo, J.; Kang, H.; Joo, T.; Hwang, J.; Shin, S. K., Shell and Ligand-Dependent Blinking of CdSe-Based Core/Shell Nanocrystals. *PCCP* **2010,** *12,* 9312-9319.

(14) Peterson, M. D.; Cass, L. C.; Harris, R. D.; Edme, K.; Sung, K.; Weiss, E. A., The Role of Ligands in Determining the Exciton Relaxation Dynamics in Semiconductor Quantum Dots. *Annu. Rev. Phys. Chem.* **2014,** *65,* 317-339.

(15) Issac, A.; Krasselt, C.; Cichos, F.; von Borczyskowski, C., Influence of the Dielectric Environment on the Photoluminescence Intermittency of CdSe Quantum Dots. *ChemPhysChem* **2012,** *13,* 3223-3230.

(16) Bixby, T. J.; Cordones, A. A.; Leone, S. R., CdSe/ZnS Quantum Dot Intermittency in N,N '-Diphenyl-N,N '-Bis(3-Methylphenyl)-(1,1 '-Biphenyl)-4,4 '-Diamine (Tpd). *Chem. Phys. Lett.* **2012,** *521,* 7-11.

(17) Nirmal, M.; Dabbousi, B. O.; Bawendi, M. G.; Macklin, J. J.; Trautman, J. K.; Harris, T. D.; Brus, L. E., Fluorescence Intermittency in Single Cadmium Selenide Nanocrystals. *Nature* **1996,** *383,* 802-804.

(18) Efros, A. L.; Nesbitt, D. J., Origin and Control of Blinking in Quantum Dots. *Nat. Nanotechnol.* **2016,** *11,* 661-671.

(19) Gomez, D. E.; van Embden, J.; Mulvaney, P.; Fernee, M. J.; Rubinsztein-Dunlop, H., Exciton-Trion Transitions in Single CdSe-CdS Core-Shell Nanocrystals. *ACS Nano* **2009,** *3,* 2281-2287.

(20) Lee, S. F.; Osborne, M. A., Photodynamics of a Single Quantum Dot: Fluorescence Activation, Enhancement, Intermittency, and Decay. *J. Am. Chem. Soc.* **2007,** *129,* 8936-8937.

(21) 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.

(22) Stefani, F. D.; Zhong, X. H.; Knoll, W.; Han, M. Y.; Kreiter, M., Memory in Quantum-Dot Photoluminescence Blinking. *New. J. Phys.* **2005,** *7,* 197.

(23) Verberk, R.; van Oijen, A. M.; Orrit, M., Simple Model for the Power-Law Blinking of Single Semiconductor Nanocrystals. *Phys. Rev. B* **2002,** *66,* 233202.

(24) Kuno, M.; Fromm, D. P.; Johnson, S. T.; Gallagher, A.; Nesbitt, D. J., Modeling Distributed Kinetics in Isolated Semiconductor Quantum Dots. *Phys. Rev. B* **2003,** *67,* 12304.

(25) Tang, J.; Marcus, R. A., Mechanisms of Fluorescence Blinking in Semiconductor Nanocrystal Quantum Dots. *J. Chem. Phys.* **2005,** *123,* 054704.

(26) Frantsuzov, P. A.; Marcus, R. A., Explanation of Quantum Dot Blinking without the Long-Lived Trap Hypothesis. *Phys. Rev. B* **2005,** *72,* 155321.

(27) Frantsuzov, P. A.; Volkan-Kacso, S.; Janko, B., Model of Fluorescence Intermittency of Single Colloidal Semiconductor Quantum Dots Using Multiple Recombination Centers. *Phys. Rev. Lett.* **2009,** *103,* 207402.

(28) Kern, S. J.; Sahu, K.; Berg, M. A., Heterogeneity of the Electron-Trapping Kinetics in CdSe Nanoparticles. *Nano Lett.* **2011,** *11,* 3493-3498.

(29) 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.

(30) Schmidt, R.; Krasselt, C.; Gohler, C.; von Borczyskowski, C., The Fluorescence Intermittency for Quantum Dots Is Not Power-Law Distributed: A Luminescence Intensity Resolved Approach. *ACS Nano* **2014,** *8,* 3506-3521.

(31) Knappenberger, K. L.; Wong, D. B.; Xu, W.; Schwartzberg, A. M.; Wolcott, A.; Zhang, J. Z.; Leone, S. R., Excitation-Wavelength Dependence of Fluorescence Intermittency in CdSe Nanorods. *ACS Nano* **2008,** *2,* 2143-2153.

(32) Kim, S.; Fisher, B.; Eisler, H. J.; Bawendi, M., Type-Ii Quantum Dots: CdTe/CdSe(Core/Shell) and CdSe/ZnTe(Core/Shell) Heterostructures. *J. Am. Chem. Soc.* **2003,** *125,* 11466-11467.

(33) Boldt, K.; Kirkwood, N.; Beane, G. A.; Mulvaney, P., Synthesis of Highly Luminescent and Photo-Stable, Graded Shell CdSe/$Cd_xZn_{1-x}S$ Nanoparticles by *In Situ* Alloying. *Chem. Mater.* **2013,** *25,* 4731-4738.

(34) Park, Y. S.; Bae, W. K.; Padilha, L. A.; Pietryga, J. M.; Klimov, V. I., Effect of the Core/Shell Interface on Auger Recombination Evaluated by Single-Quantum-Dot Spectroscopy. *Nano Lett.* **2014,** *14,* 396-402.

(35) Cragg, G. E.; Efros, A. L., Suppression of Auger Processes in Confined Structures. *Nano Lett.* **2010,** *10,* 313-317.

(36) Park, Y. S.; Bae, W. K.; Pietryga, J. M.; Klimov, V. I., Auger Recombination of Biexcitons and Negative and Positive Trions in Individual Quantum Dots. *ACS Nano* **2014,** *8,* 7288-7296.

(37) Osborne, M. A.; Fisher, A. A. E., Charge-Tunnelling and Self-Trapping: Common Origins for Blinking, Grey-State Emission and Photoluminescence Enhancement in Semiconductor Quantum Dots. *Nanoscale* **2016,** *8,* 9272-9283.

(38) Klimov, V. I.; Mikhailovsky, A. A.; McBranch, D. W.; Leatherdale, C. A.; Bawendi, M. G., Quantization of Multiparticle Auger Rates in Semiconductor Quantum Dots. *Science* **2000,** *287,* 1011-1013.

(39) Yu, W. W.; Qu, L. H.; Guo, W. Z.; Peng, X. G., Experimental Determination of the Extinction Coefficient of CdTe, CdSe, and CdS Nanocrystals. *Chem. Mater.* **2003,** *15,* 2854-2860.

(40) Donega, C. D.; Koole, R., Size Dependence of the Spontaneous Emission Rate and Absorption Cross Section of CdSe and CdTe Quantum Dots. *J. Phys. Chem. C* **2009,** *113,* 6511-6520.

(41) Xie, R. G.; Kolb, U.; Li, J. X.; Basche, T.; Mews, A., Synthesis and Characterization of Highly Luminescent Cdse-Core CdS/$Zn_{0.5}Cd_{0.5}S$/ZnS Multishell Nanocrystals. *J. Am. Chem. Soc.* **2005,** *127,* 7480-7488.

(42) Li, J. J.; Wang, Y. A.; Guo, W. Z.; Keay, J. C.; Mishima, T. D.; Johnson, M. B.; Peng, X. G., Large-Scale Synthesis of Nearly Monodisperse CdSe/CdS Core/Shell Nanocrystals Using Air-Stable Reagents *via* Successive Ion Layer Adsorption and Reaction. *J. Am. Chem. Soc.* **2003,** *125,* 12567-12575.

(43) Chen, O.; Zhao, J.; Chauhan, V. P.; Cui, J.; Wong, C.; Harris, D. K.; Wei, H.; Han, H. S.; Fukumura, D.; Jain, R. K.; Bawendi, M. G., Compact High-Quality CdSe-CdS Core-Shell Nanocrystals with Narrow Emission Linewidths and Suppressed Blinking. *Nat. Mater.* **2013,** *12,* 445-451.

(44) Crouch, C. H.; Sauter, O.; Wu, X. H.; Purcell, R.; Querner, C.; Drndic, M.; Pelton, M., Facts and Artifacts in the Blinking Statistics of Semiconductor Nanocrystals. *Nano Lett.* **2010,** *10,* 1692-1698.

(45) Bae, Y. J.; Gibson, N. A.; Ding, T. X.; Alivisatos, A. P.; Leone, S. R., Understanding the Bias Introduced in Quantum Dot Blinking Using Change Point Analysis. *J. Phys. Chem. C* **2016,** *120,* 29484-29490.

(46) Wei, S. H.; Zhang, S. B.; Zunger, A., First-Principles Calculation of Band Offsets, Optical Bowings, and Defects in CdS, CdSe, CdTe, and Their Alloys. *J. Appl. Phys.* **2000,** *87,* 1304-1311.

(47) Shimizu, K. T.; Neuhauser, R. G.; Leatherdale, C. A.; Empedocles, S. A.; Woo, W. K.; Bawendi, M. G., Blinking Statistics in Single Semiconductor Nanocrystal Quantum Dots. *Phys. Rev. B* **2001,** *63,* 205316.

(48) Peterson, J. J.; Nesbitt, D. J., Modified Power Law Behavior in Quantum Dot Blinking: A Novel Role for Biexcitons and Auger Ionization. *Nano Lett.* **2009,** *9,* 338-345.

(49) Wang, L. W.; Zunger, A., Pseudopotential Calculations of Nanoscale CdSe Quantum Dots. *Phys. Rev. B* **1996,** *53,* 9579-9582.

(50) Early, K. T.; Nesbitt, D. J., Size-Dependent Photoionization in Single CdSe/ZnS Nanocrystals. *Nano Lett.* **2013,** *13,* 4844-4849.

(51) Blaudeck, T.; Zenkevich, E. I.; Cichos, F.; von Borczyskowski, C., Probing Wave Functions at Semiconductor Quantum-Dot Surfaces by Non-Fret Photoluminescence Quenching. *J. Phys. Chem. C* **2008,** *112,* 20251-20257.

(52) Wang, R. M.; Zhang, Y. P.; Gan, C. L.; Muhammad, J.; Xiao, M., Controlling Blinking in Multilayered Quantum Dots. *Appl. Phys. Lett.* **2010,** *96,* 151107.

(53) Gao, F.; Bajwa, P.; Nguyen, A.; Heyes, C. D., Shell-Dependent Photoluminescence Studies Provide Mechanistic Insights into the Off-Grey-on Transitions of Blinking Quantum Dots. *ACS Nano* **2017,** *11,* 2905-2916.

(54) Heyes, C. D.; Kobitski, A. Y.; Breus, V. V.; Nienhaus, G. U., Effect of the Shell on the Blinking Statistics of Core-Shell Quantum Dots: A Single-Particle Fluorescence Study. *Phys. Rev. B* **2007,** *75,* 125431.

(55) Kim, B. S.; Islam, M. A.; Brus, L. E.; Herman, I. P., Interdot Interactions and Band Gap Changes in CdSe Nanocrystal Arrays at Elevated Pressure. *J. Appl. Phys.* **2001,** *89,* 8127-8140.

(56) Yu, Z. H.; Guo, L.; Du, H.; Krauss, T.; Silcox, J., Shell Distribution on Colloidal CdSe/ZnS Quantum Dots. *Nano Lett.* **2005,** *5,* 565-570.

(57) Chen, Y.; Vela, J.; Htoon, H.; Casson, J. L.; Werder, D. J.; Bussian, D. A.; Klimov, V. I.; Hollingsworth, J. A., "Giant" Multishell CdSe Nanocrystal Quantum Dots with Suppressed Blinking. *J. Am. Chem. Soc.* **2008,** *130,* 5026-5027.

(58) Vela, J.; Htoon, H.; Chen, Y. F.; Park, Y. S.; Ghosh, Y.; Goodwin, P. M.; Werner, J. H.; Wells, N. P.; Casson, J. L.; Hollingsworth, J. A., Effect of Shell Thickness and Composition on Blinking Suppression and the Blinking Mechanism in 'Giant' CdSe/CdS Nanocrystal Quantum Dots. *J. Biophotonics* **2010,** *3,* 706-717.

(59) Zhu, H. M.; Song, N. H.; Lian, T. Q., Controlling Charge Separation and Recombination Rates in CdSe/ZnS Type I Core-Shell Quantum Dots by Shell Thicknesses. *J. Am. Chem. Soc.* **2010,** *132,* 15038-15045.

(60) Climente, J. I.; Bertoni, A.; Goldoni, G., Photoluminescence Spectroscopy of Trions in Quantum Dots: A Theoretical Description. *Phys. Rev. B* **2008,** *78,* 155316.

(61) Yi, C. Y.; Knappenberger, K. L., The Influence of Surface Passivation on Electronic Energy Relaxation Dynamics of CdSe and CdSe/CdS Nanocrystals Studied Using Visible and near Infrared Transient Absorption Spectroscopy. *Nanoscale* **2015,** *7,* 5884-5891.

FIGURE CAPTIONS

Figure 1. Schematic definition of QD states and rate constants used in the CTST model. Excitation and emission constants k_{x} and k_{r} connect the ground and NX^0 state, respectively. The exciton-electron kinetics are determined by a trap-distance and -energy dependent tunnelling rate constant k_{ion}^{+} that leaves the QD ionised in either a CX^+ or SX^+ state depending on a surface-to-core volume trapping-probability. In the CX^+-state, the Auger-rate, k_{A} dominates recombination leaving the QD dark, but in SX^+ the core is neutral and PL emission persists. QD blinking is associated with back-tunnelling rate constants k_{on}^{-} and k_{off}^{-} for electron-recombination at the excess-hole (magenta) on either the QD-core in CX^+ or surface in SX^+. Additional PL modulation associated with grey-state emission is accounted for by exciton-hole (blue) tunnelling between the QD-core and surface, where the core-surface equilibrium is governed by the tunnelling rates, k_{h}^{+} and k_{h}^{-} respectively. Following biexciton formation in the SSX^+-state, Auger recombination leads to a hot-electron that quenches the excess surface-hole at a rate, k_{c}, which is dependent on the hole-to-core volume ratio.

Figure 2. Shell-size dependent spectroscopy in core-shell CdSe-CdS QDs and the effective exciton-radius. a) Absorption and PL spectra ($\lambda_{ex} = 473$ nm) of core CdSe QDs (in toluene) as a function of CdS shell monolayer (ML) number. Epitaxial shell growth was performed by successive adsorption reactions of S and Cd precursors for 1 to 4 CdS MLs. Actual ML number is determined from TEM sizing and a CdS lattice spacing of 0.36 nm (Figure S2 in SI). b) and c) TEM micrographs of the as synthesised nanocrystals and corresponding particle size distributions with averages 0 ML = 3.4 $\pm$ 0.2 nm, 0.9 ML = 4.1 $\pm$ 0.3, 2.1 ML = 4.9 $\pm$ 0.3 nm and 3.5 ML = 5.9 $\pm$ 0.2 nm. d) The effective QD radius of confinement, R_x as a function of the QD band-gap energy $E_{QD} = hc/\lambda$, where λ is the first-exciton peak from the absorption spectra in (a) for each CdS shell thickness (inset). e) The "exciton-radius" R_x as function of CdS ML number (n) derived from the root of the quadratic $hc/\lambda(n) = 1.74 + 0.45/R_x^2 + 0.5/R_x$, where $\lambda(n) = 555 + 11.5n$. Schematic definition of the effective "exciton-radius" R_x (inset), in relation to the QD-core and shell radii, R_c and R_s.

Figure 3. Shell-size dependent blinking in CdSe-CdS QDs. a) Extracts from experimental single-QD PL trajectories of core-shell CdSe-CdS QDs and b) PL intensity histograms as function of CdS shell ML number. c) Probability density distributions (PDDs) of on and off-times extracted from experimental trajectories with a 2σ threshold above the mean intensity of the background peak PL intensity histograms from (b). The PDDs represent the average from over 30 QDs and a total of around 40000 on-off events for each CdS shell thickness. Densities have been have been scaled for clarity, 0 ML = 1000X (magenta), 0.9 ML = 100X (blue), 2.1 ML = 10X (green), 3.5 ML = 1X (red). d) Histograms of the power-law exponent α_{on} and α_{off} derived from fitting the PDDs in individual QDs with the TPL $P(t) = At^{-\alpha}e^{-t/\tau_c}$. e) Corresponding on and off-time PDDs derived from the stochastic simulation of PL intensity trajectories of single-QDs using the modified CTST model, wherein QD size-sensitive properties ae made dependent on the effective "exciton-radius", R_{x}. e) PDDs for on and off-times extracted from simulated trajectories and processed as per (c) with scaling 0 ML = 1000X (pink), 0.9 ML = 100X (cyan), 2.1 ML = 10X (olive), 3.5 ML = 1X (orange).

Figure 4. Exciton and excess charge-carrier controlled blinking statistics. Dependence of the truncated power-law parameters describing blinking statistic in core-shell CdSe-CdS QDs on shell ML number: a) the on-time PDD power-law exponent, α_{on}; b) off-time PDD power-law exponent, α_{off} and c) the cut-off time τ_{c} characterising the exponential truncation of the on-time PDDs. Values from experiment (blue) and simulation (red) represent the mean and standard deviation from the population of single CdSe-CdS QDs sampled for each shell-thickness. Theoretical values (green) derived directly from the CTST model are evaluated using Equation 1. Grey lines in (a) and (b) are for guidance only and in (c) $R_{\mathrm{x}}^{-3.3}$ function (see text) is mapped to ML number (see Figure 1e). d) Dependence of the mean experimental on-time $\langle\tau_{\mathrm{on}}\rangle$ (blue points) on the effective "exciton-radius", R_{x} along with $\langle\tau_{\mathrm{on}}\rangle$ derived the CTST-model (cyan) with contributing components $(1-p_{\mathrm{s}})^{-1}$ (magenta) and $\langle k_{\mathrm{on}}\rangle^{-1}$ (orange) from simulation. e) As in d) but for mean off-times $\langle\tau_{\mathrm{off}}\rangle$ from experiment (blue points) and the CTST-model (cyan) along with components, p_{s}^{-1} (magenta) and $\langle k_{\mathrm{off}}\rangle^{-1}$ (orange). Note the component functions have been arbitrarily scaled to show R_{x} dependence. f) Biexciton formation rate constant from simulation (blue points) and the functional dependency, $R_{\mathrm{x}}^{6.3}$ (cyan) from fitting the rate constant with the influence of h_x surface-sampling included. Also shown, to highlight the effects of charge carrier dynamics, is the $R_{\mathrm{x}}^{11.5}$ (magenta) dependence of biexciton formation in the absence of h_x-tunnelling.

Figure 5: Shell-size dependent spectroscopy and blinking in core-shell CdSe-ZnS QDs. a) Absorption and PL spectra ($\lambda_{ex} = 473$ nm) of core CdSe QDs (in toluene) as a function of ZnS shell monolayer (ML) number. Epitaxial shell growth was performed by successive adsorption reactions of S and Cd precursors for 1 to 8 ZnS ML. b) Particle size distributions (PSDs) obtained from low-resolution TEM with averages 0 ML = 3.4 $\pm$ 0.2 nm, 4.2 ML = 6.1 $\pm$ 0.4, 5.8 ML = 6.9 $\pm$ 0.3 nm and 8.4 ML = 8.5 $\pm$ 0.3 nm. c) Probability density distributions (PDDs) of on-times and d) off-times extracted from experimental trajectories. The PDDs represent the average from over 30 QDs and a total in excess of 30000 on-off events for each ZnS shell thickness. Densities have been have been scaled for clarity, 0 ML = 1000X (magenta), 4.2 ML = 100X (blue), 5.8 ML = 10X (green), 8.4 ML = 1X (red). e) Histograms of cut-off times, $\tau_c(\mathrm{on})$, derived from fitting the on-time PDDs of individual QDs with the TPL, $P(t) = At^{-\alpha}e^{-t/\tau_c}$.

Figure 6. Shell-structure dependent power-law truncation in CdSe-ZnS QDs. a) Size dependent first-exciton absorption for core-shell CdSe-ZnS (blue) and CdSe-CdS (red). Shell radii $R_s = D/2$ are derived from TEM-PSDs in Figure 5b and Figure 2c and ZnS ML (inset axis) from the number of SILAR capping cycles. An effective shell-radius and ZnS ML number is defined by mapping each exciton wavelength to the corresponding CdS radius at the same wavelength (grey lines). b) Cut-off times derived from TPL fitting to on-time PDDs extracted from experimental (blue) CdSe-ZnS single PL trajectories and calculated (red) from the CTST model (Equation 1) based on the effective ZnS ML number in (a). Line (grey) shows fit to CdSe-CdS cut-off times (from Figure 4c) for comparison. Inset for comparison are cut-off times (cyan) determined from as synthesised ML number and mean-size from TEM-PSDs. (c) and d) TEMs of core CdSe with 3.5 ML CdS shell and 8.4 ML ZnS capping respectively. Scale bars are 20 nm. Insets show expanded ROIs (yellow) highlighting in (c) a typical CdSe-CdS QD of mean diameter (orange circle) from the PSD (Figure 2c) and in (d) a CdSe-ZnS QD with a mean size (cyan circle) from the PSD (Figure 5b) along with the effective size (orange circle) derived from the first-exciton absorption. e) Variation of the QD shell-radius (black), $R_s = R_c + 3.1n$ (black) with ZnS ML number n. Core-exciton radius R_x as derived from over-sized (solid blue) and reduced-shell (solid red) radii, along with tunnelling-lengths, $d = R_s - R_x$, for over-sized (dotted blue) and effective (dotted red) shell-radii. f) Corresponding R_x dependence of the biexciton formation rate for over-sized (blue) and effective (red) shell-sizes, respectively. Representations of the CdSe-ZnS core-shell QDs with an over-sized (cyan) and a reduced shell-thickness (orange), show the shift in the h_x-equilibrium (open circle) between QD-core and surface with different shell-sizes relative to the effective core-exciton size (yellow).

Table 1. The shell-size dependent exciton radius and truncated power-law (TPL) fitting parameters.

QD and exciton sizing			Experimental			Simulation			Model
ML	D (nm)	R_x (nm)	α_{on}	α_{off}	$\tau_c(on)$	α_{on}	α_{off}	$\tau_c(on)$	$\tau_c(on)$
0	3.4	1.59	1.6	1.6	4.9	1.7	1.7	9.0	5.1
0.9	4.1	1.69	1.4	1.7	3.0	1.5	1.8	3.6	3.2
2.1	4.9	1.87	1.3	1.8	2.8	1.2	1.8	2.4	2.3
3.5	5.9	2.09	1.0	1.8	1.9	0.7	1.7	1.5	1.9

[D] QD diameters obtained from the particle size distributions (Figure 2c). Error in $D \leq \pm 0.3$ nm.

[R_x] Exciton radii derived from root $hc/\lambda(n) = 1.74 + 0.45/R_x^2 + 0.5/R_x$ (Figure 2e).

[$\alpha_{on/off}$] Mean power-law exponents extracted from fitting the TPL to experimental and simulated on and off-time PDDs. Error in both α_{on} and $\alpha_{off} \leq \pm 0.2$.

[$\tau_c(on)$] Mean truncation time (in seconds) extracted from TPL fitting to experiment and simulation. Error in $\tau_c(on) \sim 60\%$.