

Electronic Supplementary Information

***In-situ* enhancement of the blue photoluminescence of colloidal Ga₂O₃ nanocrystals by promotion of defect formation in reducing conditions**

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I. EXPERIMENTAL PROCEDURES

A. Synthesis of Ga₂O₃ Nanocrystals

All reagents are commercially available and were used as received. Gallium acetylacetonate (Ga(acac)₃, 99.99 %) was purchased from Strem Chemicals. Oleylamine (70 %) and tri-*n*-octylphosphine oxide (TOPO, 90 %) were purchased from Sigma-Aldrich, and hexane (99.9 %) from Fischer Scientific. All gasses (compressed argon (>99 %), oxygen (high purity, grade 4.3, 99.993%) and hydrogen (high purity, grade 5.0, 99.999%) were purchased from Praxair.

A detailed procedure for the synthesis of colloidal γ -Ga₂O₃ NCs has been previously described (see ref. 8 in the communication text). In a typical synthesis, Ga(acac)₃ (0.5 g) was mixed in a round-bottom flask with oleylamine (7.0 g), and stirred under argon at ca. 80 °C until the precursor was fully dissolved. The solution was degassed, and subsequently heated to different temperatures (220 to 310 °C) while continuously stirring in a flow of argon. This reaction mixture was refluxed at the desired

temperature in the inert atmosphere for different lengths of time (1-30 hours). The resulting suspension was cooled to room temperature, and then precipitated and washed three times with ethanol. The NCs, collected as a white powder, were capped with TOPO and dispersed in hexane.

The reaction was also carried out in a mixture of oxygen and argon ($O_2/Ar=3/7$ flow ratio) as an oxidizing environment, and hydrogen and argon ($H_2/Ar=3/7$) as a reducing environment, while keeping the content of the reaction mixture as described above. The nanocrystals were prepared under oxidizing and reducing conditions at 220 and 310 °C for direct comparison with the NCs prepared in argon. The post-synthesis treatment of the NC powders was the same as for NCs prepared in argon.

B. Measurements and Data Analysis. The crystal structure of the prepared samples was characterized by powder X-ray diffraction (XRD). XRD patterns were collected with INEL powder diffractometer equipped with a position-sensitive detector, using monochromatic Cu K α radiation. Transmission electron microscopy (TEM) imaging was performed with a JEOL-2010F microscope operating at 200 kV. The optical absorption spectra were collected with a Varian Cary 5000 UV-vis-NIR spectrophotometer. Photoluminescence (PL) spectra were recorded with a Varian Cary Eclipse fluorescence spectrometer. For a direct comparison of PL intensities, the concentrations of colloidal NCs in hexane were adjusted to exhibit absorption of 0.1 at 230 nm. For the delayed PL measurements, the samples were excited at 230 nm with a pulsed Xenon flash lamp, and the emission intensity at each point was recorded with various delay times (0.1, 0.2, 0.5 and 1ms) after excitation. Relative quantum yields of γ -Ga₂O₃ NC samples were calculated using quinine bisulfate (QBS) as the reference substance. A solution of QBS

was prepared in 1 N H₂SO₄ as previously reported (ref. S1). The quantum yield of QBS under these conditions was determined to be 0.55.

II. Figures

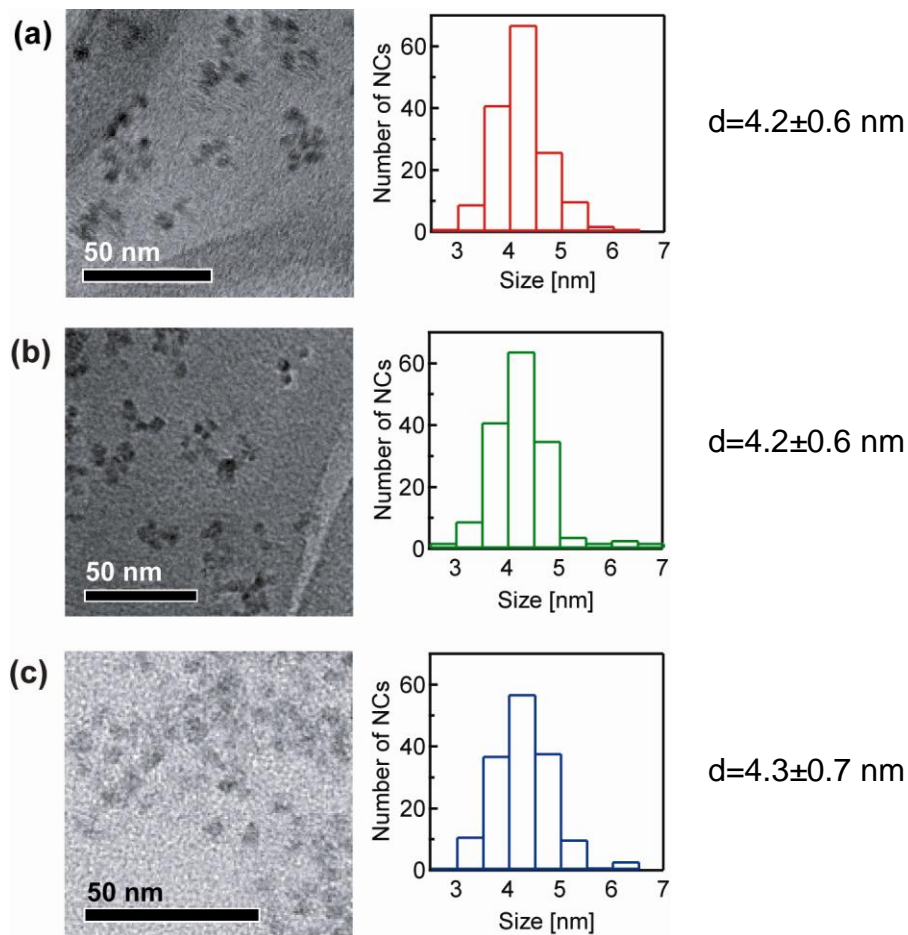


Figure S1. TEM images (left) and size distribution histograms (right) of γ -Ga₂O₃ NCs synthesized at 220 °C for (a) 1, (b) 7 and (c) 30 hours. The average NC sizes are indicated in the figure. The data demonstrate negligible change in the average NC size with increasing heating time.

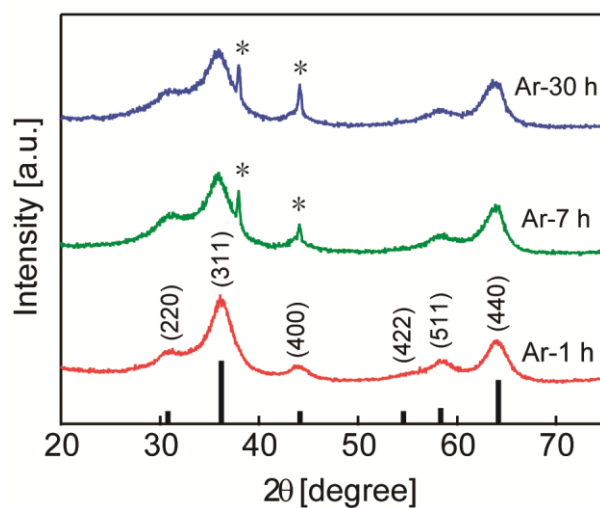


Figure S2. XRD patterns of γ -Ga₂O₃ NCs synthesized at 220 °C in argon flow for different durations, as indicated in the graph. The vertical red lines represent the XRD pattern of bulk γ -Ga₂O₃ NCs (JCPDS 20-0426). The stars indicate the peaks from Al sample holder.

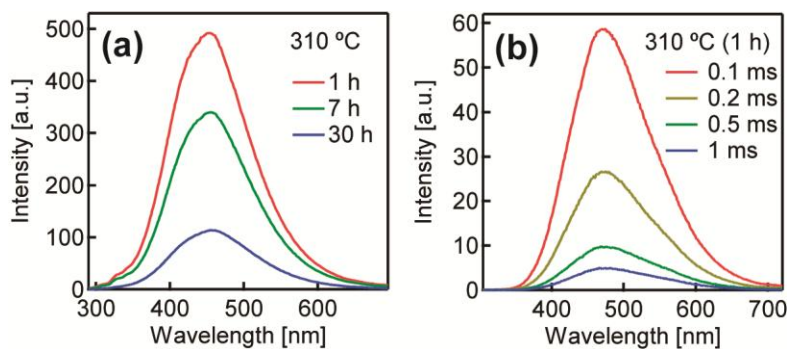


Figure S3. (a) PL spectra of Ga₂O₃ NCs synthesized at 310 °C for 1 (red), 7 (green) and 30 hours (blue). The spectra correspond to the same NC concentrations as those in Fig. 1a. (b) Delayed PL spectra of the same NCs prepared for 1 hour, obtained 0.1 (red), 0.2 (olive), 0.5 (green) and 1.0 ms (blue) upon excitation with 230 nm pulse.

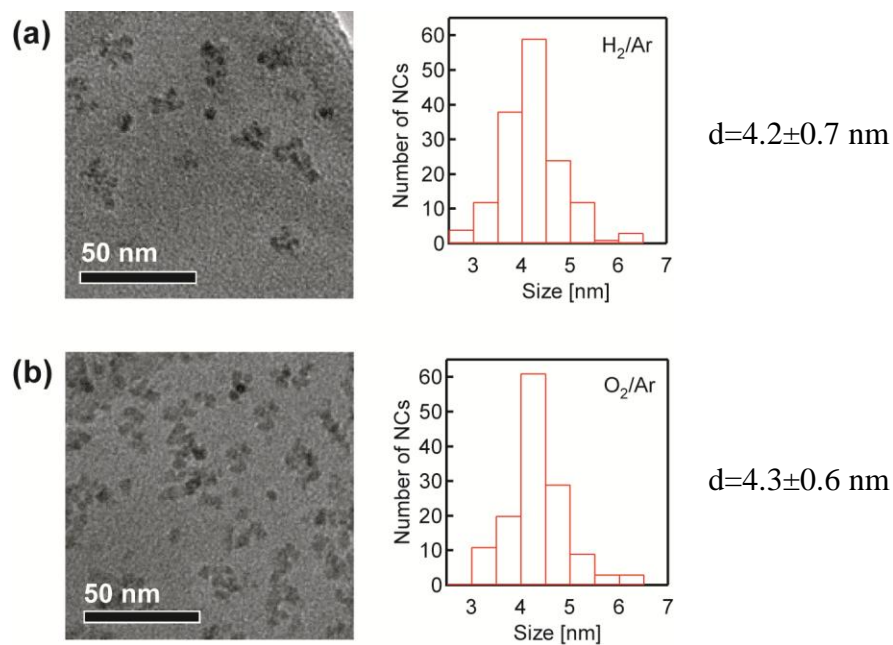


Figure S4. TEM images (left) and size distribution histograms (right) of γ -Ga₂O₃ NCs synthesized at 220 °C for 1 hour in (a) H₂/Ar and (b) O₂/Ar mixture. The average NC sizes are indicated in the figure. The data demonstrate negligible change in the average NC size in oxidizing or reducing conditions.

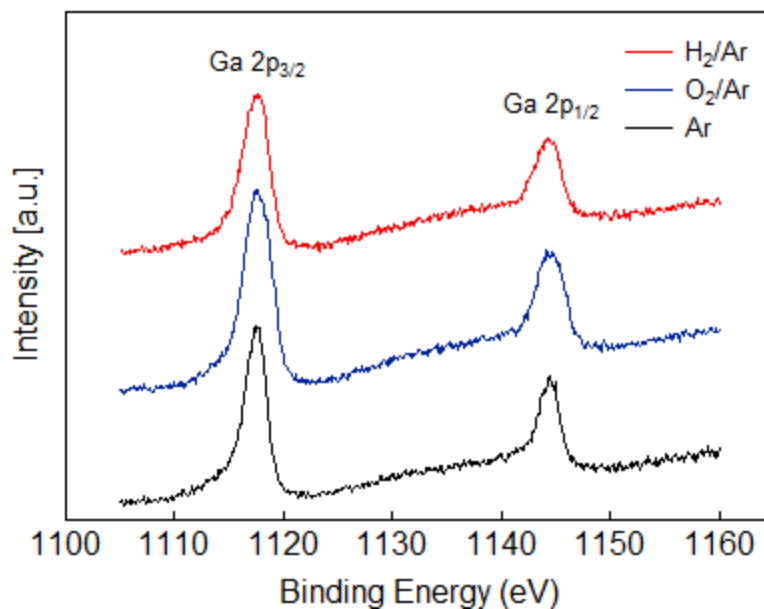


Figure S5. X-ray photoelectron spectra of Ga₂O₃ NCs synthesized at 220 °C for 1 hour in H₂/Ar (red), O₂/Ar (blue) or Ar (black) atmosphere collected in Ga 2p region. The spectra show no obvious difference indicating a negligible change in the average local environment of Ga³⁺ sites. These results confirm that very small percent change in the concentration of oxygen vacancies causes a large change in the observed PL.

III. REFERENCES

S1 J. E. Gill, *Photochem. Photobiol.*, 1969, **9**, 313.