Supporting Information

1. Core-shell synthesis and hybrid sol-gel preparation

1.1 Chemicals

5-Amino-1-pentanol (AP, 95%), zirconium(IV) isopropoxide (70 wt% in 1-PrOH), titanium(IV) isopropoxide (97 %), acetylacetone (ACAC, 99%) were purchased from Sigma–Aldrich. Hexane, chloroform, PrOH (propanol), EtOH (ethanol), and MeOH were all of analytical grade and purchased from Univar. All chemicals and solvents were used without further purification.

1.2 Synthesis

CdSe nanocrystal (NC) preparations were adapted from those reported by van Embden *et al.*[1]. Briefly CdO and oleic acid were heated in ODE to 80 °C and degassed for 30 mins. The solution was then heated to 310 °C under nitrogen until a colourless solution resulted. At this point a solution of TOPSe, TMPPA and ODE was swiftly injected. The growth temperature was set to 240 °C and growth of the subsequent nascent crystallites continued for 30 mins. The resulting NCs dimensions could be controlled by changing the relative concentration of TMPPA and oleic acid as described by van Embden and Mulvane. The nanoparticles were washed via a chloroform-MeOH-Acetone extraction.

Shelling of the NC's was performed utilizing a modified SILAR method[2,3]. 7.62 x 10^{-6} mole of NC's were degassed in 72.5 g ODA and 72.5 g ODE at 80 °C for at least 1 hour. The temperature was then slowly ramped to between 210-240 °C for the subsequent growth of a CdS-ZnS shell. 0.1M stock solutions of ODE-S, ODE-CdTMPPA (0.8M TMPPA) and ODE-ZnTMPPA (0.8 M TMPPA) were used. The first layer to be grown was a half monolayer of Cd as suggested by Rengue et al. From thereon alternate layer-by-layer deposition of S, Cd and Zn occurred. A total of 3 monolayers (CdS x1, ZnS x2) were grown based on the wurtzite c_o-axis lattice parameter. Following the final Zn layer, the NC's were annealed at 240 °C for 30 mins and cooled to 100 °C overnight. The extraction method described by Li et al. was used to remove excess salts and the resulting CdSe-ZnS NC's were finally dispersed in chloroform[2].

To render the NC's soluble in alcohol solutions, a similar procedure to that utilized by Petruska et al. was used[4]. The NC's were firstly precipitated from chloroform with AP. These NC's were then redispersed in a 1:1 by volume of EtOH/$CHCl_3$ mixture with 0.1M AP to promote a thorough ligand exchange. The solution was allowed to gently stir for 12-24 hours. Following this time the

NC's were precipitated with excess hexane. The AP functionalized particles were then redispersed in MeOH and were colloidally stable for over 1 month.

The sol-gel solution of the ZrO_2 film was prepared by mixing $Zr(OPr)_4$ (1 mL, x mole), acetylacetone (0.23 mL) and i-PrOH (6 mL). The sol solution was allowed to hydrolyse for ~1 hour prior to use. QD doped thin films were made by adding 100 μL of sol-gel sol-solution to 200 μL of a solution of QDs in MeOH. These solution were allowed to stir for an additional ~1 hour prior to the spin coating process. All the films in this study were spin coated at 3500 rpm for 20 seconds in Ar atmosphere to prevent degradation. The films were then treated at 100 °C for 2 min and at 250°C for a further 5 min. Multilayer films could in this way be deposited. Further details of incorporating nanocrystals into sol-gel hosts is given elsewhere[5].

2. Optical Characterization

2.1 Linear Characterization

UV-Visible spectra are recorded with a Cary 5 spectrometer (Varian) and the fluorescence spectra are measured with the fluorimeter FluoroMax P (Jobin-Yvon).

Transmittance at normal incidence and ellipsometry quantities Ψ and Δ have been measured using a J.A. Woollam V-VASE Spectroscopic Ellipsometer in vertical configuration, at three different angles of incidence (65°, 70°, 75°) in the wavelength range 300-900 nm. Optical constants n and k and film thickness have been evaluated from Ψ, Δ and transmittance data using WVASE32 ellipsometry data analysis software, fitting the experimental data with Cauchy dispersion and Gaussian and Tauc-Lorentz oscillators for non absorbing region, QDs absorption peak and UV absorption edge, respectively.

2.2 TPIF

TPIF experiments are performed using a tunable Ti:Sapphire femtosecond laser system (Coherent Mira 900-F), with pulses of duration approximately 130 fs, with 76 MHz repetition rate and a 700 to 930 nm varying wavelength. The laser beam is focused on the sample, contained in a 10 mm quartz cell, via a 40 cm focal length lens, following the experimental setup described by Rumi et al.[6]. The input irradiance at the sample is varied up to 100 MW/cm^2. TPA spectrum is obtained for QDs solution at concentration in the range 2×10^{-6} to 2×10^{-5} M.

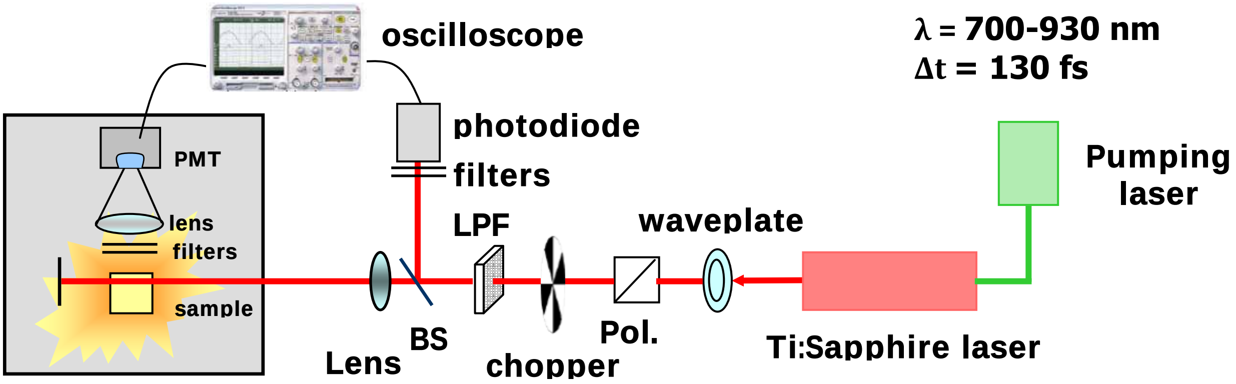

Figure 1. TPIF Experimental set-up.

For each exciting wavelength investigated, the quadratic trend of the TPE signal versus impinging light intensity is verified and recorded, and the TPA cross-section (σ_{TPA}) is obtained using the expression[7]:

$$\sigma_s = \frac{q_s}{q_r}\frac{C_r}{C_s}\left(\frac{n_s}{n_r}\right)^2 \frac{F_r}{F_s}\sigma_r$$

where C_i are the concentration for the sample (suffix s) and the reference (suffix r) solutions, q_i the coefficients of the quadratic fit, n_i the solvent refractive indices, F_i the fluorescence quantum yields, and σ_i is the TPA cross section. TPA data for the reference chromophore (Fluorescein in H_2O pH>11 C~3×10^{-5} M), were as published by Xu et al.[8]. The QDs solution concentration is about 2×10^{-6} M.

2.3 ASE

ASE and lasing emission are performed with an amplified Ti:Sapphire laser system. It delivers 150 fs pulses, with a maximum of 0.7 mJ per pulse energy, at ~ 800 nm and a repetition rate variable between 1 KHz to 10 Hz. With a BBO doubling crystal and a cut-off filter a 400 nm wavelength beam is obtained. The intensity of the input beam is continuously varied with a half wave plate in series with a polarizer, and a set of neutral density filters. The spatial profile of the input beam was measured using a CCD camera (Pulnix TM-7CN), placed on the beam focus, and the pulse energies are sampled with a pyroelectric detector (Molectron J3-05).

For ASE measurements the input beam is focused with a 200 mm focal length cylindrical lens onto the slide samples. Sample's edge emitted beam is detected in a lateral configuration (see figure 2 and 3) by an optical fiber connected to a micro-spectrometer (Ocean Optics HR2000).

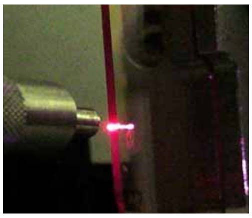

Figure 2. ASE signal lateral detection.

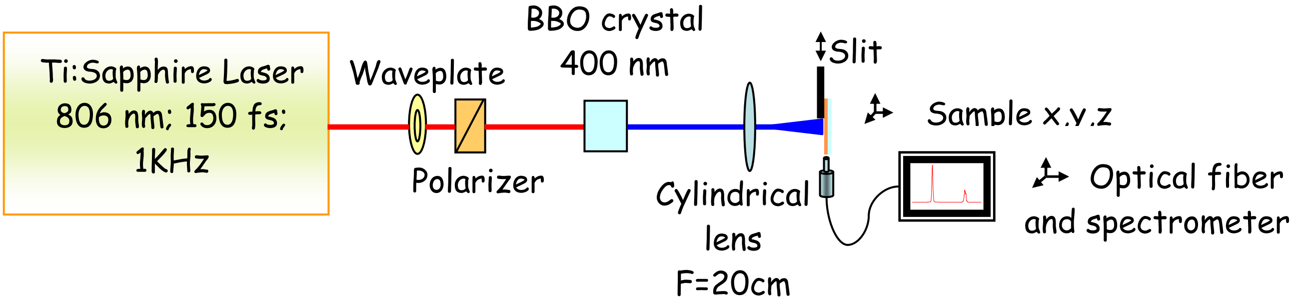

Figure 3. ASE Experimental set-up.

2.4 Lasing

For lasing measurements the input beam is focused with a 100 mm spherical focal lens onto the slide samples. The sample is back illuminated and the emitted signal is recorded with a 0° geometry (figure 4), using the optical fiber connected to micro-spectrometer, a cut off filter is used to remove the residual pumping laser beam.The device emission was detected in a plane parallel to the grating grooves containing the exciting beam (figure 5).

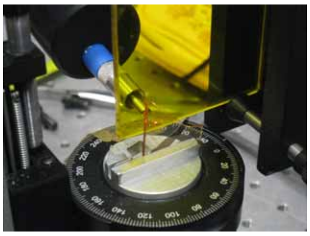

Figure 4. Lasing signal detection at 0°.

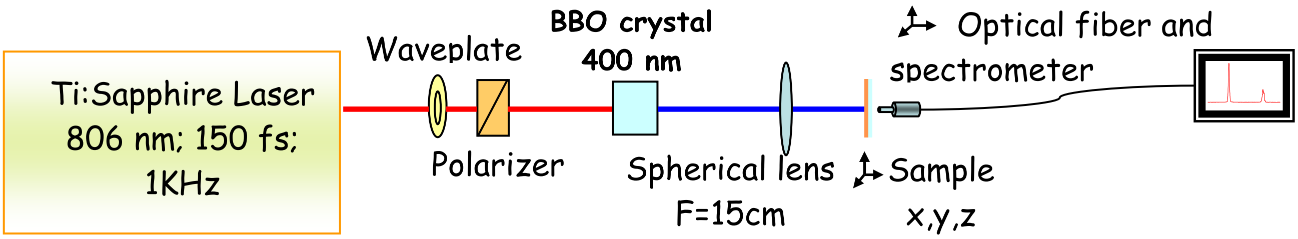

Figure 5. Lasing Experimental set-up.

References:

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[4] Petruska, M. A., Malko, A. V., Voyles, P. M., and Klimov, V. I., *Advanced Materials* **15** (7-8), 610 (2003).

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