Supporting Information

Anomalous Photocatalytic Activity of Nanocrystalline γ-Phase Ga_2O_3 Enabled by Long-Lived Defect Trap States

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Determination of the apparent quantum efficiency (AQE):

The apparent quantum efficiency (ϕ_X) was calculated based of the following equation (Chem. Rev. **1995**, *95*, 69-96):

$$\phi_X \equiv \frac{\pm(d[X]/dt)}{d[h\nu]_{inc}/dt}$$

ϕ_X: the apparent quantum efficiency for chemical species (Rh-590)

d[X]/d*t*: the initial rate of formation or loss of chemical species (mol/Ls or mol/m^{3}s)

d[*hν*]/d*t*: the incident photon flux per unit volume (moles of photon/m^{3}s)

d[X]/d*t* can be extracted from a plot of [Rh-590] (mol/L) versus time (seconds). The slope of this plot equals d[X]/d*t*.

d[*hν*]/d*t* is determined by measuring the power of irradiation per unit area at the same height as the top of the Rh-590 solution and determining the photon flux per unit volume of the dye solution.

Table S1. Rate of Photocatalytic Degradation of Rh-590 and Apparent Quantum Efficiency (AQE) for Photocatalysts Prepared by Annealing γ-Ga_2O_3 Nanocrystals at Different Temperatures.

Annealing T (°C)	d[X]/d*t* [mol/sL]	AQE [%]
400 ºC	$(5.6\pm0.1)\cdot10^{-9}$	0.142±0.001
600 ºC	$(4.9\pm0.1)\cdot10^{-9}$	0.124±0.001
650 ºC	$(6.3\pm0.3)\cdot10^{-9}$	0.160±0.020
800 ºC	$(1.9\pm0.3)\cdot10^{-9}$	0.049±0.010

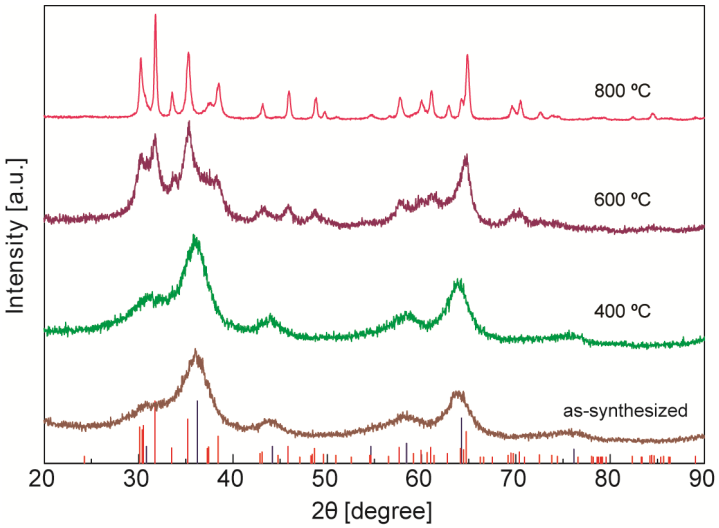

Figure S1. XRD patterns of Ga_2O_3 NCs synthesized at 300 ºC and annealed at different temperatures as indicated in the graph. Blue and red sticks represent the patterns of bulk γ-Ga_2O_3 and β-Ga_2O_3, respectively.

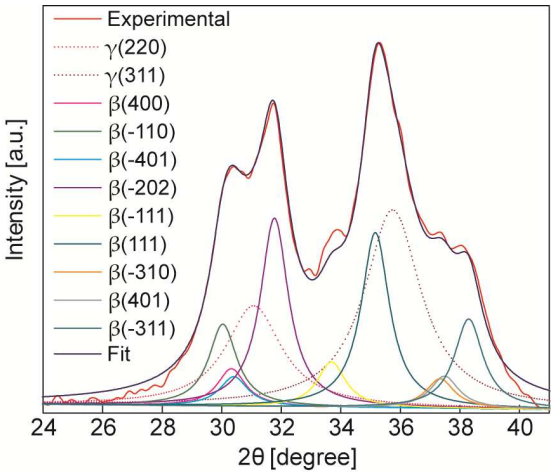

Figure S2. Deconvolution of the XRD peaks for Ga_2O_3 NCs synthesized at 200 ºC and annealed at 600 ºC. The presence of both β- and γ-phase is clearly observed between 25° and 40°, and specific peaks for both phases are designated in the graph.

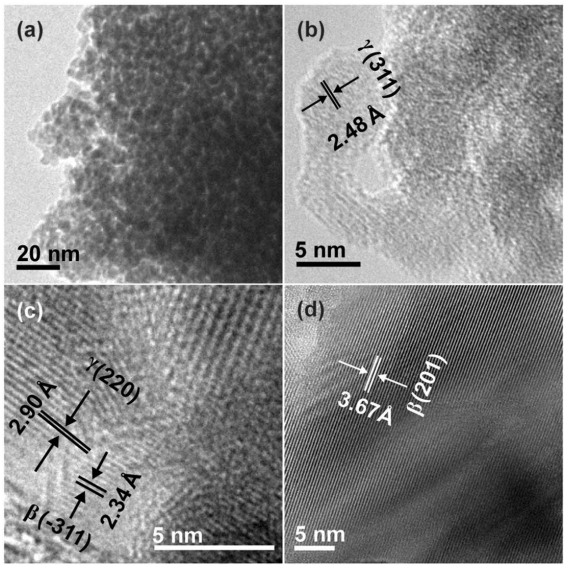

Figure S3. TEM images of Ga_2O_3 NCs synthesized at 300 ºC and annealed at (a, b) 400 ºC, (c) 600 ºC, and (d) 800 ºC.

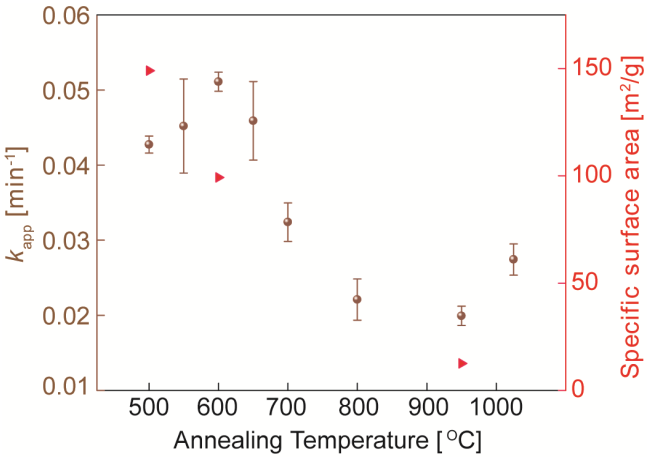

Figure S4. Ga_2O_3 NC annealing temperature dependence of the apparent rate constant of Rh-590 degradation (brown spheres) and the specific surface area of the photocatalyst (red triangles) for the NCs synthesized at 300 ºC. The measurements were performed in the annealing temperature range corresponding to the mixed γ-Ga_2O_3 and β-Ga_2O_3 phases.

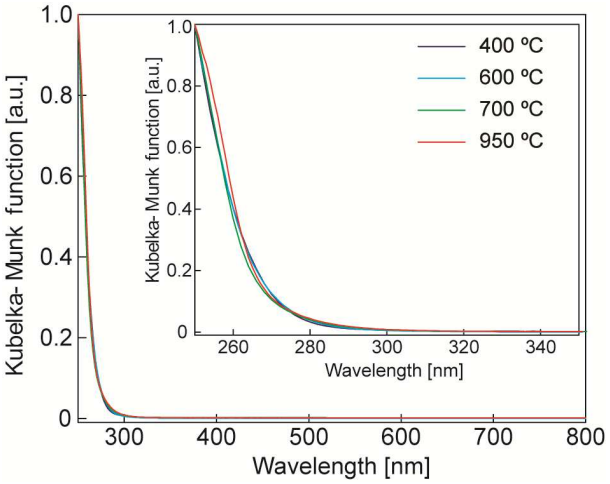

Figure S5. Diffuse reflectance spectra of Ga_2O_3 NCs annealed at different temperatures, as indicated in the graph. Inset: magnified band edge absorption region. The spectra of all samples are nearly identical indicating negligible difference in the band gap energy between γ- and β-phase.

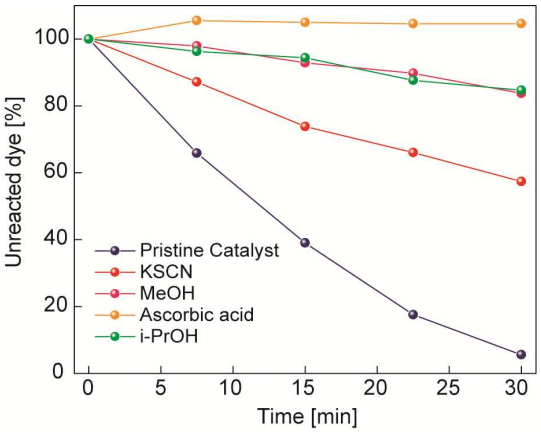

Figure S6. Photocatalytic degradation of Rh-590 by γ-Ga_2O_3 in the presence of different scavengers. The photocatalyst was prepared by annealing Ga_2O_3 NCs at 400 ºC.

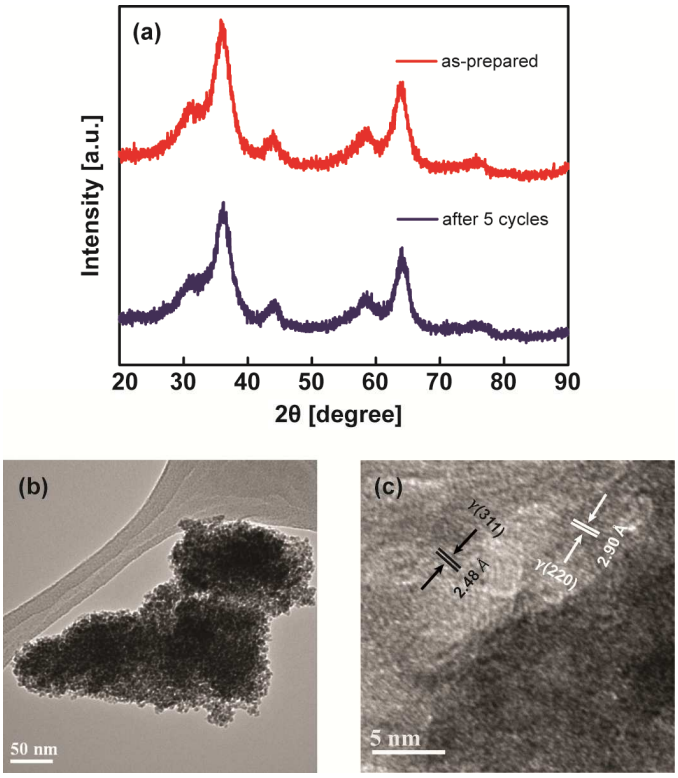

Figure S7. (a) XRD patterns of γ-Ga_2O_3 photocatalyst as-prepared (upon annealing at 400 °C) and after 5 photocatalytic cycles. (b) Overview TEM image of γ-Ga_2O_3 photocatalyst after 5 cycles. (c) High-resolution TEM image of the sample in (b). The XRD and TEM data indicate no change in the structure and morphology of the photocatalyst after multiple photocatalytic cycles.

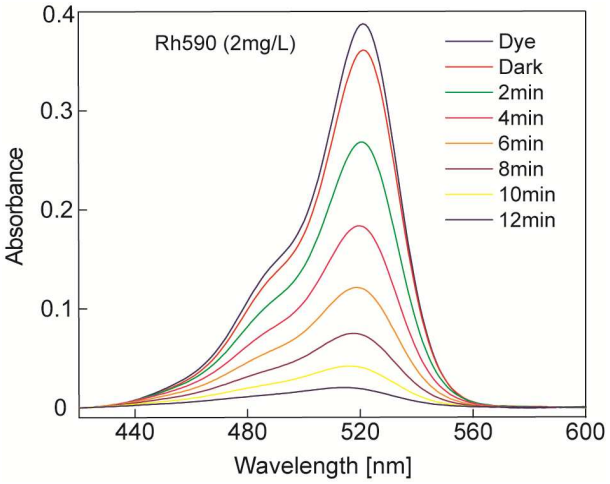

Figure S8. Absorption spectra of Rh-590 solution (2 mg/L) monitored over time in the presence of γ-Ga_2O_3 photocatalyst under UV excitation. The photocatalyst was prepared by annealing as-synthesized NCs at 400 ºC.

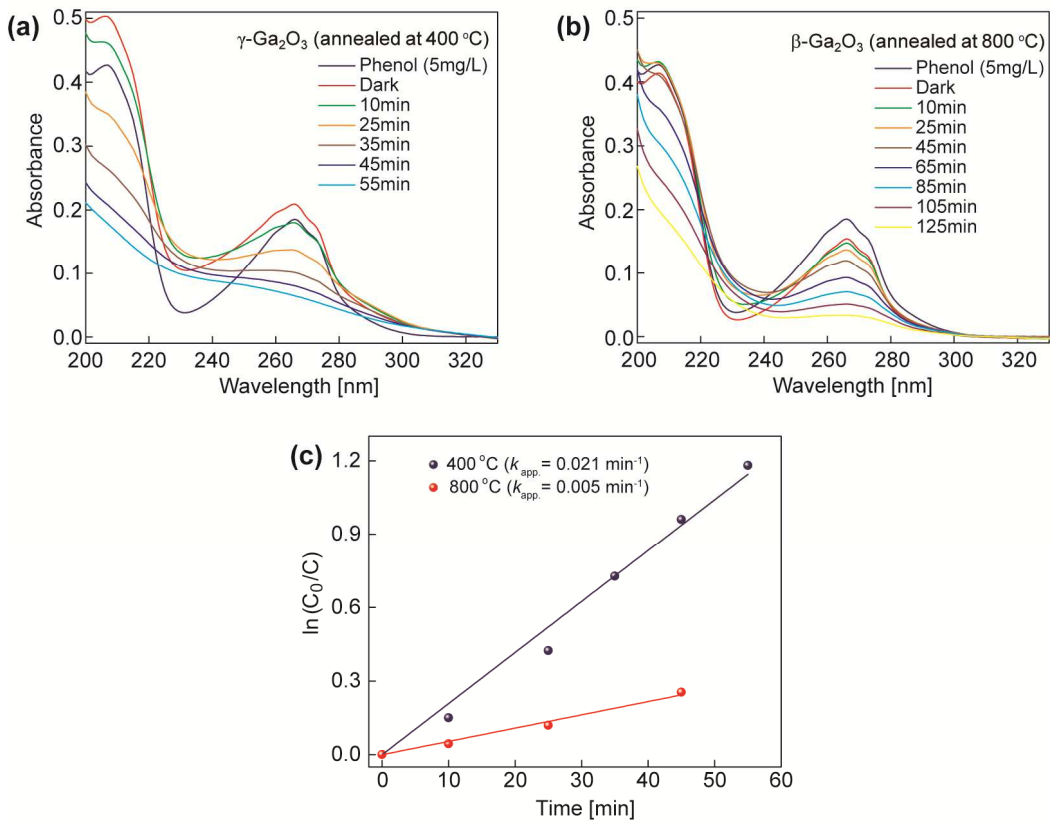

Figure S9. (a,b) Absorption spectra of phenol solutions (5 mg/L) monitored over time in the presence of Ga_2O_3 nanocrystalline photocatalysts under UV excitation: (a) γ-Ga_2O_3 prepared by annealing as-synthesized NCs at 400 ºC, and (b) β-Ga_2O_3 prepared by annealing as-synthesized NCs at 800 ºC. Exposure times corresponding to different spectra are indicated in the graphs. (c) Langmuir-Hinshelwood plot for the photocatalytic degradation of phenol with Ga_2O_3 prepared by annealing as-synthesized NCs at 400 ºC and 800 ºC. Straight lines are linear fits to the experimental data using eq. 5 in the main text. The k_{app} is ca. 4 times higher for the Ga_2O_3 sample annealed at 400 ºC, confirming anomalous photocatalytic activity of γ-phase Ga_2O_3.