SUPPORTING INFORMATION

Giant Nanocrystal Quantum Dots: Stable Down-Conversion Phosphors that Exploit a Large Stokes Shift and Efficient Shell-to-Core Energy Relaxation

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Experimental: (I) Device fabrication procedure:

Surface treatment. Thin ITO glass slides (Delta technologies limited) are plasma cleaned. This is followed by surface treatment of the glass slides by immersing the slide in a mixture of 30 µL of heptadecafluoro 1,1,2,2 tetra(hydrodecyl) trichlorosilane in 30 mL of n-hexadecane for 50 seconds, followed by rinsing with chloroform and drying under a flow of nitrogen. Similar surface treatment procedure is utilized for thin cover glass (Fisher Scientific).

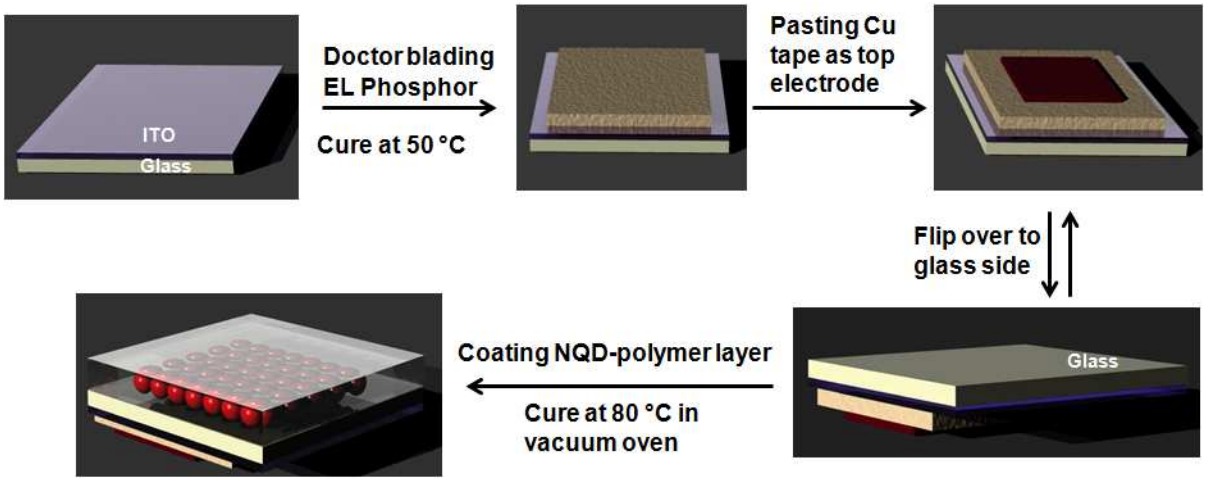
NQD:polymer composite. We incorporated our NQDs into poly(lauryl methacrylate) (PLMA) as previously described[1] to form homogenous and optically clear NQD-PLMA composites. To this end, a weighed amount of g-NQD or NQD is mixed with a monomer solution [lauryl methacrylate (2.0 mL), ethylene dimethacrylate (0.5 mL), and AIBN (10 mg)] and stored in a refrigerator for 30 mins to allow undispersed NQDs to settle to the bottom. To prepare PLMA-NQD composite films, 40 µL of this solution is dropped on the glass side of the ITO-coated glass slide, forming a prominent droplet. A surface-treated cover glass is placed on top of the droplet, carefully to avoid trapping air bubbles and to facilitate formation of homogenous films. The resulting sandwich structure is baked in a vacuum oven for more than 8 hrs at 80 °C at -10 mm of Hg in an argon environment. We assessed composite-film homogeneity by acquiring PL spectra from various locations in the films. We observed that emission intensity was essentially uniform across the films.

EL phosphor layer. EL powder phosphor is added to binder polymer (γ-butyrolactone) in 1:1.2 ratios by weight. The components are blended thoroughly before being drop-cast and doctor bladed into thin films (250-450 µm) on the ITO side of the surface-treated ITO-glass slides. These slides are then allowed to cure in an oven for more than 5 hours at 55 °C.

Electrodes and AC biasing. Conducting copper tape (3M), pasted on the EL phosphor layer, acts as the top electrode while copper wire attached onto ITO, using Ag paste, acts as a bottom electrode. For AC biasing of the EL phosphor, a DC power source and a JKL Inverter are utilized.

White LEDs (WLEDs). Same working protocol is utilized to make WLEDs using red g-NQDs and green NQDs as the two additive color-mixing components. The weighed amounts of red and green components utilized to make different WLEDs with different CIE coordinates and CCT are listed in table format below, where tables correspond to specific figures in the main text (as indicated).

Schematic of Device Fabrication procedure



Experimental: (II) Nanocrystal quantum dot synthesis:

Cd-containing NQDs: Materials. Cadmium oxide, oleic acid (90%), 1-octadecene (ODE, 90%), 1-octadecane (OD, 90%) oleylamine, sulfur, selenium pellet, and trioctyl phosphine (TOP) were purchased from Aldrich and used without further purification. Trioctyl phosphine oxide (TOPO) (90%) was purchased from STREM and used without further purification.

CdSe Core Synthesis. The CdSe core was prepared by reported procedure with minor modifications.[2] A 100 ml round bottom (r.b.) flask equipped with a reflux condenser and a thermocouple probe was charged with 1 g of TOPO, 8 ml of ODE and 0.38 mmols of Cd-oleate under standard air free conditions. The reaction system was evacuated for 30 minutes at room temperature and 30 minutes at 80 °C, and then the temperature was raised to 300 °C under argon, following which a mixture of 4 mmol of TOP-Se, 3 ml oleylamine and 1 ml of ODE was quickly injected into the reaction system. The temperature was then lowered to 270 °C for CdSe NQD growth. After several minutes, the solution was cooled to room temperature, and CdSe nanocrystal quantum dots (NQDs) (diameter, d = 3 nm) were collected by precipitation with ethanol and centrifugation. CdSe core NQDs were re-dispersed in hexane.

CdS Core Synthesis. The CdS core was prepared by reported procedure.[3]

CdSe/nCdS Core/Shell g-NQD Synthesis. The synthesis of core/shell CdSe/nCdS g-NQDs followed the successive ionic layer adsorption and reaction (SILAR) approach pioneered by Peng and co-workers[4] with our modifications.[5] A 250 ml r.b. flask was charged with ~2×10^{-7} moles of pre-washed CdSe cores, 5 ml of oleylamine and 5 ml of OD. 0.2 M elemental sulfur dissolved in OD and 0.2 M Cd-oleate in ODE were used as precursors for shell growth. The quantity of precursors for growing each monolayer of shell was calculated according to the volume increment of each monolayer shell, considering the changing total NQD size with each successive monolayer grown (each monolayer addition increases the NQD radius by ~0.34 nm, as calculated from ½ the c parameter for the wurtzite CdS crystal structure). The reaction temperature was set at 240 °C. Growth times were 1 h for sulfur and 2.5 h for Cd^{2+} precursors. Reactions were continued until desired shell thickness was achieved. The g-NQDs were washed in a similar fashion as the CdSe cores, by precipitating 2-3 times with ethanol and re-dispersing

in hexane. Relative quantum yields (QYs) in emission were determined in comparison to a standard dye (Rhodamine 6G, 99%, Acros) and were observed to vary as a function of shell thickness.

InP NQDs: Materials. Octadecene (ODE; 90%), myristic acid (99.5%), and oleylamine (approximate C18-content, 80-90%) were acquired from Acros Organics. Indium (III) acetate (99.99+%-In), tri-n-octylphosphine (TOP; 97%) and tris(trimethylsilyl)phosphine ($(TMS)_3P$; 98%) were purchased from Strem Chemicals; selenium pellet came from Aldrich and zinc stearate (ZnO 12.5-14%) was procured from Alfa Aesar.

Methods. InP/ZnSe core/shell NQDs were synthesized using a modification of a previously reported method.[6] In brief, cores were produced through the hot injection of $(TMS)_3P$ into an indium myristate solution, while shells were added via repeated SILAR deposition of zinc stearate and TOP:Se with thermocycling. An indium myristate stock solution was prepared by heating 4 mmol indium (III) acetate, 14.4 mmol myristic acid, and 50 mL of ODE to 120 °C under vacuum. A 0.1 M zinc stearate solution was prepared by dissolving 7.23 g zinc stearate in 100 mL ODE at 120 °C under vacuum. Selenium pellet was stirred at room temperature in TOP overnight in the glovebox to produce the 0.1 M TOP:Se precursor. For the core reaction, 2.5 mL of indium myristate were heated to 100 °C and degassed in a three-necked round bottomed flask; subsequent to backfilling with argon, the temperature was raised to 188 °C and a mixture of 0.75 mL oleylamine, 0.75 mL ODE, and 26 µL $(TMS)_3P$ (0.1 mmol) was rapidly injected. The temperature was lowered to 178 °C and another 26 µL of $(TMS)_3P$ in 1 mL ODE was added dropwise to the reaction solution. Two minutes after the initial injection, heat was removed and 5 mL of degassed ODE were added to rapidly cool the reaction. The cores were found to have a 1S peak at 473 nm, corresponding to a core diameter of ~1.7 nm.[6] With the entire core solution at 100 °C, 4.2 mL zinc stearate were added, followed 10 min later by the same volume of TOP:Se. The temperature was raised to 220 °C for 30 min. Three times the reaction solution temperature was lowered to 150 °C for the addition of zinc stearate (5.5 mL, 7.1 mL, and 8.8 mL), followed 10 min later by TOP:Se, before the temperature was returned to 220 °C for a 30 min anneal. The resulting core/shell NQDs were stored in the mother liquor at 4 °C until they were needed.

References:

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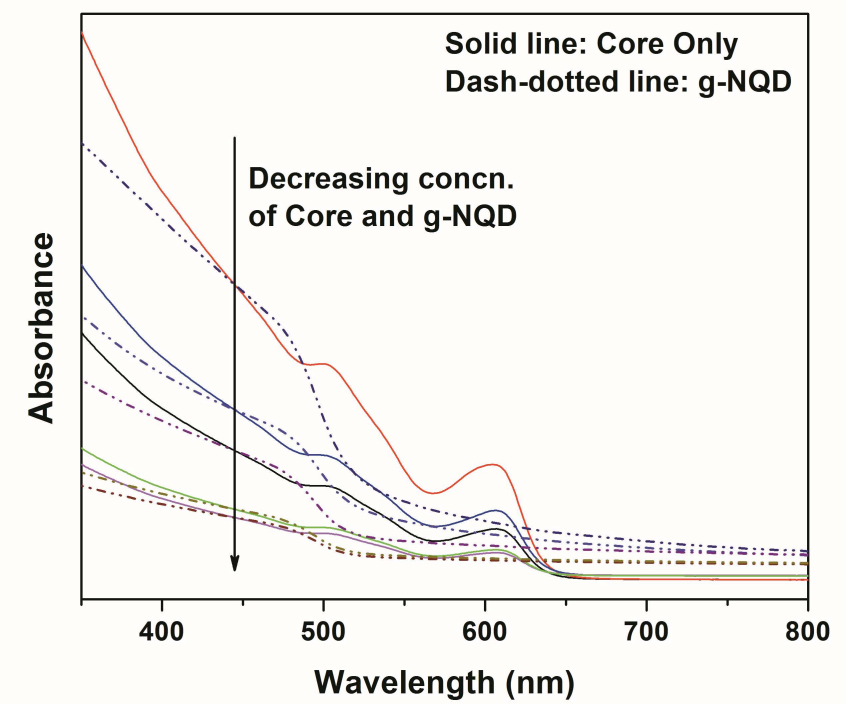

Figure S1. Absorption profiles of core-only NQD and g-NQD films for different "matching" concentrations (overlapping at 445 nm).

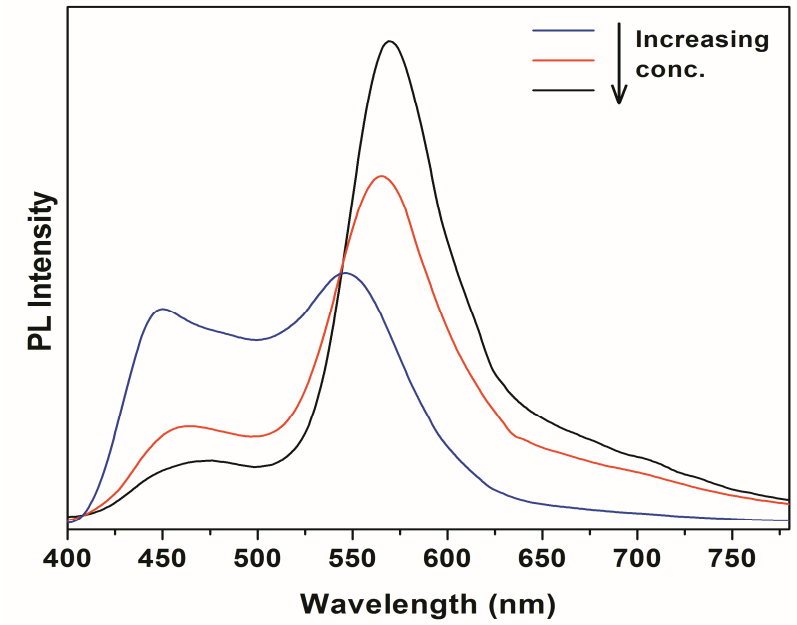

Figure S2. Photoluminescence spectra demonstrating successful optical down-conversion for InP/ZnSe green NQD-based devices at various concentrations.

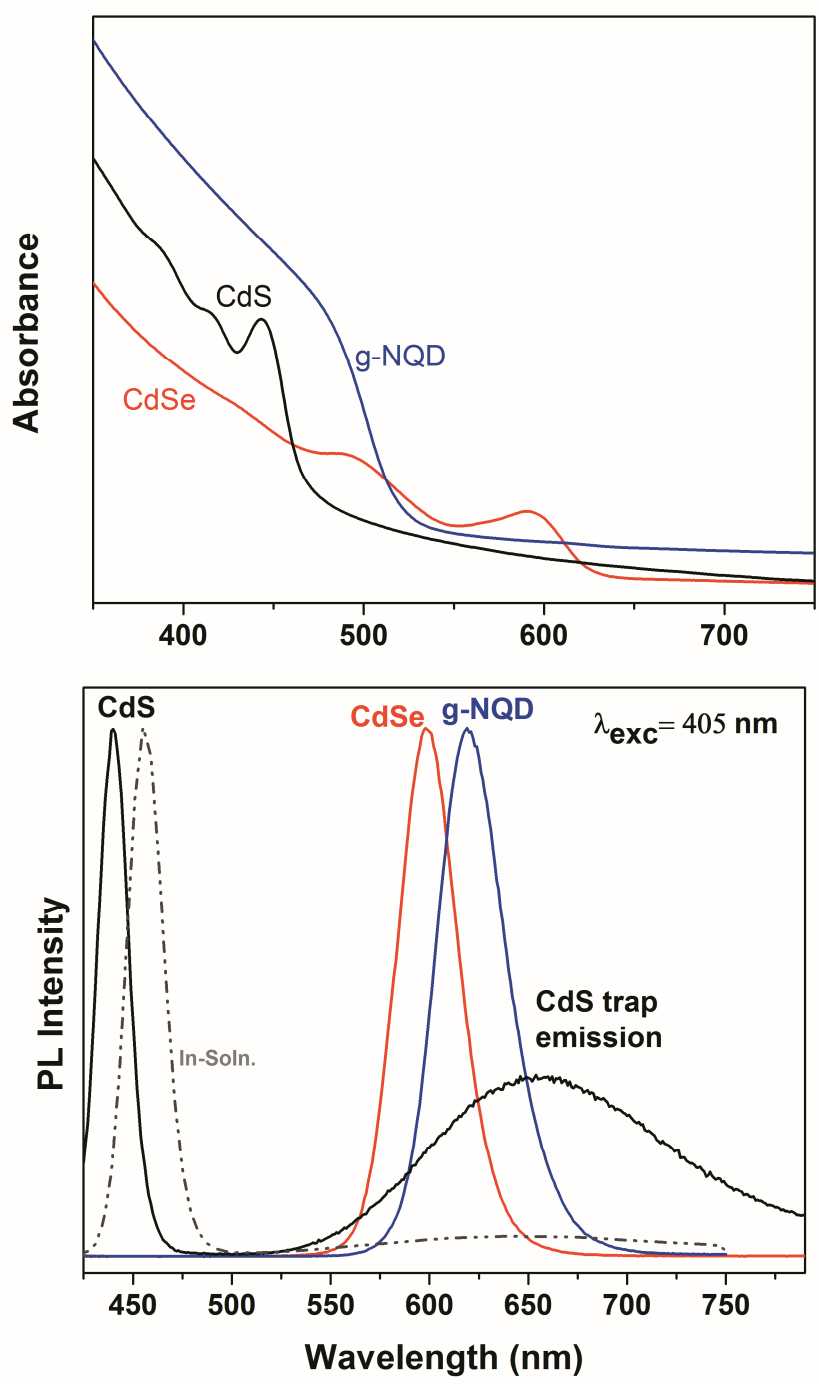

Figure S3. Absorption (top) and emission (bottom) spectra of films of CdSe NQDs (red), CdS NQDs (black) and CdSe/CdS g-NQDs (blue) on glass. The in-solution CdS emission spectra with minimal trap state emission is plotted as dash-dotted grey curve.

Tables summarizing concentration of active species (mg/250 µL of monomer solution; EL phosphor layer thickness of 450 µm) utilized for experiments reported in various figures in the main text.

For Figure 2b:

Spectrum Index	Concentration of g-NQD (mg/250 µL of monomer solution)
Blue trace	3.4
Red trace	12.5
Green trace	16.8

For Figure 3b and c:

Optical Density	g-NQD (mg/250 µL of monomer solution)	Core only QD (mg/250 µL of monomer solution)
2.1 (C5)	14.8	17.3
1.2 (C4)	8.9	14.1
0.9 (C3)	8.1	11.8
0.5 (C2)	4.7	8.1
0.4 (C1)	3.1	6.4

For Figure 5:

Active species	Concentration (mg/250 µL of monomer solution)
Core only NQD	13.1
g-NQD 4 shell	11.3
g-NQD 11 shell	10.2
g-NQD 16 shell	10.7

For Figure 6:

Spectrum CCT (K)	Red g-NQD (mg/250 µL of monomer solution)	Green NQD (mg/250 µL of monomer solution)
3200 / orange	8.3	7.3
4403 / black	7.1	7.7
4684 / red	6.8	7.6
5800 / green	3.3	9.7
4200 / blue	5.2	9.4

For Figure S2:

Spectrum Index	Concentration of green NQD (mg/250 µL of monomer solution)
Blue	7.5
Red	14.5
Black	16.7