Supplemental Information

Blue Light Emission Enhancement and Robust Pressure Resistance of Gallium Oxide Nanocrystals

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Experimental Section

Materials

Gallium acetylacetonate ($Ga(acac)_3$, 99.99%) and oleylamine (OA, 70%) purchased from Aladdin and used as received without further purification.

Synthesis of Ga_2O_3 nanocrystals (NCs).

The synthesis of Ga_2O_3 NCs was performed in oleylamine (OA) as a coordinating solvent. In a 100 mL three-neck round bottom flask 0.5 g of gallium acetylacetonate ($Ga(acac)_3$) was mixed with 8.5 mL of OA. Under an Ar atmosphere, the mixture stirred continuously for 1 hour at room temperature, after which the Ga source was dissolved at 80 ℃. The mixture was heated to 310 ℃ at an average of 3 ℃ per minute and held for 1 hour. The NCs were then precipitated with an equal volume of ethanol and centrifuged at 3000 rpm for 5 min. The obtained white powder was washed 3 times with ethanol followed by centrifugation.

High pressure generation.

High-pressure were generated by a symmetric diamond anvil cell (DAC) with a culet size of 400 μm. Then we drilled a 150 μm-diameter hole in the center of T301 stainless steel gasket as the sample chamber, which was preindented to 45 μm. The sample and a small ruby ball were loaded into the gasket cavity. The standard ruby fluorescent technique was carried out to determine the actual pressure. Silicon oil (Dow Corning, 10 cSt) was used as the pressure transmitting medium to provide the hydrostaticity.

PL and absorption spectra.

The in situ high-pressure PL and absorption spectra were collected with the help of an optical fiber spectrometer (Ocean Optics, QE65000). The pressure-dependent PL spectra were measured by a semiconductor laser with an excitation wavelength of 355 nm. We took the PL micrographs of the samples upon compression with a camera (Canon Eos 5D mark II) installed on a microscope (Ecilipse TI-U, Nikon). In situ high-pressure absorption spectra were measured by a deuterium halogen light source. The PLQY of Ga_2O_3 NCs at ambient pressure was determined using an integrating sphere incorporated into the FLS920 spectrofluorometer. All high-pressure measurements were conducted at room temperature.

ADXRD patterns.

In situ high-pressure angle-dispersive X-ray diffraction (ADXRD) patterns were measured at beamline 15U1, Shanghai Synchrotron Radiation Facility (SSRF). Portions of this work were performed at the 4W2 High Pressure Station in Beijing Synchrotron Radiation Facility (BSRF). The monochromatic wavelength of the synchrotron radiation was 0.6199 Å and we used CeO_2 as the standard sample for the calibration. The pattern of intensity versus diffraction angle 2θ was plotted based on the FIT2D program, which integrated and analyzed the 2D images collected. All the high-pressure experiments were conducted at room temperature.

Calculation details.

The actual molecular formula of γ-Ga_2O_3 should be $Ga_{2.67}O_4$[PDF#20-0426], and we used the optimized γ-$Ga_{21.38}$ O_{32} (a=b=c=8.220 Å) for theoretical simulations. Band-structure calculations of Ga_2O_3 NCs were accomplished using Materials Studio 8.0 program. Calculations were performed within the framework of density functional theory (DFT) by using plane-wave pseudopotential methods. Geometry optimization was calculated using the plane-wave pseudopotential method with the generalized gradient approximation (GGA) based on density functional theory with CASTEP package. The plane-wave cutoff energy of 571.40 eV and Monkhorst-Pack grid for the electronic Brillouin zone integration was 3×3×3. The self-consistent field (SCF) tolerance was set as 1.0×10^{-6} eV/atom. The convergence thresholds between optimization cycles for maximum force, maximum stress and maximum displacement are set as 0.05 eV/Å, 0.1 GPa, and 2.0×10^{-3} Å, respectively.

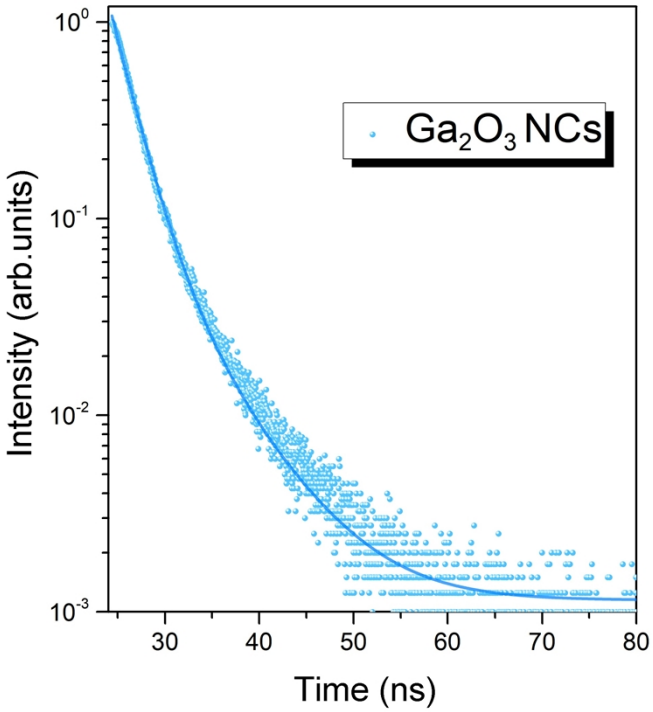

Figure S1. Fluorescence lifetime of as-prepared Ga_2O_3 NCs.

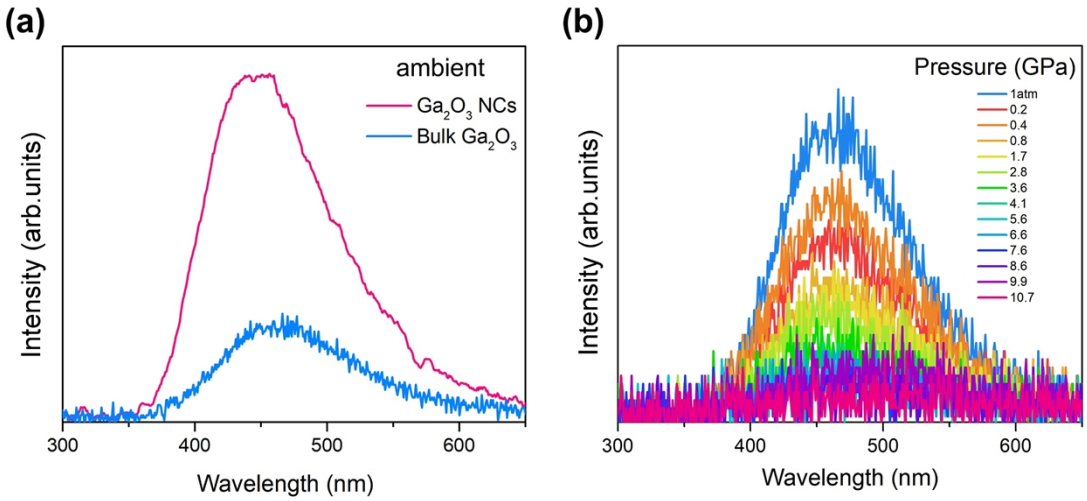

Figure S2. a) PL spectra of ambient Ga_2O_3 NCs and bulk Ga_2O_3. b) PL spectra of bulk Ga_2O_3 with increasing pressure.

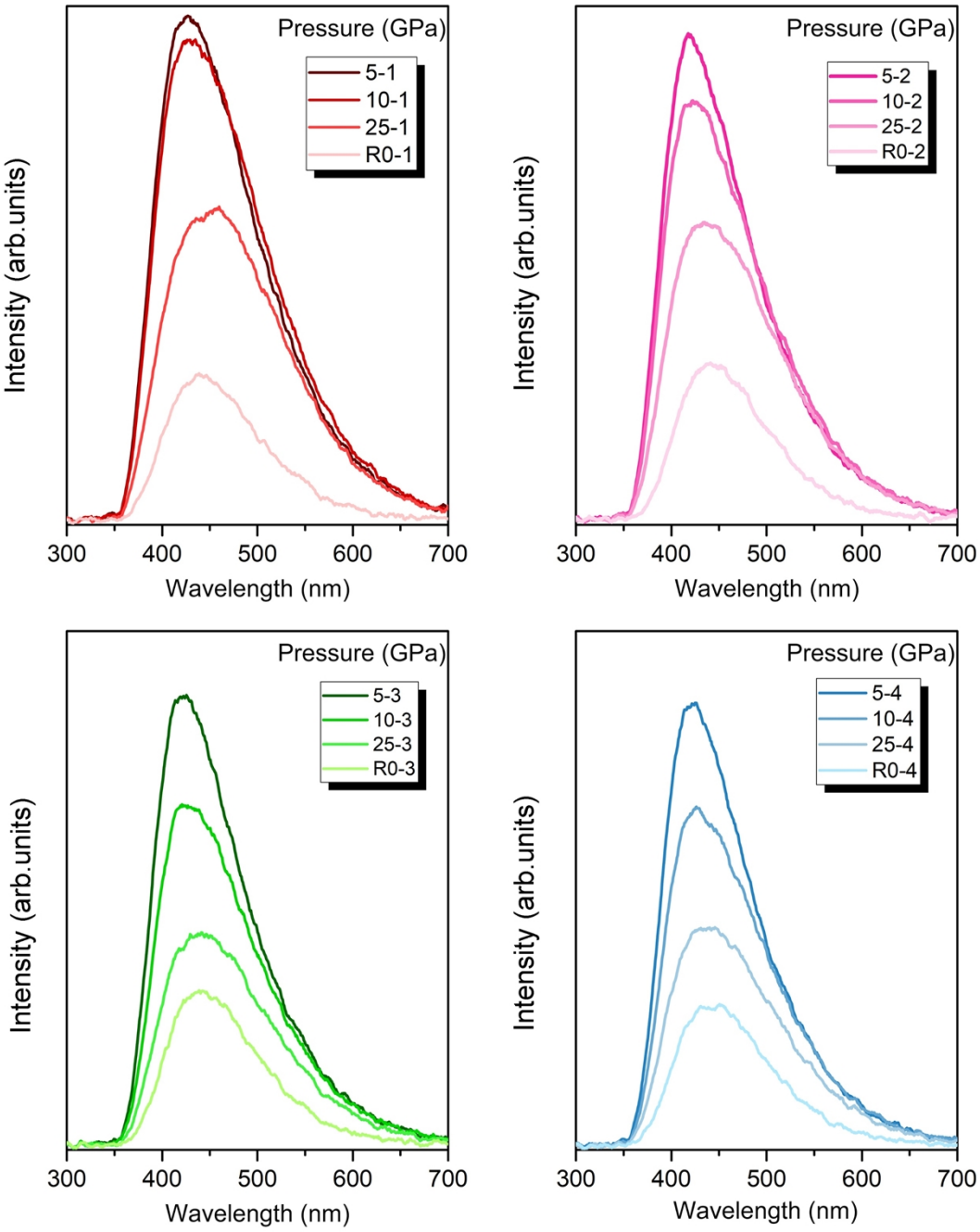

Figure S3. Repeated compression emission spectra of Ga_2O_3 NCs with four pressure-treated cycle times.

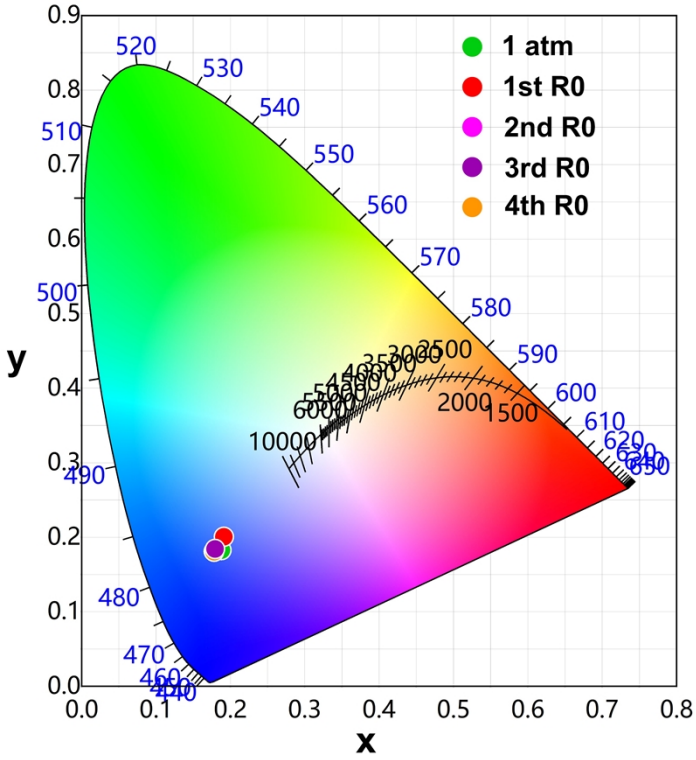

Figure S4. Chromaticity coordinate diagram of the ambient and the cyclic four pressure experiment of Ga_2O_3 NCs.

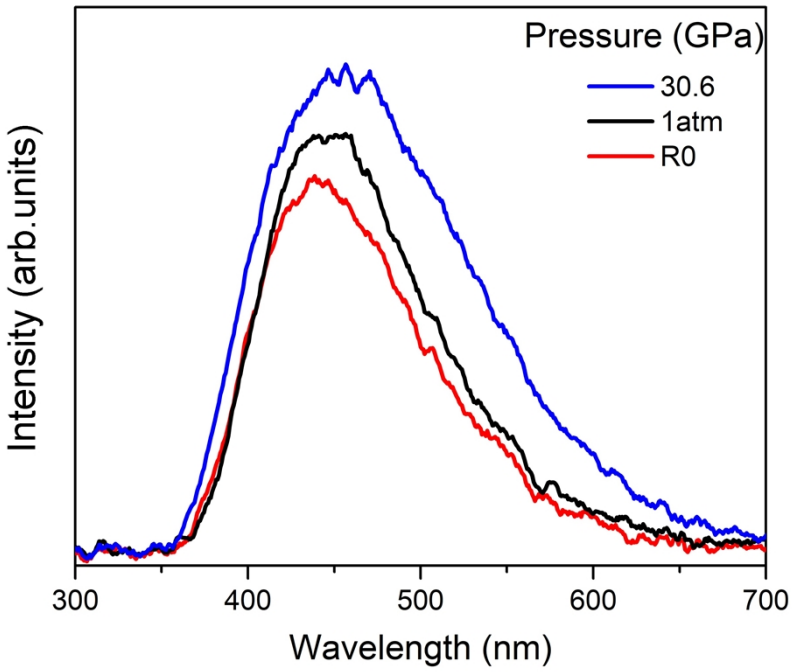

Figure S5. Emission spectra of Ga_2O_3 NCs at ambience, 30.6 GPa and decompression.

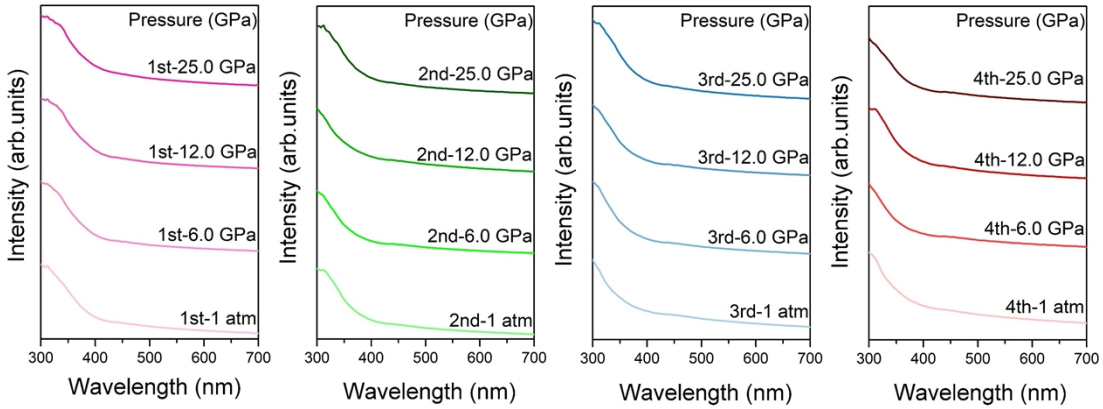

Figure S6. Absorption evolution of Ga_2O_3 NCs during the pressure cycle.

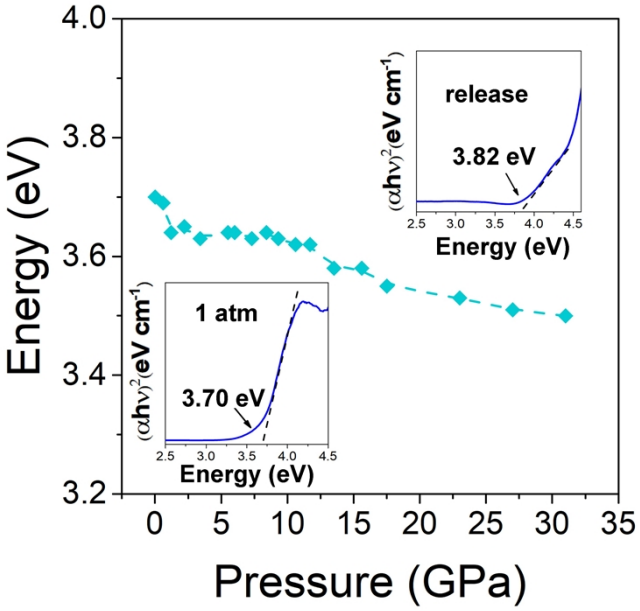

Figure S7. Absorption energy evolution of Ga_2O_3 NCs upon compression. The inset shows absorption energy of Ga_2O_3 NCs under ambient conditions and completely release of pressure.

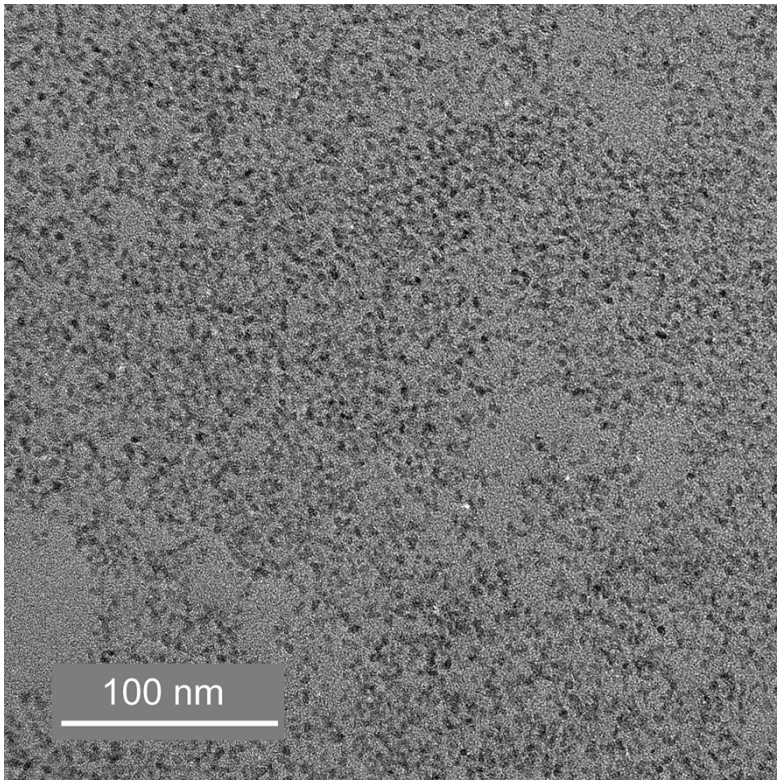

Figure S8. TEM image of the Ga_2O_3 NCs after releasing pressure to ambient conditions.

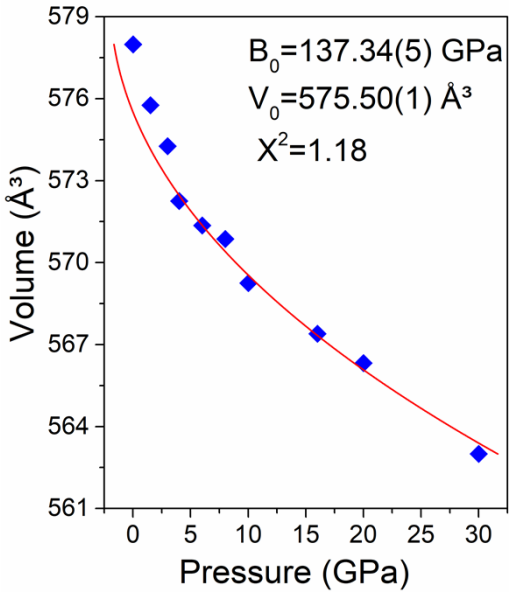

Figure S9. Fitting the experimental pressure-volume data of Ga_2O_3 NCs by Birch-Murnaghan equation.

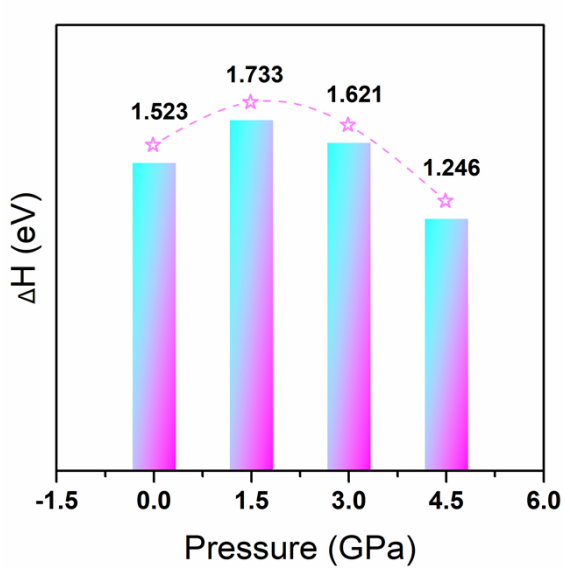

Figure S10. Calculated oxygen vacancy formation energies of Ga_2O_3 NCs at different pressures.

Table S1. Lattice parameter changes under pressure.

Pressure (GPa)	*a*=*b*=*c* (Å)	Volume (Å^3)
1atm	8.3299	577.9887
1.5	8.3276	577.5184
2.0	8.3139	574.6728
4.0	8.3023	572.2583
6.0	8.2979	571.3614
8.0	8.2956	570.8678
10.0	8.2877	569.2569
16.0	8.2787	567.4009
20.0	8.2735	566.3261
30.0	8.2573	563.0012