Electronic Supplementary Material (ESI) for Nanoscale.

Drastic difference between hole and electron injection through the gradient shell of $Cd_xSe_yZn_{1-x}S_{1-y}$ quantum dots

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Supporting information:

1. Experiment section

2.1 Sample preparation: $Cd_xSe_yZn_{1-x}S_{1-y}$ gradient CSQDs were prepared by following a method described by Bae *et. al.*[1] and reproduced in our previous work.[2-5] Briefly, we use a single-step hot injection method where both Cd^{2+} and Zn^{2+} oleate in 1-octadecene solution were heated up to 325 °C. Then Se^{2-} and S^{2-} in 3 ml of trioctylphosphine (TOP) solution were swiftly injected into the cation precursor solution. To obtain gradient CSQDs with different shell thicknesses, the growth process was terminated by cooling the solution down using an ice bath after 5 sec, 1, 3, 5, 10, and 15 min reaction. For sensitization, the surface capping agent of doubly purified QDs was exchanged from oleic acid (OA) to a bifunctional linker molecule, mercaptopropionic acid (MPA) and re-dispersed in ethanol that was used as a solution to sensitize the photocathode. NiO mesoporous films were prepared according to the method by Sumikura *et al.*[6] Briefly, the precursor containing $NiCl_2$ and the triblock co-polymer F108 dissolved in ethanol was spin-coated onto a glass substrate and then calcined in air at 400 °C for 30 min. In order to fabricate the photocathode, the NiO films were immersed in MPA capped-QDs solution for 12 hours.

1.2 Materials Characterization: The size of the QDs was analyzed by the high-resolution transmission electron microscopy (HR-TEM) images recorded on a JEOL3000F microscope equipped with an Oxford SDD X-ray analyzer as discussed in our previous work.[5]

1.3 Time-solved Photoluminescence: The excitation source for the time-resolved PL setup is drawn from a Titanium:Sapphire passively mode-locked femtosecond laser (Spectra-Physics, Tsunami), emitting at 820 nm with an 80 MHz repetition rate and a 150 fs pulse length. The laser pulses were frequency-doubled to 410 nm by a harmonic generator (Photop technologies, Tripler TP-2000B). The excitation fluence was 1.1×10^{12} photons/cm^2/pulse.

Time-resolved PL spectra were detected by a streak camera (C6860, Hamamatsu) coupled to a Chromex spectrograph, triggered by Ti:Sapphire laser. A long-pass wavelength filter from 490 nm was used in front of the spectrograph to cut off the scattering from the excitation pulses.

1.4 Transient Absorption: Transient absorption (TA) spectra were recorded using a pump-probe setup described in our previous studies.[2, 4-5] Briefly, laser pulses (800 nm, 80 fs pulse length, 1 kHz repetition rate) were generated by a regenerative amplifier (Spitfire XP pro) seeded by a femtosecond oscillator (MaiTai, both Spectra Physics). Excitation pulses at the wavelength of 450 nm were acquired using an optical parametric amplifier (Topas C, Light Conversion). The excitation photon fluence was kept at 1.1×10^{12} photons/cm^2/pulse to avoid photodamage and possible multiple exciton recombination. The probe pulses (a broad supercontinuum spectrum) were generated from the 800-nm pulses in a sapphire plate and split by a beam splitter into a probe pulse and a reference pulse. The probe pulse and the reference pulse were dispersed in a spectrograph and detected by a diode array (Pascher Instruments). Thin film samples were measured in a nitrogen atmosphere to avoid possible oxidation of QDs.[7]

1.5 Photoelectrochemical cell measurements: Photocell measurements were carried out using an in-house designed electrochemical cell. NiO and CSQDs-NiO films were freshly prepared on FTO electrodes. These nanofilm**s** on FTO electrodes were employed as photoanodes (or working electrodes), and a Pt plate was utilized as a counter electrode in the 1M Na_2S, 1M S, and 0.1M NaOH electrolyte water solution saturated with Ar. An ORLED RL18 (100 mW cm^{-2}) equipped with a UV cut filter (λ > 400 nm) was applied to provide simulated solar light for photocurrent response experiments. The photocurrent-time curves were recorded using an electrochemical workstation (CHI 760, USA).

2. Band alignment characterization:

The band alignment of the CSQDs with regards to CBM and VBM was determined using our established strategy for pure QDs involving both XPS and XAS measurements carried out in Beamline I311 and I811 in MAX IV Laboratory. In brief, alignment of VBM is first determined by the edge of XPS valence spectra, while the alignment of the CBMs is estimated by the XANES representing the allowed transition from core level to CB. The absolute positon of the CBM and VBM was finally calibrated by the reference sample whose band gap is already known. In the XPS characterization of CSQD samples, the photon energy of the excitation X-ray is 130 eV which results in the electron mean free path for shell materials less than 1 nm. This means that the photoelectrons probe the surface of our CSQD samples with various shell thicknesses.

3. TA results:

Figure S1 presents the normalized TA decay kinetics at the band-edge absorption excited at 410 nm for neat QDs and QDs attached to a NiO film. Within the early time scale (100 ps) the decay kinetics remains almost the same for neat QDs and CSQDs/NiO. The minor fast decay component in the early time scale (<10 ps) in Core/glass and Core/NiO NPs is due to electron trapping in some of the QDs. The density of the excited electron states at the band-edge transition of CdSe QDs is significantly smaller than the corresponding density of the hole states (in the effective-mass approximation, the lowest excited electron state is only two-fold degenerate). In addition, the hole states are more closely spaced in QDs. As a result, the signal of TA bleaching is dominated by the state filling of electrons instead of holes. Therefore, we can conclude that no electron depopulation processes occur from excited QDs (e.g. electron injection, electron trapping) in the CSQDs/NiO system.

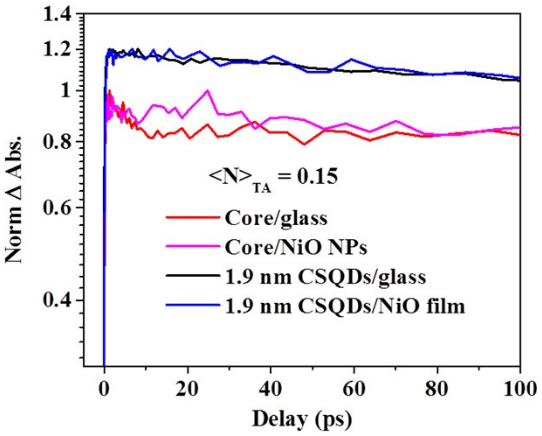

Figure. S1. Normalized TA decay kinetics for bare core CdSe QDs on glass and attached to NiO NPs (red and pink lines, respectively) and (black and blue for CdSe–ZnS gradient CSQDs with 1.9 nm shell thickness on glass and attached to NiO NPs, respectively)

4. Results of the theoretical simulation with different effective mass used:

Table S1. Parameter used for theoretical simulation:

Electron	CdSe	ZnS	ligand
Effective mass (m0)	0.13	0.25	1
Conduction band (eV)	-3.5	-3	-1.8

Hole	CdSe	ZnS	ligand
Effective mass (m0)	0.45	0.1 or 0.2 or 1.3	1
Valence band (eV)	-6.2	-6.4	-7.9

Shell thickness (nm)	0	0.6	1.3	1.6	1.9	2.3
Ratio (CdSe/ZnS)	0.86	0.42	0.33	0.27	0.22	0.19

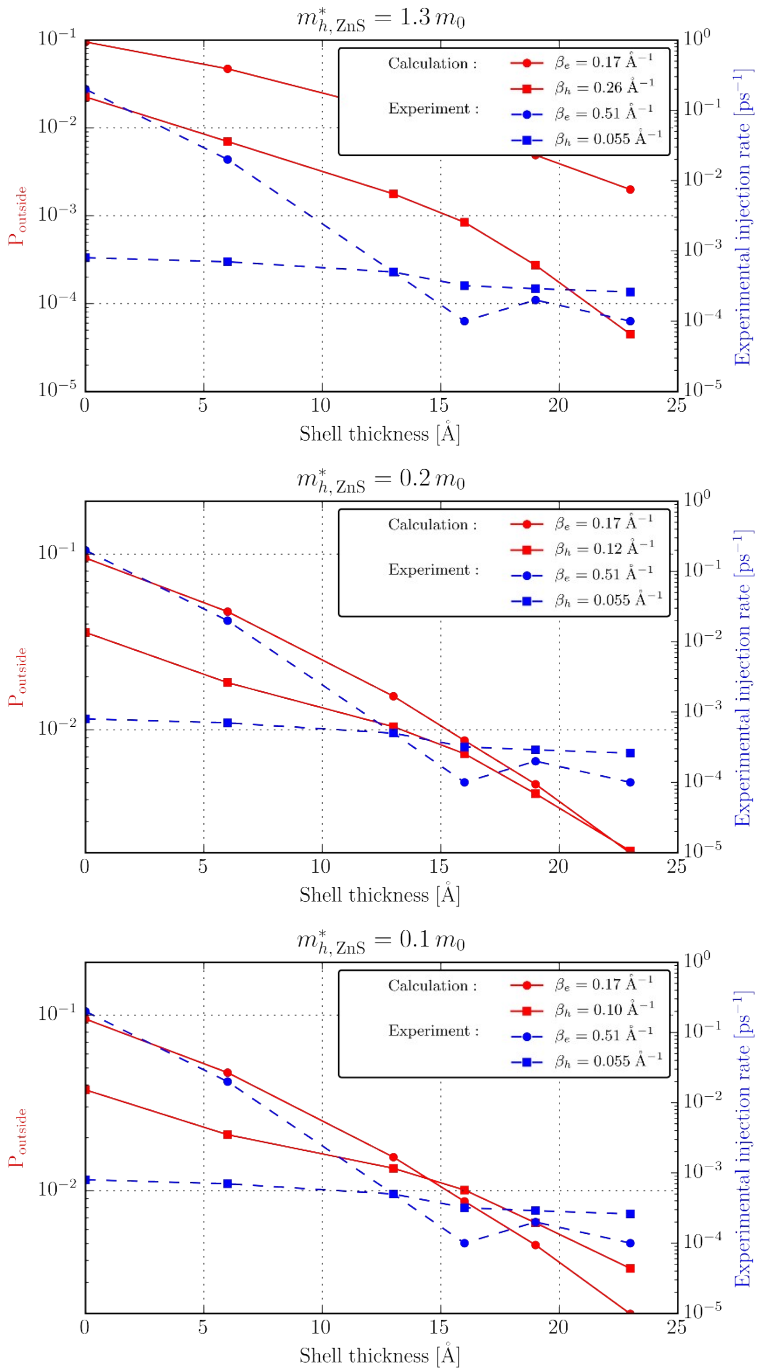

Figure. S2. Calculated probability of being found outside of the quantum dot for the electron (black) and the hole (blue) with different hole effective mass selected.

5. Confirmation of the gradient CSQDs structures:

In order to further confirm the gradient core-shell structure of the as-obtained QDs, we first synthesized the pure-core CdSe QDs with the sample injection temperature and the precursor concentration corresponding to the CSQDs growth. The absorption spectra in Fig. S3A show that the growth of the CdSe QDs stops between 1 min and 3 min. Both line-shapes and absorbances stay constant after that. First, this confirms the high chemical reactivity of Cd and Se precursors. Second, this indicates that the red shift of the 1S exciton peaks and the increase of the red band-edge tails in Fig. 1A should be attributed to the addition of Zn and/or S ions to the QDs.

Previously, it has also been reported that, at high growth temperature, the Zn ions may diffuse through the QDs, resulting in a spatial redistribution of the chemical composition.[8] Therefore, we conducted the synthesis of CSQDs at low injection temperature (270^{o}C) where such diffusion is not energetically activated according to the literature.[9] The trend in time evolution from the absorption spectra during the growth period in this case is quite similar to what is observed in the high temperature synthesis (Fig. S2B). However, after 5 min, there is no visible spectral changes either in emission or in absorption, demonstrating a stabilized confinement of the core independently of the shell building. This points to some small degree of ion diffusion, since wavefunction leakage can also be observed after 5 min as a probable consequence of confinement loss in core when ion diffusion increases the effective size. However, we also conducted XPS valence band measurements using higher X-ray photon energy (1000 eV), similar to these presented in Fig. 3B in the main text. Here, the escape depth was 1.5 nm. As shown in Fig. S3C, the VBM energy position measured in this case is totally different from what is obtained using low photon energy (130 eV). However, the VBM for the pure-core samples probed using these two different photon energies are very similar, indicating a homogenous core structure. When the shell thickness increases, the VBM probed at 130 eV is always lower than that measured at 1000 eV. In other words, the electronic bandgap close to the surface is larger than in the inner volume. This strongly supports a gradient core-shell instead of a homogenous alloy structure for our CSQDs.

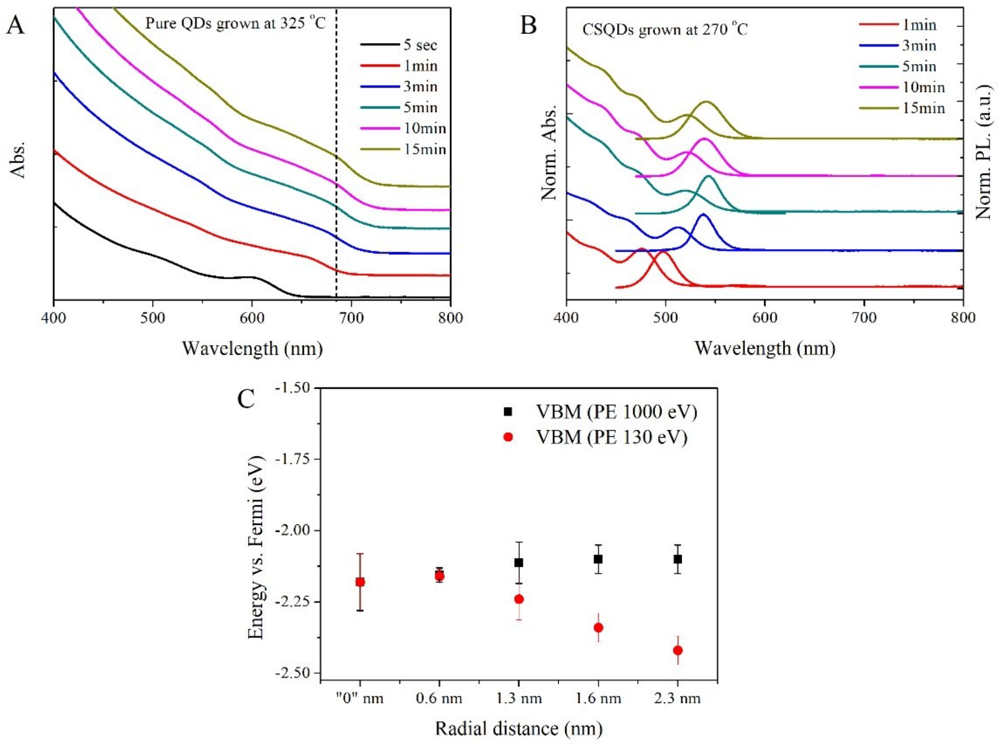

Fig. S3. A) UV-vis absorption spectra of CdSe QDs grown at 325 °C and B) absorption and emission spectra of CSQDs grown at 270 °C, C) VBM position extracted from XPS valence band edges using photon energy of 1000 eV and 130 eV, corresponding to the escape depth of 0.7 nm and 1.5 nm, respectively.

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