

Supporting Information for:

Incorporation of Fluorescent Quantum Dots for 3D Printing and Additive Manufacturing Applications

Cole D. Brubaker,^{†,‡} Talitha M. Frecker,^{#,‡} James R. McBride,[#] Kemar R. Reid,[§] G. Kane Jennings,[▽]
Sandra J. Rosenthal,^{#,||,°,§,▽,*} Douglas E. Adams^{†,⊥,*}

Departments of [†]Civil and Environmental Engineering, [#]Chemistry, ^{||} Physics and Astronomy,
[°]Pharmacology, [§]Interdisciplinary Materials Science, [▽]Chemical and Biomolecular Engineering,
[⊥]Mechanical Engineering, Vanderbilt University, Nashville, Tennessee 37235, United States.

Corresponding Authors

*Douglas Adams: douglas.adams@vanderbilt.edu

* Sandra Rosenthal: sandra.j.rosenthal@vanderbilt.edu

Fluorescence lifetime measurements

For time-resolved photoluminescence (TRPL) measurements, the QD films were excited at low power ($\sim 30\text{mW/cm}^2$) using a 405 nm pulsed source (100 ps pulse duration) with a repetition rate of 1 MHz. Photoluminescence from the films was filtered with an appropriate long-pass filter and directed onto a single-photon avalanche photo-diode (SPAD, Micro Photon Devices, PD-050-0TC). A time-correlated single photon-counting unit (TCSPC, PicoHarp 300) was used to generate a histogram of photon arrival times. Lifetimes were determined by fitting the histogram of arrival times to a tri-exponential function:

$$I_{PL}(t) = \sum_i A_i \exp(-t/\tau_i) \quad (1)$$

The average lifetime, τ_{avg} was calculated using the fit components as follows:

$$\tau_{avg} = \sum_i^n \frac{A_i \tau_i}{\sum_i^n A_i} \quad (2)$$

Decay curves were fit with the following equation, where A_i and τ_i are the decay amplitudes and lifetimes, respectively.

$$I(t) = \sum_{i=3}^n A_i e^{-\left(\frac{t}{\tau_i}\right)} \quad (3)$$

For samples in solution TRPL measurements were performed on diluted solutions with optical densities below 0.1 at the lowest-energy absorption transition.

Figures:

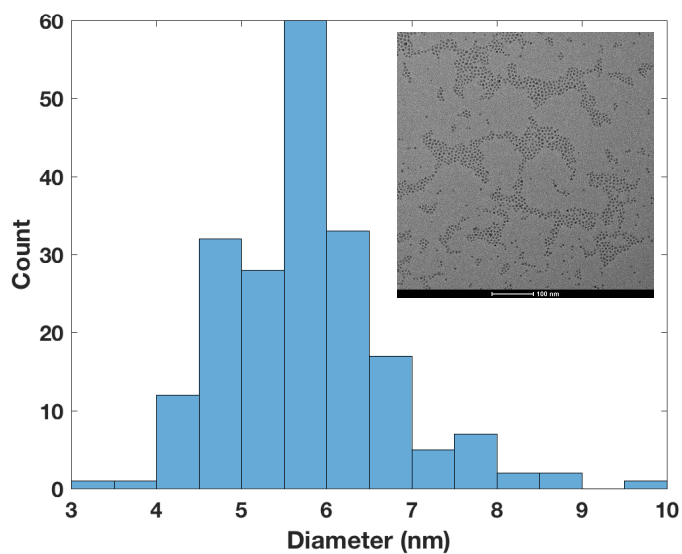


Figure S1. Size distribution and TEM image of CdSSe QDs in solution. Average diameter of CdSSe QDs in solution is 5.74 ± 0.95 nm.

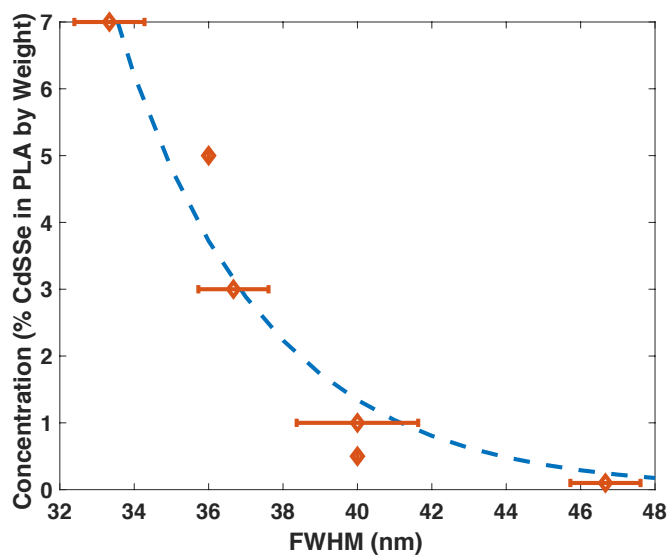


Figure S2. Full width half maximum (FWHM) analysis of photoluminescence spectra for PLA/CdSSe QD 3D-printed films at varying concentrations of CdSSe QDs in PLA by weight.

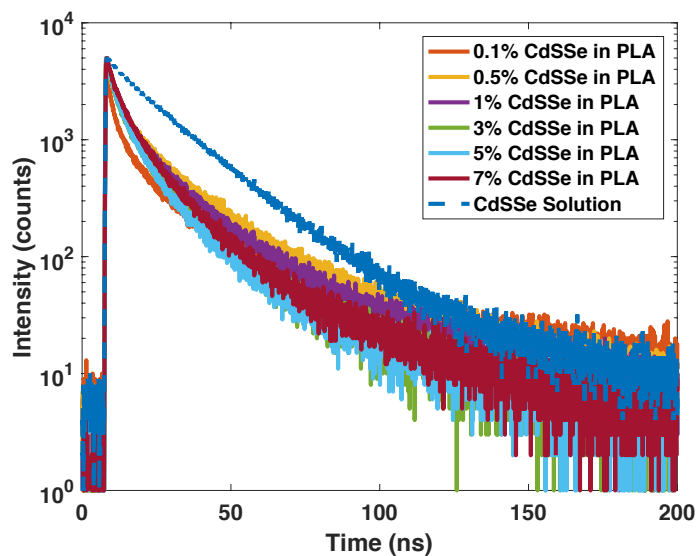


Figure S3. Lifetime analysis of 3D-printed PLA/CdSSe QD films and CdSSe QDs in solution.

Table S1. Lifetime analysis of 3D-printed PLA/CdSSe QD films and CdSSe QDs in solution.

Parameter	CdSSe solution	0.1%	0.5%	1.0%	3.0%	5.0%	7.0%
A₁ (counts)	210.7	377.8	642.6	517.1	326.7	248.8	252.0
T₁ (ns)	46.811	33.541	31.656	30.920	30.392	32.506	34.977
A₂ (counts)	4183.3	1308.9	1801.1	1861.9	1980.2	2002.8	2152.4
T₂ (ns)	19.112	7.905	10.499	10.490	9.265	9.579	11.117
A₃ (counts)	560.9	2675.2	2426.6	2625.4	2696.4	2790.5	2607.1
T₃ (ns)	4.395	1.247	1.869	2.009	2.251	2.459	3.006

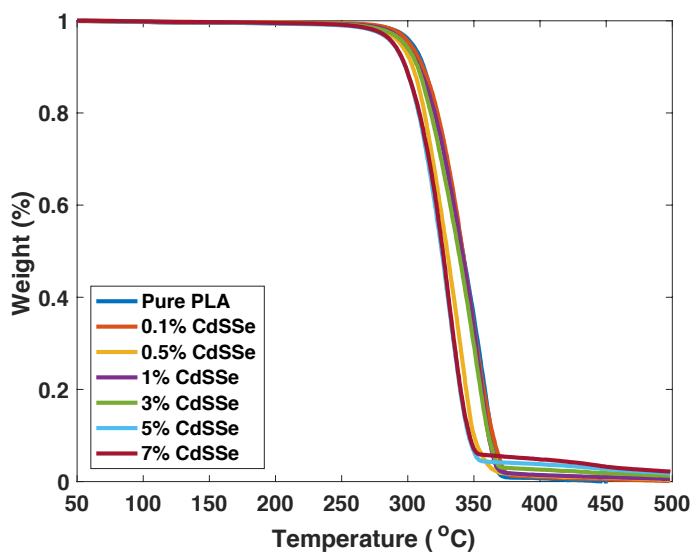


Figure S4. Thermogravimetric analysis response of 3D-printed pure PLA and PLA/CdSSe QDs films at various concentrations of CdSSe in PLA by weight (0.1%, 0.5%, 1%, 3%, 5%, 7%). All films studied showed good thermal stability in the range of temperatures used for materials processing and 3D-printing.

Table S2. Differential scanning calorimetry results

	Glass Transition Temperature (°C)	Crystallization Temperature (°C)	Melting Temperature (°C)
Pure PLA	59.4 ± 1.0	106.5 ± 1.4	172.5 ± 1.3
0.1% CdSSe QD in PLA	59.0 ± 0.8	104.7 ± 1.9	170.8 ± 1.3
0.5% CdSSe QD in PLA	59.1 ± 4.4	101.9 ± 1.6	171.3 ± 3.7
1% CdSSe QD in PLA	59.2 ± 3.0	100.2 ± 2.1	172.1 ± 2.9
3% CdSSe QD in PLA	53.4 ± 1.5	95.7 ± 1.9	166.8 ± 1.5
5% CdSSe QD in PLA	52.4 ± 0.3	92.4 ± 0.4	165.5 ± 1.7
7% CdSSe QD in PLA	51.0 ± 1.1	93.3 ± 0.4	163.2 ± 1.0

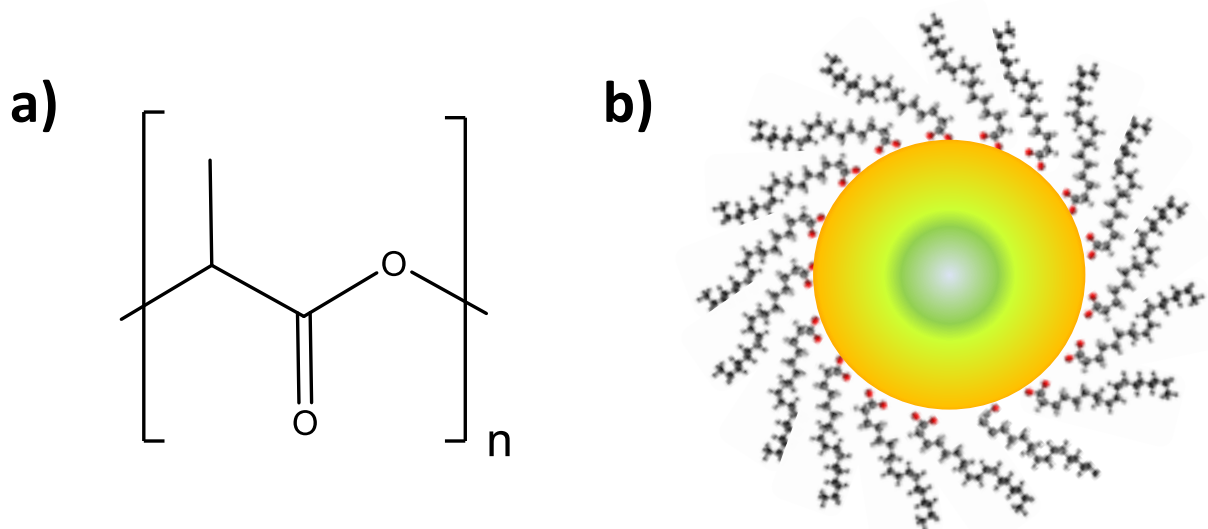


Figure S5. a) Chemical structure of polylactic acid polymer host matrix and b) schematic representation of cadmium sulfur selenide graded alloy quantum dots and corresponding oleic acid surface ligands.

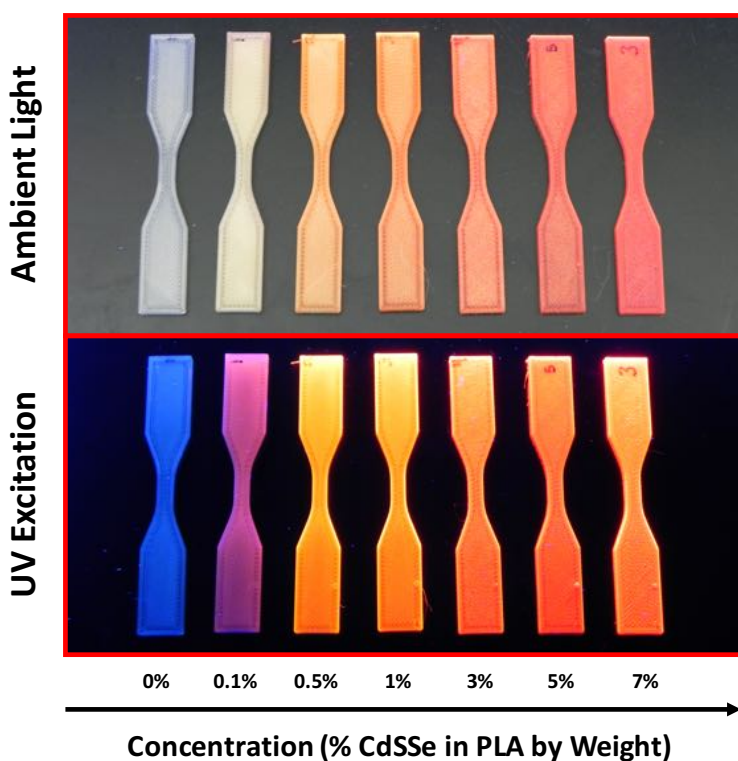


Figure S6. 3D-printed ASTM D638 Type V tensile dogbone specimen with varying of concentration of CdSSe in PLA by weight under ambient light and UV excitation (top and bottom, respectively). Blue coloration on pure PLA sample (0% CdSSe in PLA by weight) is due to reflection of UV excitation source on the 3D-printed sample.

Table S3. Mechanical properties of 3D-printed pure PLA and PLA/CdSSe QD tensile test specimens

	Average Ultimate Tensile Strength (MPa)	Average Strain at Break (mm/mm)	Average Tensile Modulus (MPa)	Average Toughness ($\times 10^8$ J/m³)
Pure PLA	62 \pm 1.0	0.26 \pm 0.02	447 \pm 43	11 \pm 1.4
0.1% CdSSe QD in PLA	58 \pm 1.0	0.23 \pm 0.03	342 \pm 29	7.2 \pm 0.99
0.5% CdSSe QD in PLA	55 \pm 0.81	0.23 \pm 0.03	354 \pm 38	7.6 \pm 0.95
1% CdSSe QD in PLA	50 \pm 0.26	0.19 \pm 0.01	342 \pm 11	5.5 \pm 0.52
3% CdSSe QD in PLA	42 \pm 1.0	0.20 \pm 0.02	336 \pm 21	5.3 \pm 0.47
5% CdSSe QD in PLA	29 \pm 0.71	0.16 \pm 0.01	319 \pm 14	3.0 \pm 0.19
7% CdSSe QD in PLA	22 \pm 0.60	0.11 \pm 0.01	345 \pm 12	1.5 \pm 0.30