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Linking microscale morphologies to localised performance in singlet fission quantum dot photon multiplier thin films

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1. Synthesis of oleic acid capped lead sulfide colloidal quantum dots (PbS-OA).

A master batch of oleic acid-capped PbS nanocrystals was synthesised by the method of Hines & Scholes[1]. Lead oxide (PbO, 99.999%) was purchased from Alfa Aesar. Ethanol and 1-butanol (Hi-Dry anhydrous) were purchased from Romil. All other chemicals were purchased from Sigma-Aldrich. All materials were used as received without further purification. Lead oxide (1.25 g, 5.6 mmol), oleic acid (OA, 90%, 4 mL, 12.6 mmol) and 1-octadecene (ODE, 90%, 25 mL, 78 mmol) were placed in a 3-necked round-bottomed flask and degassed under vacuum (<10-2 mbar) at 110 °C for 2 hours with stirring, forming a colorless solution. In a nitrogen glovebox, a syringe was prepared containing ODE (13.9 mL, 43 mmol) and hexamethyldisilathiane (TMS_2S, 95%, 592 µL, 2.8 mmol). The flask was put under nitrogen flow and the syringe contents rapidly injected into the flask at 110 °C and allowed to cool. Upon cooling to 60 °C, the reaction mixture was transferred to an argon glovebox. The as-formed nanocrystals were precipitated with ethanol/butanol and centrifuged at 12000 *g*. The nanocrystals were then suspended with hexane and precipitated again with ethanol. The purified nanocrystals were suspended in toluene for storage.

2. OA-TetCAL ligand exchange

Ligand exchange of synthesised OA-capped PbS nanocrystals with TIPS-tetracene-carboxylic acid was performed as follows. TIPS-tetracene carboxylic acid was dissolved in toluene (20 mg mL^{-1}) and added to PbS nanocrystals in toluene (50 mg mL^{-1}). The mixture was stirred at room temperature overnight before precipitation with acetone and centrifugation at 12000 *g*. The exchanged nanocrystals were resuspended in toluene and the purification was repeated, with final resuspension in toluene to form a reddish-black solution.

3. Film formation + Encapsulation

Glass or silicon substrates were cleaned by sonication for 10 mins in a DI water and detergent (Decon90) mixture, followed by acetone and then isopropanol before being blown dry with compressed N_2.

Stock solutions of PbS-TET-CA (100 mg mL^{-1}) and three TIPS-Tc concentrations (222, 250, 333 mg mL^{-1}) were prepared in toluene. Films denoted as comprising TIPS-Tc (200 mg mL^{-1}) with PbS-Tet-CA loadings (10, 20 or 40 mg mL^{-1}) were prepared by mixing 20, 40 or 80 µL of the PbS-TET-CA stock solution with 180, 160 or 120 µL of the respective 222, 250, 333 mg mL^{-1} TIPS-Tc solutions.

Solutions of TIPS-Tc and PbS-TET-CA nanocrystals were prepared in toluene and under N_2 at varying concentrations. These were coated onto the glass or silicon substrates using a doctor blade at rT in a glovebox. Samples prepared on glass, where encapsulated through deposition of a ring of polyisobutylene onto the rim of a separate glass slide that was then placed over the coating. A low level of force was applied until a firm seal between the two glass slides was formed.

4. X-ray scattering

Grazing incidence x-ray scattering measurements were carried out on a Xeuss 2.0 instrument equipped with an Excillum MetalJet liquid gallium X-ray source. Films prepared on glass were collected for 900 s using collimating slits of 0.5 × 0.6 mm ("high flux" mode).
Alignment was performed via three iterative height (z) and rocking curve (Ω) scans, with the final grazing incidence angle set to Ω = 0.3°. Scattering patterns were recorded on a vertically-offset Pilatus 1M detector with a sample to detector distance of 379 mm, calibrated using a silver behenate standard to achieve a *q*-range of 0.04 – 1.85 Å^{-1}. Data reduction was performed using the instrument-specific *Foxtrot*. Fitting of QD with the *q*-range of 0.1 – 0.25 Å^{-1} features was performed using *SasView*.

4.2 Small-angle scattering models

4.2.1. Sphere model

PbS nanocrystal cores are adequately modelled as spherical scattering particles. The form factor of such particles, expressed as the scattering intensity as a function of the magnitude of the scattering vector, q, is given by

$$I(q) = \frac{scale}{V}\left[3V(\Delta\rho)\frac{\sin(qr) - qr\cos(qr)}{(qr)^3}\right]^2 + background$$

where r and V are the radius and volume of the sphere, $\Delta\rho$ is the scattering length density contrast difference between the solvent and the spherical particle. For data that has been correctly normalised onto an absolute intensity scale in units of cm^{-1} the $scale$ represents the volume fraction of scattering particles.

4.2.2 Structure factors

In a many-particle system like a solution or nanocomposite of colloidal quantum dots, scattering may arise from inter-particle correlations as well as from the primary particles themselves. This scattering is taken into account by a *structure factor* $S(q)$ that multiplies the form factor at each point in q, i.e.

$$I(q) = F(q)S(q)$$

4.2.2.1 Hard sphere structure factor

The hard sphere structure factor is not used in the current study but is important in the development of the sticky hard sphere structure factor described in the next subsection. It is a calculation of the interparticle structure factor for monodisperse spherical particles interacting through excluded volume interactions. This is calculated using the Percus-Yevick closure[2] where the inter-particle potential is given as:

$$U(r) = \begin{cases} \infty & r < 2R \\ 0 & r \geq 2R \end{cases}$$

4.2.2.2 Sticky hard sphere structure factor

The sticky hard sphere structure factor (as implemented in SasView version 4.2.2) is a calculation of the interparticle structure factor for monodisperse spherical particles interacting via a narrow, attractive, potential well. This is calculated using a perturbative solution to the Percus-Yevick closure[3, 4]. The inter-particle potential is given by

$$U(r) = \begin{cases} \infty & r < \sigma \\ -U_0 & \sigma \le r < \sigma + \Delta \\ 0 & r > \sigma + \Delta \end{cases}$$

where the stickiness parameter quantifying the attractiveness of the well is given by

$$\epsilon = \frac{1}{12\tau}\exp\left(U_0/k_B T\right)$$

where U_0 is the depth of the potential well. The stickiness ϵ is also dependent upon the perturbation parameter τ, which sets the width of the well via the relation $\tau = \Delta/(\sigma + \Delta)$. Here, σ is the classical hard sphere radius of $2R$ and Δ is the width of the potential well.

4.2.3 Lognormal polydispersity distribution

The lognormal distribution as implemented in SasView 4.2.2[5] was used to describe the polydispersity in the radii of quasi-spherical PbS quantum dot cores. It is usually obtained from a SAXS measurement which provides the optimal contrast. The lognormal distribution is a function of r for which $\ln r$ has a normal distribution.

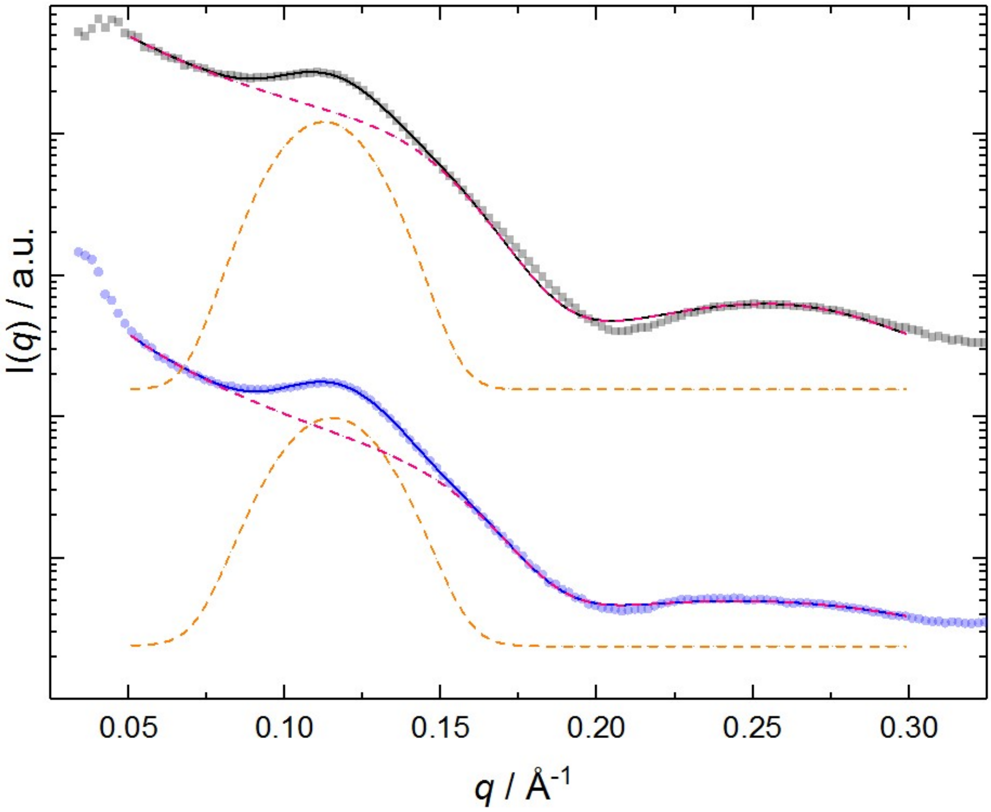
$$f(r) = \frac{1}{Norm}\frac{1}{r\sigma}\exp\left(-\frac{1}{2}\left(\frac{\ln r - \mu}{\sigma}\right)^2\right)$$

In this notation, r represents the radius of the quasi-spherical quantum dot core, $Norm$ is the normalisation factor, $\mu = \ln r_{med}$ and r_{med} is the median value of the lognormal distribution and σ describes the width of the underlying normal distribution.

4.3 Model fitting of radially integrated data

*SI Table 1: Results from the fits of the GISAXS data for PbS-TetCAL:TIPS-T, fitted to a sphere*sticky-hard-sphere model, with lognormal polydispersity or a sphere*sticky-hard-sphere model, with lognormal polydispersity + Guassian peak model. Radius (22.236 Å) and polydispersity co-refined (0.114 Å) (fixed) between all three datasets.*

PbS-TetCAL:TIPS-T /mg ml^{-1}	Sphere*sticky-hard-sphere					Gaussian peak		
	Scale	Background	Vol fraction	Perturbation	Stickiness	Scale	Peak position (Å^{-1})	Sigma (Å^{-1})
10:200	5.26	16.97	0.08	0.089	0.142	NA	NA	NA
20:200	2.16	23.76	0.147	0.016	0.11	445.8	0.115	0.015
40:200	2.69	15.59	0.149	0.083	0.149	449.5	0.113	0.014



*SI Figure 1: Radially integrated grazing incidence scattering data for 20:200 (blue circles) and 40:200 (grey circles) PbS-TetCAL:TIPS-T blend films, with model fits (solid blue and black lines, respectively) and the separate sphere*sticky-hard-sphere (pink dashed line) + Gaussian peak (orange dashed line) components of the model employed.*

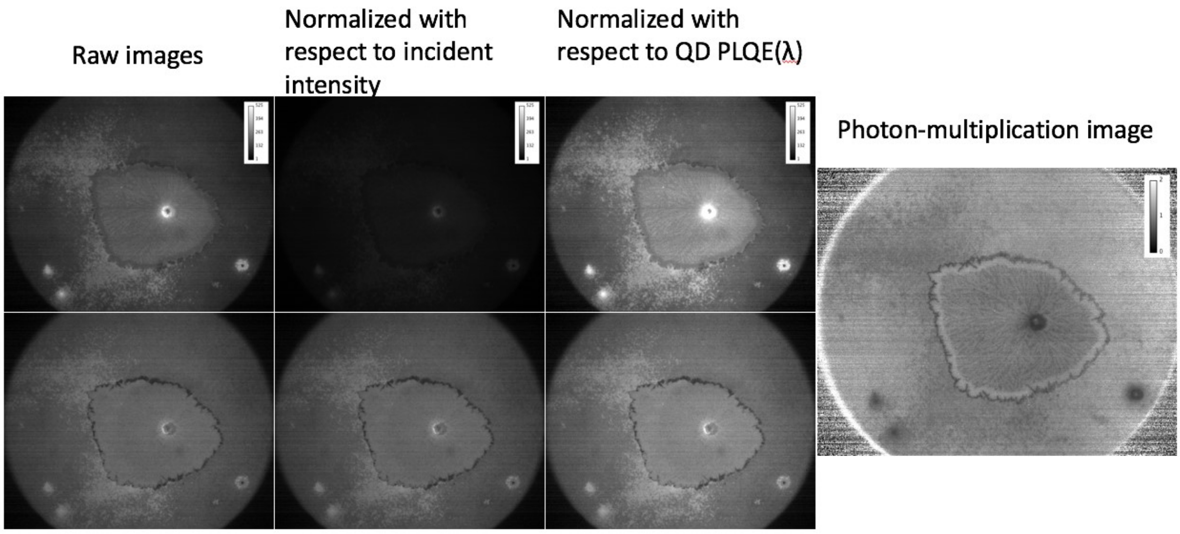
5. Polarised optical microscopy

Polarized optical microscopy micrographs were obtained using polarised white light illumination, with the analysing polariser at aligned at 90° to the polarised illumination using either; A plan 2.5x/0.06. N-achroplan 10x/0.25 or *LD Plan NeoFluer x20/0.4 objectives with a Axiocam 105 colour camera giving field of views of 2440 x 1820, 610 x 455 and 305 x 227 µm, respectively.*

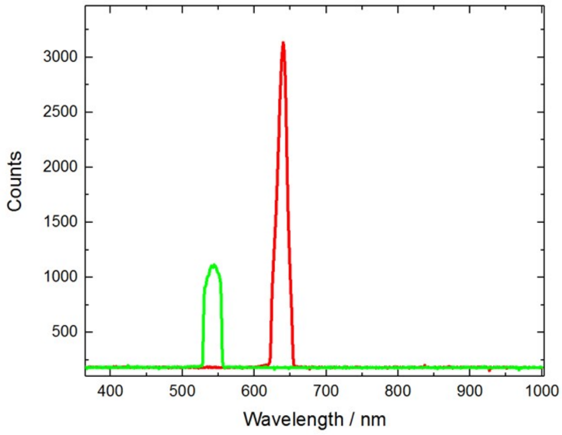
6. IR fluorescence

IR fluorescence was performed on a Zeiss Axio Scope.A1 in reflection mode utilizing either LED-module neutral white f. Axio, EX BP 550/25, BS FT 570 or LED-module 625nm f. Axio, EX BP 640/30, BS FT 660. For both excitation wavelengths a 1000 nm shortpass filter was placed between the LED illumination source and excitation bandpass filter and a 1000 nm longpass filter placed between the dichroic mirror and the detector. *A IR sensitive camera (InGaAs Hamamatsu Model Number: C12741-03) coupled with a LD Plan NeoFluer x20/0.4 objective provided micrographs with a field of view of 1823 x 2442* µm.

The intensity of the incident excitation source was normalized utilizing a UV/VIS spectrophotometer (Ocean Optics USB2000+) with an optical fibre attachment aligned at the centre of the focused illumination in the sample plane. Data were normalized with respect to the wavelength dependence of QD PLQE using previously published data on this system.[6]



SI Figure 2: Image processing steps to obtain "photon-multiplication image" from fluorescence images excited via 640 nm (top row) and 550 nm (bottom) row.



SI Figure 3: UV/VIS spectra of fluorescence excitation at 550 and 640 nm. Peak areas were obtained using OriginLab 2017's peak analyser function, with values obtained used to normalize fluorescence images with respect to the incident illumination intensity.

7. Steady-State Absorption

A Shimadzu UV-3600Plus spectrometer was used to measure the absorbance spectra of a representative TIPS-Tc:PbS-TET-CA film.

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