## **Supporting Information**

## Size-Tunable Phosphorescence in Colloidal Metastable γ-Ga<sub>2</sub>O<sub>3</sub> Nanocrystals

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### I. Experimental Details

A. Chemicals Used for Nanocrystal Synthesis

All reagents and solvents used for the synthesis of  $Ga_2O_3$  nanocrystals are commercially available. Gallium acetylacetonate (99.99 %) was purchased from Strem Chemicals. Oleylamine (70 %) and tri-*n*-octylphosphine oxide (90 %) were purchased from Aldrich Chemical Co. Toluene (99.98 %, EMD Chemicals), hexanes (99.9 %, Fischer Scientific) and absolute ethanol were all used as received.

B. Nanocrystal Characterization and Spectroscopy

The crystallization and phase of the nanocrystals were analyzed by X-ray diffraction (XRD). XRD patterns were collected with INEL powder diffractometer with a position-sensitive detector, utilizing monochromatic Cu *Ka* radiation ( $\lambda$ =1.5406 Å).

Transmission electron microscopy (TEM) images were obtained on FEI Titan 80-300 Cryo-In-situ microscope operating at 300 kV. The specimens were prepared by dropping dilute colloidal suspensions of NCs in toluene on copper grids (300 mesh) with lacey formvar/carbon support films purchased from Ted Pella, Inc.

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The absorption spectra of  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> NCs dispersed in hexane were collected with a Varian Cary 5000 UV-vis-NIR spectrophotometer. Quartz cuvettes (*Spectrosil*, Starna Cells Inc.) having the transparency range 170-2700 nm and the standard 1 cm optical path length were used for collecting the absorption spectra.

Photoluminescence measurements were recorded with a Varian Cary Eclipse Fluorescence Spectrophotometer. For delayed photoluminescence spectra the samples were excited at the maximum of the excitation band with pulsed Xenon flash lamp and the emission intensity at each point in a spectrum was recorded 2 ms after the excitation. The total decay time for each data point before the sample was excited again was 0.02 s. The time-resolved data were collected upon excitation of nanocrystals into the band gap using Xenon flash lamp. The data points were collected at the peak of the low-energy component (delayed photoluminescence spectra) with the initial delay of 3 µs and the data collection time (gate time) of 1 µs for each point.

#### II. Analysis

The phosphorescence time decay was modeled using donor-acceptor pair (DAP) model. The theoretical development of this model is described in detail in reference 15 of the text. The main assumption of the model is that all donors and acceptors are initially neutral. In this model the total intensity emitted at time t after excitation is given by:

$$I(t) = \left\{ 4\pi N \int_{0}^{\infty} W(r) \exp\left[-W(r)t\right] r^{2} dr \right\} \times \left\{ \exp\left[4\pi N \int_{0}^{\infty} \left\{ \exp\left[-W(r)t\right] - 1\right\} r^{2} dr \right] \right\}$$
(S1)

where *N* is the majority defect concentration (in this case the donors), *r* is the separation between a donor and an acceptor, and W(r) is the radiative recombination rate of an electron on a donor and a hole on an acceptor, which are at the distance *r* form each other. The expression for W(r) is:

$$W(r) = W_{\text{max}} \exp\left[-\frac{2r}{R_d}\right]$$
(S2)

where  $R_d$  is the Bohr radius of the donor (in  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> it is ca. 18 Å).

In our system donor-acceptor separation (r) is limited by the NC size. The upper integration limit in the expression for I(t) (equation S1) is therefore changed to reflect an average NC diameter for different samples in the calculations of the corresponding decay kinetics. It has been suggested that donors and acceptors are located mainly in the surface region (see for example reference 5), indicating that the location of defects may also play an important role in the phosphorescence decay process. Detailed studies of the dependence of the defect location on the photoluminescence are currently underway in our laboratory and will be reported elsewhere.

# III. Figures



**Figure S1.** Overview TEM image of  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> nanocrystals synthesized at 310°C, as described in the text. Inset: Nanocrystal size distribution; the distribution was determined from TEM images by measuring the diameters of ca. 200 nanocrystals. The average nanocrystal size was determined to be  $6.0 \pm 1.1$  nm.



**Figure S2.** TEM images (left panels) and size distribution diagrams (right panels) of  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> nanocrystals synthesized at different temperatures. The size distributions were determined from high resolution TEM images by measuring ca. 200 nanocrystals. Scale bars in TEM images are 50 nm. The average nanocrystal sizes are: (a)  $3.3 \pm 0.5$ , (b)  $4.2 \pm 0.9$ , (c)  $5.1 \pm 1.1$ , and (d)  $5.5 \pm 1.2$  nm. Inset in (a) shows high resolution image of a single nanocrystal (scale bar, 5 nm).



**Figure S3.** Absorption (solid lines) and excitation (dashed lines) spectra for a series of  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> nanocrystals. The average NC sizes are shown in the graph. The band edge energies are essentially unchanged for all samples indicating negligible effect of quantum confinement in Ga<sub>2</sub>O<sub>3</sub> in the studied size range.



**Figure S4.** Absorption and photoluminescence spectra of 6.0 nm  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> nanocrystals showing large Stokes shift consistent with the localized nature of the observed photoluminescence.



**Figure S5.** Photoluminescence spectra of bulk  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> powder (black trace) and 6.0 nm  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> nanocrystals (red trace). The blue shift of the photoluminescence of bulk  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>, which is opposite from the shifts observed for increasing sizes of  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> nanocrystals (Figure 2a), may be attributed to the difference in the structure and energy levels of internal defects in  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> (bulk) and in  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> (nanocrystals).



**Figure S6.** The exponential (blue line) and bi-exponential (red line) best fits to the experimental phosphorescence decay curve for  $6.0 \text{ nm } \gamma$ -Ga<sub>2</sub>O<sub>3</sub> NCs (black trace). The phosphorescence decay clearly follows non-exponential behavior and cannot be fit either by single exponential or bi-exponential functions. Refer to Table S2 for comparison of residual chi-square values for all fits and NC sizes.



**Figure S7.** Calculated phosphorescence decay curves (black lines) for  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> NCs with the diameters of 6.0 (red dots), 4.2 (green dots) and 3.3 nm (blue dots) using DAP model (see Analysis section in Supporting Information). Using the established values for the Bohr radius ( $R_d$ ) and  $W_{max}$  constant of 18 Å and 10<sup>7</sup> 1/s, respectively, the obtained values of N as the fitting parameter are shown in Table S1. The obtained values of N for different nanocrystal sizes are in agreement with a decrease in donor-acceptor separation with decreasing nanocrystal size estimated from the photoluminescence energy shifts. Refer to Table S2 for residual chi-square values and comparison to exponential fits.



**Figure S8.** The comparison of the PL spectra of 6.0 nm  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> NCs collected at room temperature (red trace) and 100 K (blue trace) upon excitation in the maximum of the excitation band. Only insignificant changes in the PL spectra are observed at temperatures below 100 K. These results are in agreement with the findings by Harwig et al. (reference 5 in the paper). Below ca. 120 K PL spectra are dominated by high-energy (UV) component. As the temperature increases the low-energy (blue) emission is observed owing to the energy migration processes. Quenching of the UV luminescence occurs at lower temperatures than the energy migration.



**Figure S9.** Photoluminescence spectra of 6.0 nm  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> NCs before (blue trace) and after (red trace) thermal annealing at 500°C. Upon annealing the PL band exhibits a red shift and a decrease in intensity. Both of these effects indicate a larger separation between donors and acceptors, and therefore a decrease in the number of point defects when NCs are annealed. Thermal annealing leads to removal of the point defects, such as oxygen vacancies, which are responsible for blue emission in Ga<sub>2</sub>O<sub>3</sub>.

Nanocrystal diameter [nm]	<i>W<sub>max</sub></i> [1/s]	Average number of donors per NC (N)
3.3	10 <sup>7</sup>	2.9
4.2	10 <sup>7</sup>	3.4
6.0	10 <sup>7</sup>	3.8

**Table S1.** The average number of donors in a nanocrystal calculated from DAP model

**Table S2.** Chi-square  $(\chi^2)$  residual values for exponential, bi-exponential, and DAP

model fits

Nanocrystal diameter [nm]	Exponential	Bi-exponential	DAP
3.3	0.00484	0.00030	0.00024
4.2	0.01675	0.00127	0.00088
6.0	0.03951	0.00216	0.00126