

Electronic Supplementary Information

Remarkable Enhancement of Photoluminescence and Persistent Luminescence of NIR Emitting ZnGa₂O₄:Cr³⁺ Nanoparticles

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S1. Experimental

S1.1 Materials: Zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O, 98%), gallium nitrate hydrate (Ga(NO₃)₃·xH₂O, 99.9%), chromium nitrate nonahydrate (Cr(NO₃)₃·9H₂O, 99%), urea (NH₂CONH₂, 99.0-100.5%), ammonium hydroxide solution (28.0-30.0% NH₃ basis) were purchased from Sigma Aldrich. Ethyl alcohol (technical grade) were purchased from Fisher Scientific. All the chemicals were of analytical grade reagents and used directly without further purification in this work.

S1.2 Synthesis

S1.2.1 Synthesis of ZGOC NPs using urea as precipitant with Zn to Ga precursor ratio = 1:1

2.0 mmol of Zn(NO₃)₂·6H₂O with 2 mmol of Ga(NO₃)₃·xH₂O and 0.004 mmol of Cr(NO₃)₃·9H₂O with a desired amount of urea were dissolved in 30 ml water and stirred for 10 minutes. After that, the solution was transferred to a 45 mL Teflon-lined stainless-steel autoclave. The sealed autoclave was heated at 220°C for 10 h. Afterward, the system was left to cool to room temperature and the resulted NPs was precipitated out of the synthesis solution with the excess volume of ethanol-water mixture. The products were separated and purified by centrifugation and subsequently centrifuged/washed with ethanol-water mixture for two more times. The washed precipitates were dried at 110°C in a drying oven overnight and ground to obtain the ZGOC-U (Zn/Ga = 1:1) NPs.

S1.2.2 Synthesis of ZGOC NPs using urea as precipitant with Zn to Ga precursor ratio = 1:2

The synthesis procedure is similar to the one above by only changing the Zn/Ga precursor ratio to 1:2. Typically 1.0 mmol of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with 2 mmol of $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ and 0.004 mmol of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ with a desired amount of urea were dissolved in 30 ml water and stirred for 10 minutes. After that, the solution was transferred to a 45 mL Teflon-lined stainless-steel autoclave. The sealed autoclave was heated at 220°C for 10 h. Afterward, the system was left to cool to room temperature and the resulted NPs was precipitated out of the synthesis solution with the excess volume of ethanol-water mixture. The washed product was subsequently centrifuged/washed with ethanol-water mixture for two more times. The purified precipitates were dried at 110°C in a drying oven overnight and ground to obtain the ZGOC-U (Zn/Ga = 1:2) NPs.

S1.2.3 Synthesis of ZGOC NPs with addition of urea and ammonium nitrate as precipitants

Typically, 2.0 mmol of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with 2 mmol of $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ and 0.004 mmol of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ with a desired amount of urea and a desired amount of ammonium nitrate were dissolved in 30 ml water and stirred for 10 minutes. After that, the solution was transferred to a 45 mL Teflon-lined stainless-steel autoclave. The sealed autoclave was heated at 220°C for 10 h. Afterward, the system was left to cool to room temperature and the resulted NPs was precipitated out of the synthesis solution with the excess volume of ethanol-water mixture. The washed product was subsequently centrifuged/washed with ethanol-water mixture two more times. The purified precipitates were dried at 110°C in a drying oven overnight and ground to obtain the ZGOC-U-A NPs.

S2. Instrumentation

Powder X-ray diffraction (XRD) patterns of the ZnGa_2O_4 NPs were taken with a Bruker D8 ADVANCE, X-ray diffractometer with $\text{Cu K}\alpha 1$ radiation ($\lambda = 0.15406$ nm). The XRD data were collected by utilizing a scanning mode of 2θ ranging from 20° to 80° with a scanning step size of 0.04° and a scanning rate of 2.0° min^{-1} . SEM images of our NPs were taken with a Carl Zeiss sigma VP field emission scanning electron microscopy (FESEM), which is equipped with EDX capability. HRTEM was recorded using Hitachi HF 3300 TEM/STEM. PL emission and excitation spectra were recorded using an Edinburgh Instrument FLS 980 fluorimeter system having steady state xenon lamp source. Persistent luminescence was also recorded on Edinburgh Instrument FLS 980 fluorimeter system on kinetic scan mode; the NPs were excited for 5 minutes and after decay was measured up to 1 hour. For the absolute quantum yield (QY) measurements, integrating sphere

was employed in the FLS980 fluorimeter (Edinburgh Instruments). More specifically, to be consistent with all experiments performed, the same sample weight (60 mg) and monochromator slit size (2 nm for both excitation and emission monochromator) were kept identical for all experiments. Fluorescence emission and excitation spectra were collected using TE-cooled photomultiplier tube (Hamamatsu, Model R928P) after diffuse reflectance from the samples relative to a non-absorbing standard (BenFlect) at the excitation wavelength and emission spectra under the same condition. To avoid reabsorption, very thin layer of samples was used in all experiments. The fluorescence QY was measured by finding the ratio of the area under the corrected emission spectra to the difference in corrected area under the diffuse reflectance spectra of the excitation spectra from the sample and the reference. The absolute photoluminescence QY is given by:

$$QY = \frac{NP(\text{emitted})}{NP(\text{absorbed})} \frac{\int L_{\text{sample}}}{\int E_{\text{reference}} - \int E_{\text{sample}}}$$

where NP_{absorbed} is the number of photons absorbed by the sample and NP_{emitted} is the number of photons emitted from the sample, $\int L_{\text{sample}}$ is the area under the curve for the photoluminescence spectra of the sample, and $\int E_{\text{reference}}$ and $\int E_{\text{sample}}$ are the areas under the excitation spectra of the reference (BenFlect) and the sample, respectively. Including all the possible errors, such as reflectivity of the reference (< 3%), particle size effects (< 2%), and diffuse reflectance from the sample holder (< 3%), the calculated QY for ZGOC-U5-A5 NPs was 10.31%.

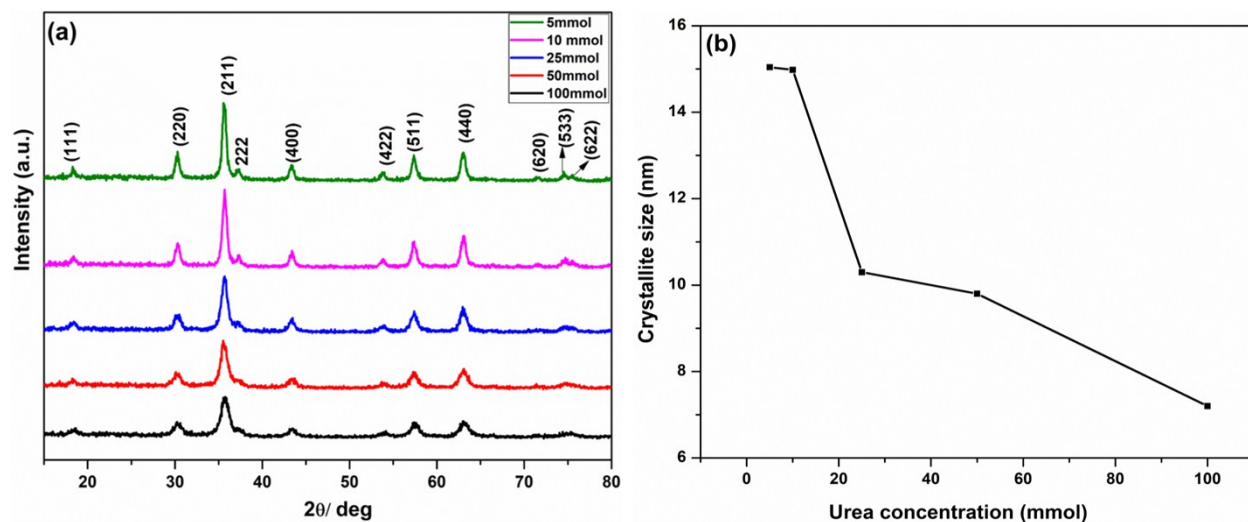


Figure S1. (a) XRD patterns of the ZGOC-U (Zn/Ga = 1:2) NPs and (b) the variation of the crystallite size as a function of urea concentration.

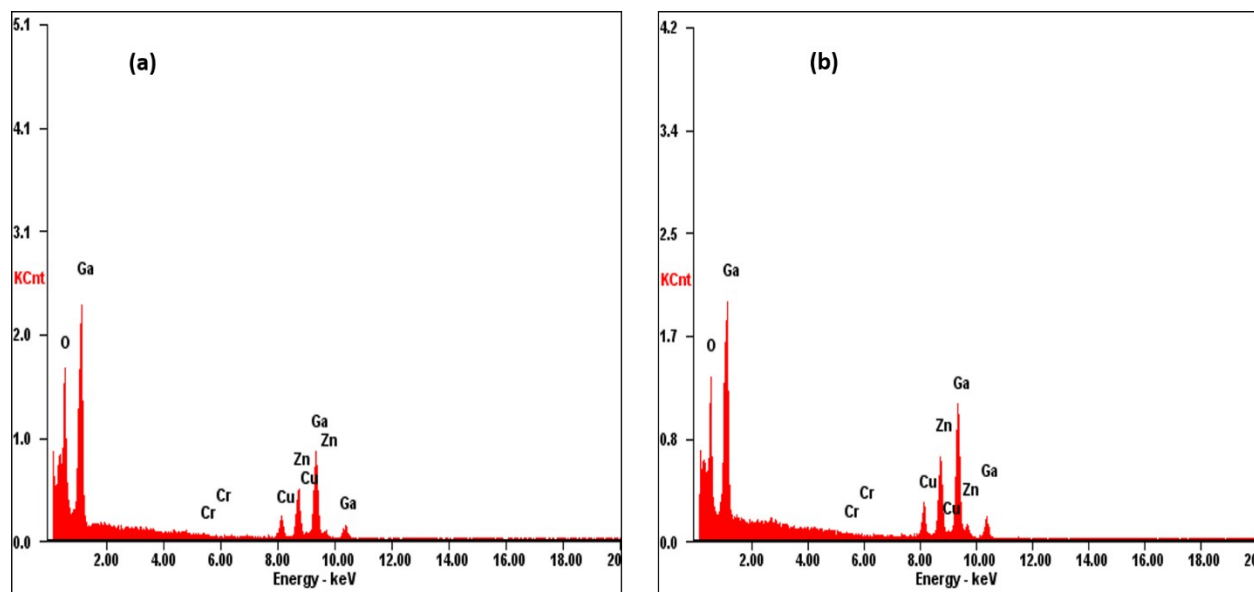


Figure S2. EDS spectra of the ZGOC-U5 NPs with Zn/Ga = (a) 1:1 and (b) 1:2.

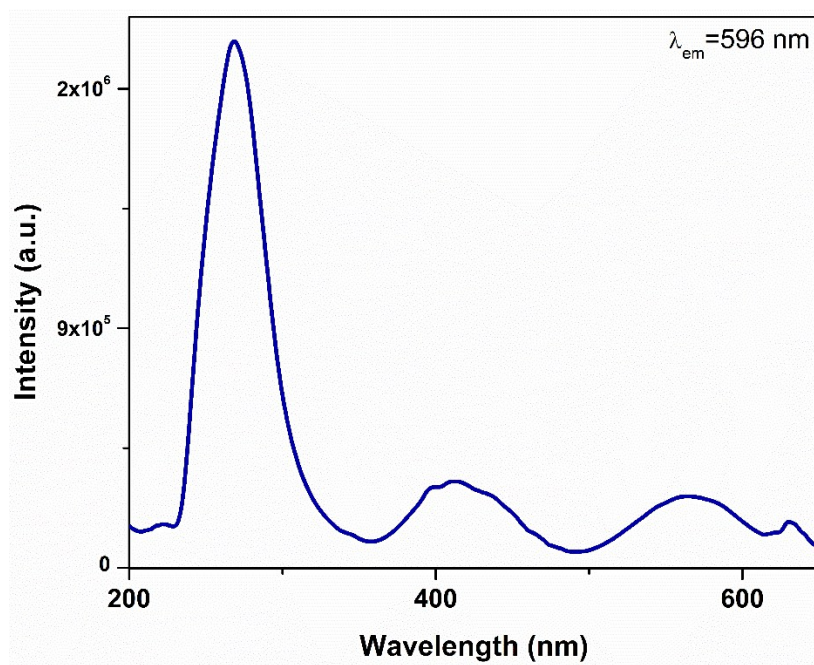


Figure S3. PL excitation spectrum of the ZGOC-U5 (Zn/Ga = 1:1) NPs.

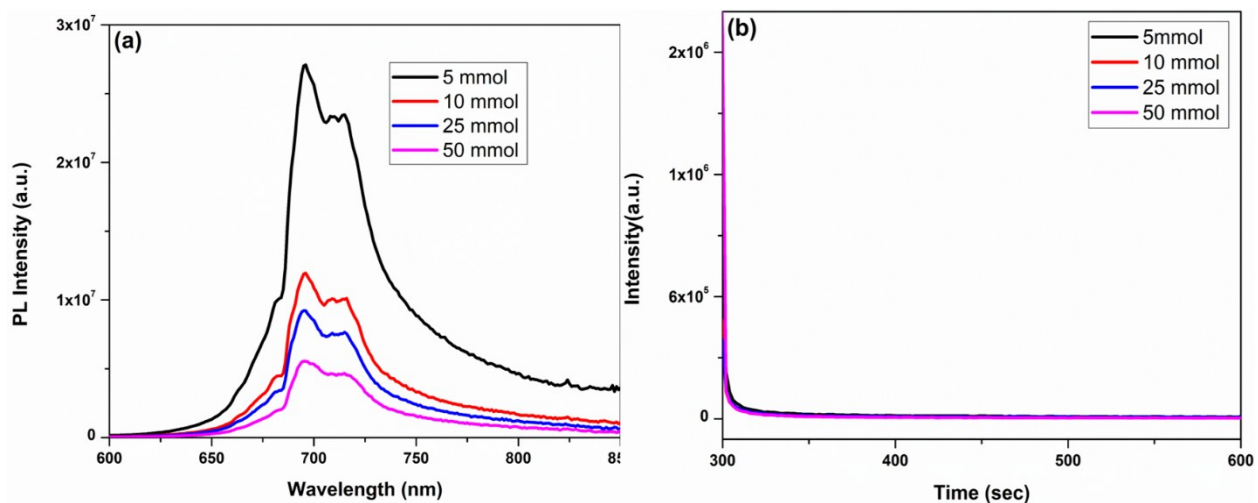


Figure S4. (a) PL emission spectra and (b) NIR afterglow decays of the ZGOC-U (Zn/Ga = 1:2) NPs synthesized with different amounts of urea added after being irradiated with 256 nm xenon lamp for 5 min.

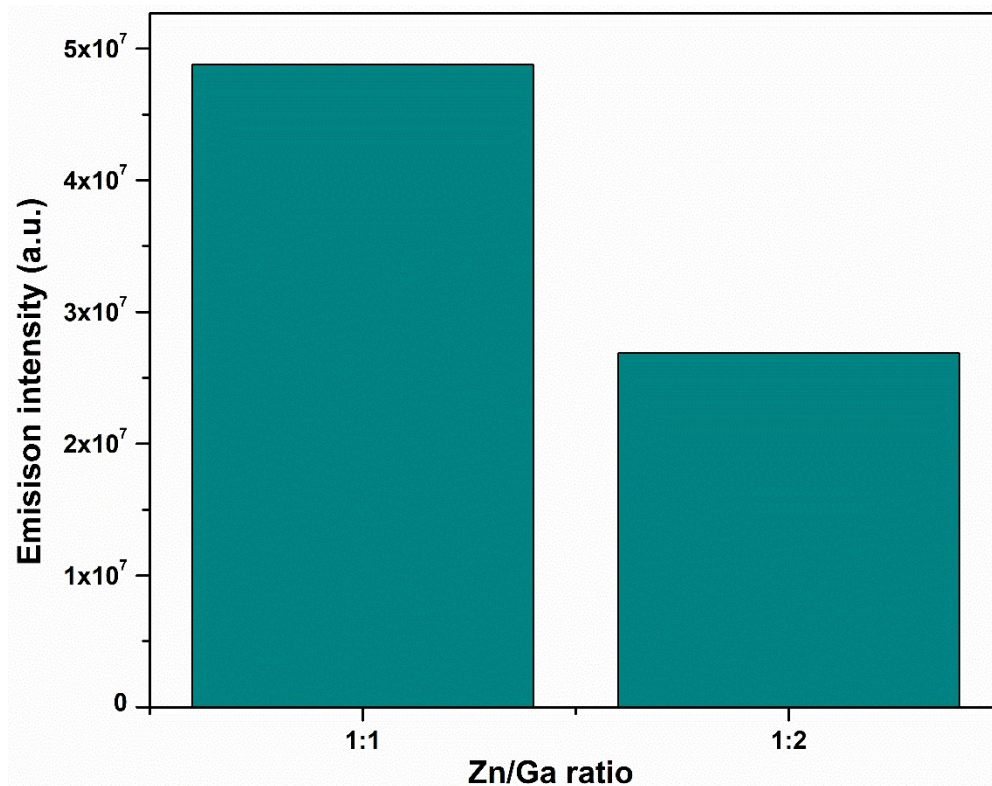


Figure S5. Comparison of the PL emission intensity of the ZGOC NPs synthesized with Zn/Ga = 1:1 and 1:2.

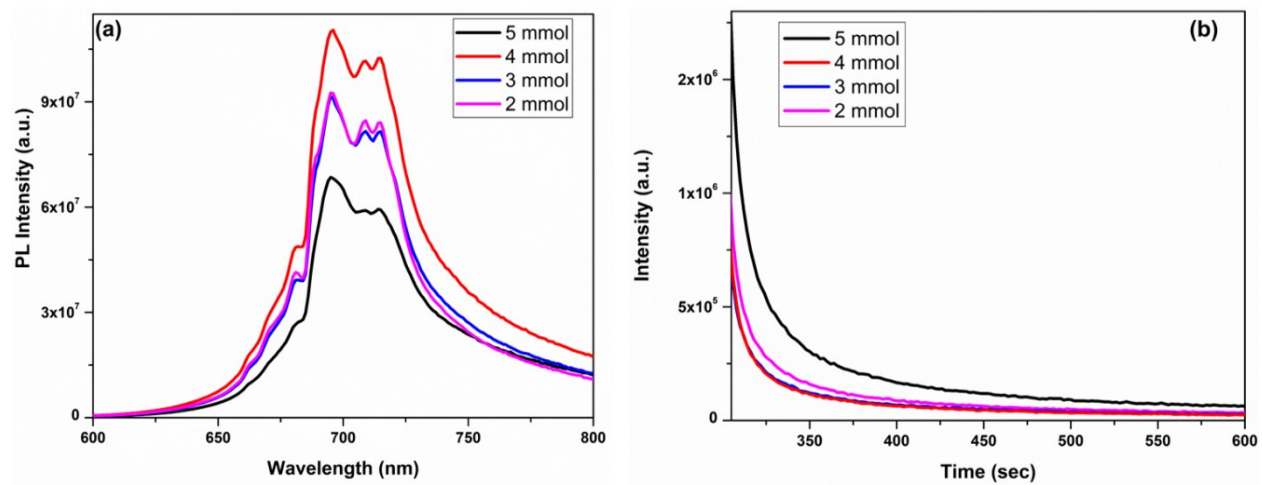


Figure S6. Effect of the added ammonium nitrate concentration on the (a) PL emission and (b) NIR afterglow decay of the ZGOC-5U (Zn:Ga = 1:1) NPs.