Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

Multiple Exciton Generation in Cluster-Free Alloy $Cd_xHg_{1-x}Te$ Colloidal Quantum Dots Synthesized in Water

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SI1. MEG thresholds in QDs.

In bulk crystalline semiconductors energy and momentum conservation conditions under the assumption of parabolic bands leads to the excess energy threshold condition for electrons to undergo impact ionization[1],[2] (ΔE_e):

$$\Delta E_e = \left(2m_e^* + m_h^*\right) \Big/ \left(m_e^* + m_h^*\right) \qquad (1)$$

However, for QDs the threshold condition is slightly different. The excess energy of the hot carriers is partitioned according to the ratio of the inverse of their effective masses. Since the electrons in $Cd_xHg_{1-x}Te$ alloys are somewhat lighter than the holes the hot electrons take the greater share of the excess energy. With their greater effective masses, the holes cool rather more efficiently (in fewer collisions with the lattice), rapidly leaving the electrons as the most likely surviving energetic carriers to undergo impact ionization. At the threshold energy (E_t=hν) the excess energy of the electrons is then:[2],

$$\Delta E_e = \frac{\left(h\nu - E_g\right)}{\left(1 + {m_e^*} \big/ {m_h^*}\right)} \qquad (2)$$

From which it follows the threshold energy is simply,[2],[3]

$$E_t = \left(2 + {m_e^*} \big/ {m_h^*}\right) E_g \qquad (3)$$

This condition arises simply from the partitioning of the excess energy between electrons and holes and energy and momentum conservation. It does not take into account competing process which will also tend to deplete the hot carrier population, such as carrier cooling and so eq.(3) is very much a lower estimate for E_t.[2]

SI 2 De-clustering of QDs

With high cation and matching ligand concentrations, clustering (the onset of gellation) of the QDs is an additional complicating factor. (3.75nm diameter) QDs entrapped in the interior of such (typically 20nm or so diameter) clusters do not receive as great a dose of Hg^{2+} with the latter diffusing less readily into the interior of the clusters. This is illustrated schematically in Fig. S1.

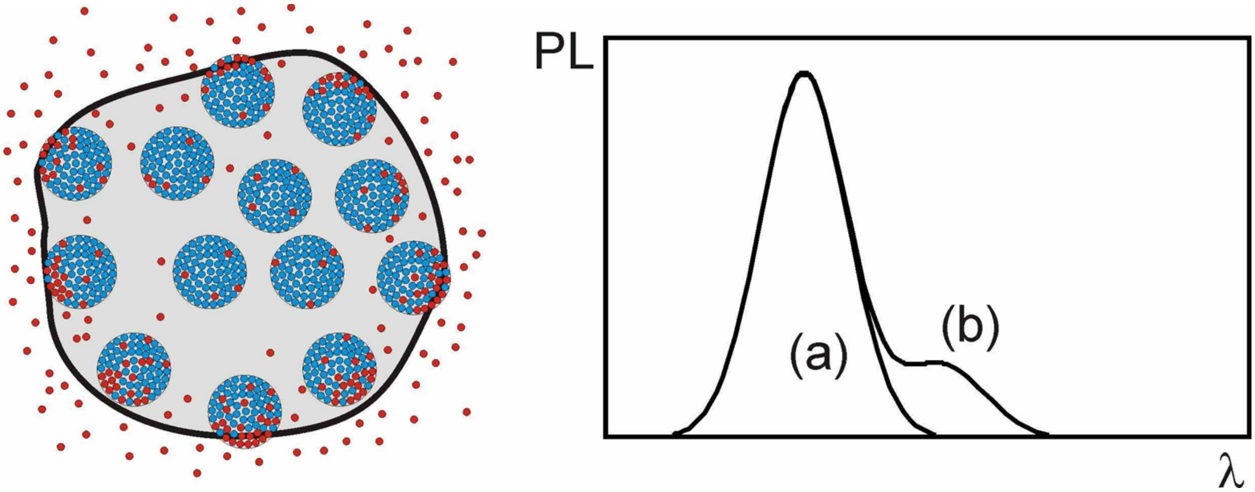


Fig. S1. Schematic representation of Hg^{2+} ions (red dots) diffusing into clusters of CdTe QDs (spheres of blue dots) to undergo ion exchange with Cd^{2+} ions. Comparatively slower/ more limited diffusion into the interior of gelled CdTe clusters leads to disparities in the degree of ion exchange of dots inside the clusters relative to those nearer the surface. This may become apparent as a broadening (a) or even bimodal (b) appearance in the PL spectrum (right).

To combat this clustering problem a method of breaking up the clusters was used in several repeated cycles during the ion exchange process. Although at the QD and cation concentrations used clustering could not be prevented, it was possible, after allowing the exchange process to proceed for a day (later in the exchange 2 days and then 3 days were allowed), to break the clusters apart. The QD solutions were then filtered to remove sequestered mercury and cadmium salts and the solution cleaned by precipitation with acetonitrile followed by centrifugation. After re-dissolving the QD precipitate in milliQ water, the exchange was continued by adding a further Hg^{2+} aliquot. This cycle was repeated a number of times and each time upon reformation of the QD clusters different QDs might find themselves at the surface or in the interior of the clusters, evening out any potential compositional variations due to poor permeation of Hg^{2+} ions into the clusters.

The de-clustering procedure is based on earlier work by Lesnyak et al.[4] and Mayilo et al.[5] In the latter case they used sodium carbonate as a source of low solubility anions to sequester divalent calcium ions from deliberately gelled QD solutions and thereby reverse the gellation. In the Lesnyak et al. study ethylenediamine tetra-acetic acid (EDTA) was used to chelate and sequester the excess divalent cations. In the present case sodium bicarbonate could be substituted since in alkaline solution (i.e. pH 10.8) the latter forms carbonate ions.

A large excess of sodium bicarbonate (e.g. 2-3 grams for 10mls of QD solution) was added and the solution agitated for 1 hr in an ultrasonic bath with ice added periodically to prevent the bath temperature from rising above 35 °C. The latter was a precaution to reduce any tendency to cause Ostwald ripening at higher bath temperatures which might increase the diameter of the QDs. This is only a consideration in order to be able to separately examine size and composition effects. After the ultrasound treatment, the un-dissolved excess of carbonates and any precipitated cadmium and mercury carbonates were removed by filtration. The filtered solution was then cleaned by precipitation with acetonitrile (several fold excess) and the precipitate collected and re-dissolved in the same volume of milliQ water. The next round of Hg^{2+} solution (as described above) was then added promptly and the solution was allowed to stand for a further period of time whilst the next stage of the ion exchange continued.

It was also believed that clustering occurred in the synthesis of the CdTe starting material as well, so prior to the addition of the first Hg^{2+} aliquot an additional de-clustering treatment was applied in the same manner as above. It was not possible to directly confirm the presence of clusters in the as-synthesised CdTe QD solution by light scattering measurements since the material's strong fluorescence emission strongly overlapped with the 633nm wavelength laser used in the Malvern light scattering instrument. However the presence of clusters was inferred from DLS measurements of other aqueous CdTe QDs (with different sizes and emission wavelengths) similarly synthesised and from the drop in optical density of the solution upon passing it through a 20nm pore size filter (Whatman Anotop 10 Plus Inorganic membrane filters). Prior to treatment, although the solutions were highly fluorescent they were also noticeably turbid by eye. After the declustering treatment they were fluorescent but clear. After treatment with sodium bicarbonate, etc, to break the clusters apart, the solution passed through the 20nm pore size filter with very little retention of the QDs.

The formation of clusters and their disintegration on treatment with sodium bicarbonate can be followed by light scattering. As already noted the CdTe starting material inconveniently had strong fluorescence at the same wavelength as the laser used in the Malvern Instruments light scattering machine (633nm). However, Fig. S2 shows how 20nm sized clusters of 4.0 nm diameter HgTe QDs (which emit in the IR) formed during a synthesis can be broken apart after treatment with an excess of sodium bicarbonate. In this earlier example the solution was stirred during bicarbonate treatment for several hours. Ultrasonic agitation for around 1 h was found to be more efficient and faster in assisting the break up and sequestration of the cations. The horizontal line on Fig. S2 corresponds to the bare HgTe QD diameter – DLS measures the hydrodynamic diameter of the QDs i.e. the diameter of the inorganic nanocrystal together with the ligand shell towed along with the QD during Brownian motion in the solution.

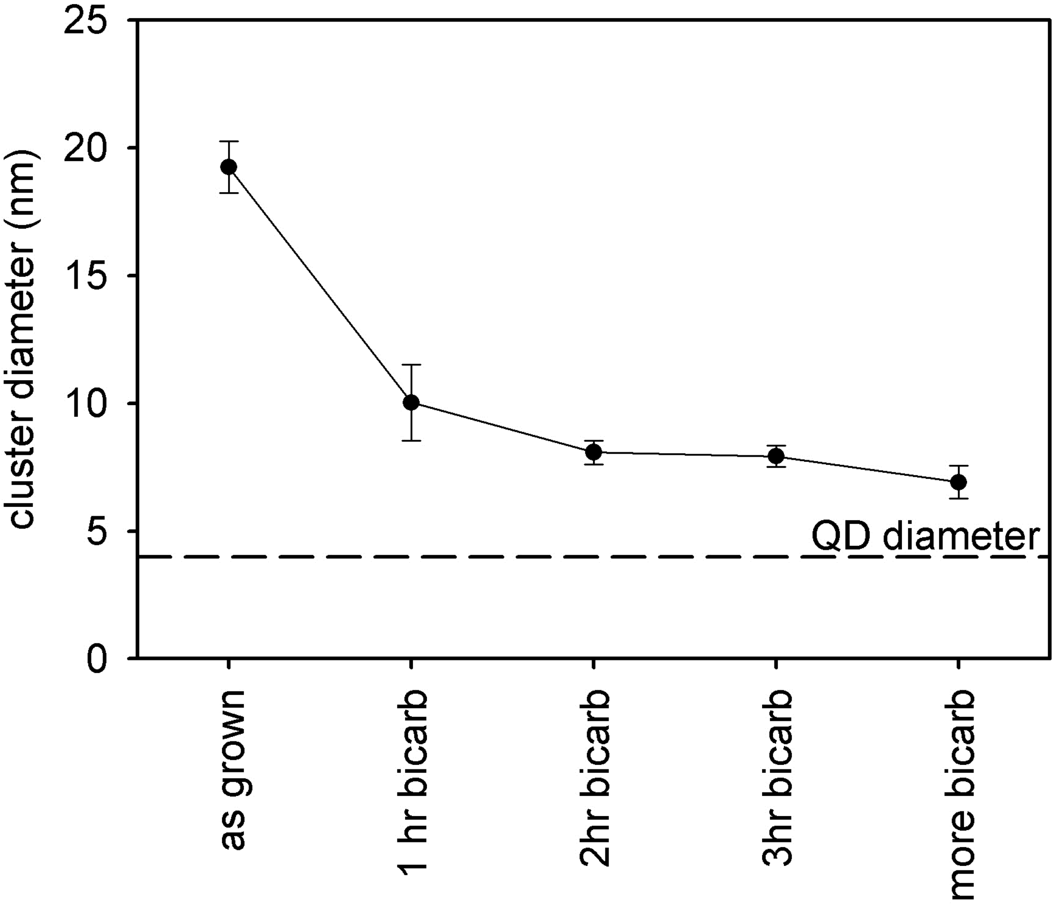
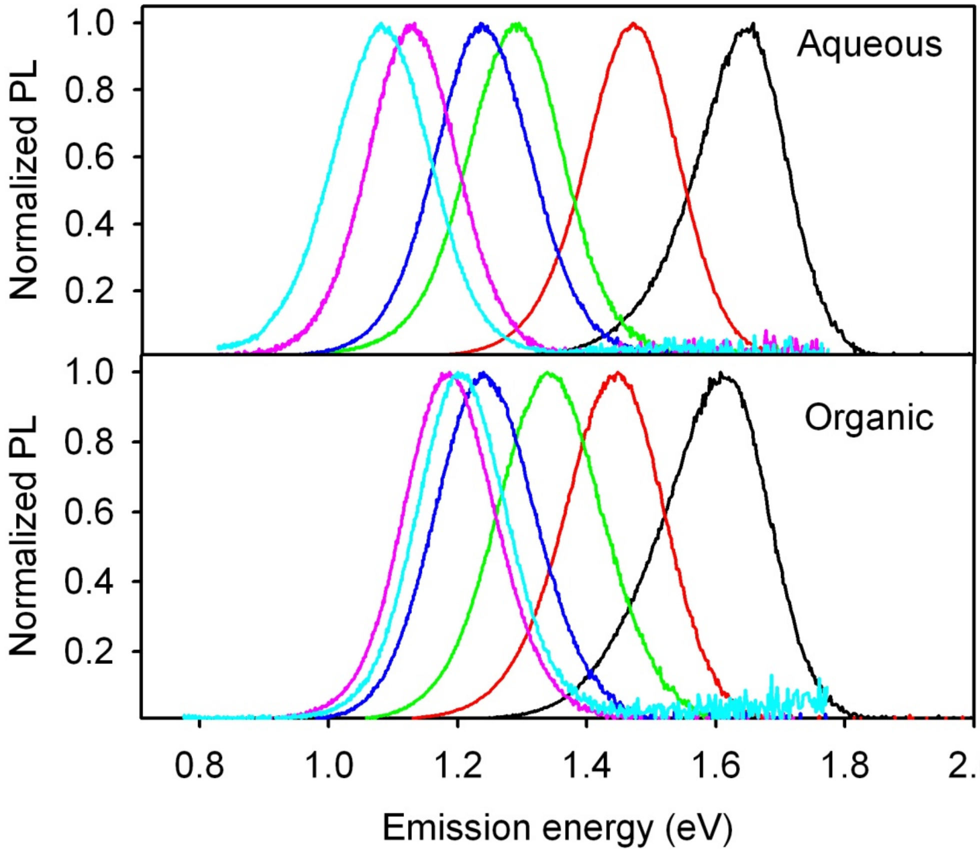


Fig. S2. Break up of 18nm diameter clusters of 4nm diameter HgTe QDs (passivated with thioglycerol) in aqueous solution on treatment with sodium bicarbonate solution. The break up of the clusters can also be effectively enhanced and accelerated using ultrasonic agitation, whilst the carbonate anion formed in alkaline solution (pH 10.8) sequesters excess Hg^{2+} ions preventing reformation of the larger gel-like particles.

SI 3 Phase transfer of QDs

When the required bandgap for each aliquot had been reached (determined approximately by the position of the PL peak), the QDs were finally de-clustered once more and then extracted by adding an equal volume of DDT. The solution was shaken vigorously several times for a few minutes each time using a lab-shaker (IKA Vortex Genius-3). On standing the DDT phase would contain much of the QDs, but separation of the two phases at this stage would not be complete. The solution was washed by adding another equal volume of water, giving the solution further vigorous shaking and decanting off the clear aqueous phase. After 3 or more such rounds, solvent (toluene or alternately tetrachloroethylene, TCE) was added and the non-turbid QD/DDT/solvent solution removed from the sample tube and retained. The remaining material in the tube was washed in this way with more solvent and further rounds of vigorous shaking until the amount of QD extracted in the solvent each time was negligible.

At this stage the concentration of DDT in the extracted solution was very high and for further studies in the IR the optical absorption was too great. To increase the QD concentration and reduce that of the DDT the solution was precipitated using methanol. Note that if the solvent to DDT ratio is high, a large excess amount of methanol might be necessary to precipitate the QDs. On the other hand, if the DDT concentration is high, initially treatment with methanol will yield a concentrated QD 'oil' rather than a solid precipitate after centrifugation. The 'oil' can be retained and the precipitation process repeated on it one or two times more after which the QDs can be collected as a solid. For optical measurements the QDs can be dissolved in toluene, or for IR measurements where the solvent has IR absorptions, TCE (or a mixture of toluene and TCE) may be preferable since TCE has no significant IR absorptions below 3μm.



Peak emission energy (eV)	FWHM/ peak wavelength (%)
1.607	12.2
1.448	12.5
1.339	14.1
1.24	14.5
1.188	14.1
1.2	13.5

Fig. S3. PL spectra of final six aliquots of $Cd_xHg_{1-x}Te$ alloy QDs taken during ion exchange process in aqueous solution (upper set) before final de-clustering and extraction into organic solvent (lower set). The relative spectral widths (FWHM/ peak wavelength as a percentage) are also listed on the right. The value for the starting solution of 3.75nm diameter CdTe QDs in aqueous solution was 8.6%. The excitation energy was 3.06eV (405nm) in each case.

Fig. S3 compares the PL spectra of a series of aliquots of $Cd_xHg_{1-x}Te$ alloy QDs both in the original aqueous solutions prior to extraction into organic solvent and afterwards. Up until the fourth aliquot the PL peaks in either phase are reasonably similar, with surface effects due to clustering in the aqueous phase and slight size selection during extraction and washing being plausible mechanisms for slight relative blue or red shifts of up to 20nm. However, the final two aliquots (which both took over a week to shift) are far less symmetric in the aqueous phase (long tails into the IR) and upon extraction into the organic phase do not appear to be shifted so far into the IR. This is interpreted as the aqueous phase QDs having a strong red shift due to significant accumulated Hg^{2+} on or very near to the QD surface rather than actually exchanged within the QD for Cd^{2+}. There is further evidence for this, along with an indication of the influence of clustering of the QDs themselves, in Fig. 4 of the main text which shows the fitted stretched exponential PL lifetimes and stretch factors for the aqueous and organic counterparts.

SI 4 The Transient Grating measurement technique.

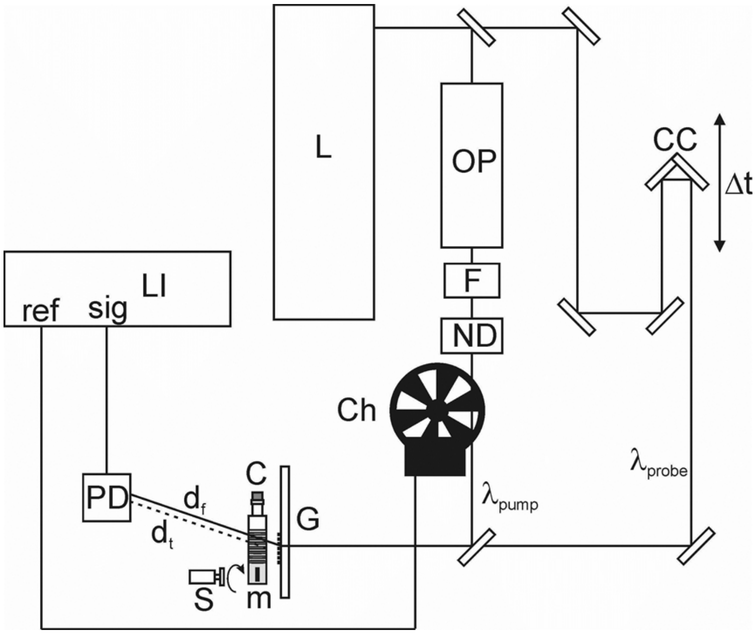


Figure S4. Transient grating experimental layout: L – regeneratively amplified Ti-sapphire laser with 1kHz repetition rate, 770nm, 150fs pulse output; OP – optical parametric amplifier to generate pump beam; F – wavelength filter to pass only required pump wavelength; ND – neutral density filters to control pump beam fluence; Ch – chopper wheel to modulate only pump beam; CC – corner cube reflector with variable position to provide differential delay Δt between pump and probe beams; G – static grating in close proximity to sample cuvette; C – sample cuvette containing liquid QD solution stirred by miniature magnet, m; S – magnetic stirrer actuator; PD – photodetector; LI – lock in amplifier locked to the chopper wheel reference signal (ref); sig – modulated signal from PD. d_f is a diffracted order beam at the probe wavelength from the fixed grating placed before and in close proximity to the cuvette whilst d_t is the same order of diffracted beam from the modulated pump induced grating created transiently in the QD sample. Although both d_f and d_t beams impinge on the photodetector only the latter gives rise to a signal modulated at the pump chopping frequency.

The experimental layout and optical beam geometry are shown in figure S4. The source laser used was a Ti-sapphire laser with an output wavelength of 775nm, a pulse repetition rate of 1 kHz and pulse width 150fs. Part of the output was used as a probe beam and the remainder used to provide a variable wavelength pump beam by converting the wavelength using an optical parametric amplifier (OPA). The latter was followed by a wavelength selective filter to remove any residual pump wavelengths, etc from the OPA output. The pump fluence at the sample was controlled by inserting neutral density filters in the pump beam path after the OPA. The pump beam was also mechanically modulated by a chopper wheel at low frequency (< laser pulse repetition frequency). In the probe beam path there is a variable delay line comprising a corner cube reflector on a programmable motorized stage so that the difference in arrival time of the pump and probe at the sample can be varied from zero to over 1ns in around 50 fs steps. Both pump and probe beams are overlapped at the sample cuvette and the solution within is stirred vigorously with a miniature magnetic stirrer bar to avoid photocharging effects. In front of the cuvette a transmission grating is placed in close proximity so that the diffracted beam pattern can induce a secondary grating pattern in the solution due to the spatially modulated pump light from the grating. The strongest component arises from the more intense pump beam and since the latter is mechanically chopped, the grating pattern induced in the QD solution by the pump beam is likewise also modulated at the chopping frequency. Both pump and probe beams are diffracted by both the static transmission grating placed before the sample and at zero differential delay by the transiently induced gratings in the solution due to their counterpart. However, with >0fs delay, only the diffracted orders of the probe beam arising from the pump induced transient grating will have the mechanical chopping frequency superimposed on the 1 KHz pulse train. The mechanically modulated probe beam can therefore be distinguished from all other diffracted beams by (a) spatial separation at the photodetector due to differences in wavelength (separates diffracted pump and probe orders) and (b) using a lock-in amplifier locked to the mechanical chopping frequency to follow only the pump induced changes to the diffracted probe beam.

It should be noted that neither pump or probe beam need to be focused with this TG grating approach and that it is therefore quite straightforward to operate at low fluence, avoiding non-linear optical effects that might otherwise give rise to transient gratings formed by other mechanisms than changes if carrier density within the QDs. In the measurements reported in the main text, it was possible to reduce the fluences to such low levels (typically a few mW average power levels) that (in the absence of carrier multiplication, e.g. with no MEG and below threshold) only one carrier pair per dot could be created – evident by the lack of any ps to tens of ps scale Auger recombination in such cases.

The pump induced grating detected by the probe beam may have both amplitude and phase grating components, due carrier population changes transiently altering both the transmission (induced absorption or bleaching) and via a Kramers-Kronig type relationship also the refractive index.[6],[7] In the TG geometry the combined diffracted orders from the two gratings may lead to either positive or negative changes in the diffracted signal intensity, particularly noticeable where the diffraction efficiencies from the amplitude and phase gratings are comparable. The change in the real component of the complete dielectric function (from which the refractive index and thereby the transiently induced phase grating follow) differs in sign on either side of an absorption peak, so this may lead to the photoinduced phase grating component changing in sign as the excitation wavelength is changed from below to above a resonance. When the excitation is far enough off resonance, as in the measurements reported in the main text when the excitation was above threshold, changes in the photoexcited carrier population due to multiple pair creation predominantly gave rise to a phase grating (transient refractive index change).

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