

Supporting Information

Persistent luminescent sub-10-nm Cr doped ZnGa₂O₄ nanoparticles by a bi-phasic synthesis route

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Experimental and Instrumentation:

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%), tert-butyl amine, ammonium hydroxide solution (28.0-30.0% NH₃ basis), triethylamine and oleic acid (90% , technical grade) were purchased from Sigma Aldrich. Hexane, chloroform and toluene were purchased from Fisher scientific. All the chemicals were of analytical grade reagents and used directly without further purification in this work.

Synthesis of Cr doped ZnGa₂O₄ NPs using Other Bases:

Synthesis procedure is similar to synthesis of Cr doped ZnGa₂O₄ NPs using tert-butylamine, only replacing tert-butylamine with ammonia solution or triethylamine. Typically, 1.0 mmol of Zn(NO₃)₂ with 1.996 mmol of Ga(NO₃)₃ and 0.004 mmol of Cr(NO₃)₃ were dissolved in 15 ml water, and ammonia solution (or triethylamine) was added to adjust the pH of the solution to desired value and stirred for 30 minutes. After that the solution was mixed with an organic solution of oleic acid (2 mL) and toluene. Similarly, the resulting mixture was transferred to a 45 mL Teflon-lined stainless steel autoclave in ambient environment without stirring. The sealed autoclave was heated at 160 °C for 24 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. The purified products were separated by centrifugation and can be easily re-dispersed in a variety of nonpolar solvent (e.g., toluene, hexane, and chloroform).

Optical Measurements: The excitation and emission spectra of the as-prepared Cr doped ZnGa₂O₄ NPs were measured using an Edinburgh Instruments FLS980 fluorometer system equipped with a Xenon lamp as an excitation source and a TE-cooled photo-multiplier tube

(Hamamatsu, Model R928P) for emission detection. All the excitation and emission spectra were corrected for the spectral sensitivity of the system and detector, as well as intensity variation in the Xe light-source using a reference diode.

For the absolute quantum yield (QY) measurements, integrating sphere was employed in the Edinburgh Instruments FLS980 fluorometer. 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 monochromators) were kept identical for all experiments. Spectra were collected after diffuse reflectance from the samples relative to a non-absorbing standard (BenFlect) at the excitation wavelength and emission spectra under the same condition. Fluorescence emission spectra in the range of 600-800 nm and excitation spectra in the range of 245-272 nm (not absorbed by the sample and reference) were collected using TE-cooled photomultiplier tube (Hamamatsu, Model R928P) as shown in Figure S4 after diffuse reflectance from the samples relative to a non-absorbing standard 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: ^{1,2}

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

where NP (absorbed) is the number of photons absorbed by the sample and NP (emitted) is the number of photons emitted from the sample, $\int L_{sample}$ is the area under the curve for the photoluminescence spectra of the sample and $\int E_{reference}$ and $\int E_{sample}$ are the area 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 is 12 ± 1.2 %.

Transmission Electron Microscopy: Low resolution Transmission Electron Microscope (TEM) images of the Cr doped ZnGa₂O₄ NPs were recorded using a Zeiss Leo 900 operated at 80 kV. Specimens were prepared by dropping a drop of the Cr doped ZnGa₂O₄ nanocrystal solution in hexane on a carbon coated copper grid, and the grid were dried in air. High resolution TEM (HRTEM) images were recorded on a Hitachi H-9500 microscope with an accelerating voltage of 300 kV.

X-ray Diffraction (XRD): Powder X-Ray diffraction (XRD) of the prepared Cr doped ZnGa₂O₄ NPs was measured by a Rigaku-MiniflexTM II X-ray diffractometer with Cu K α ₁ radiation ($\lambda = 0.15406$ nm). The XRD data were collected by using a scanning mode in the 2θ ranging from 15° to 70° with a scanning step size of 0.02° and a scanning rate of $1.0^\circ \text{ min}^{-1}$.

Supporting Data

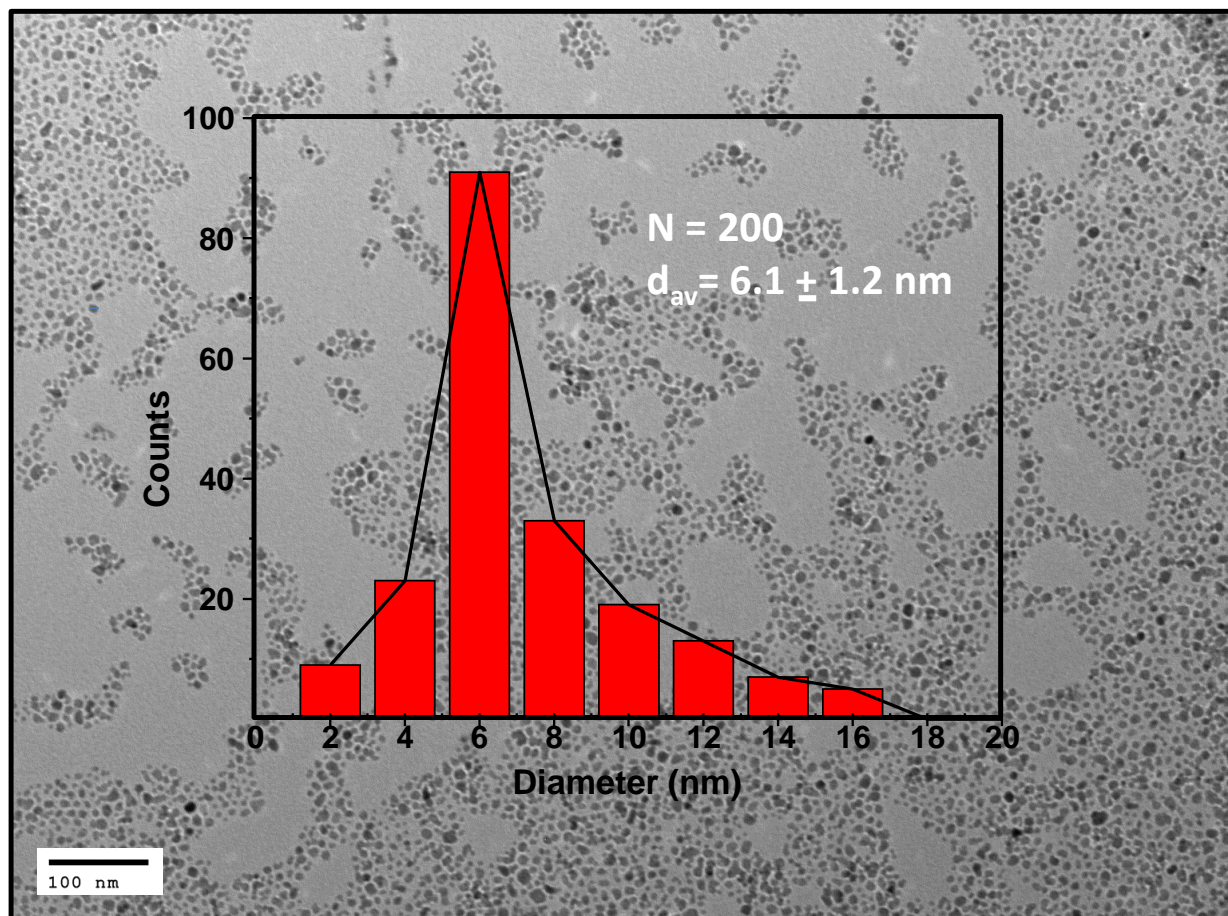


Figure S1. Low resolution TEM image of the as-synthesized Cr:ZnGa₂O₄ NPs. The inserted histogram represents particle size distribution with average particle size of 6.1 ± 1.2 nm.

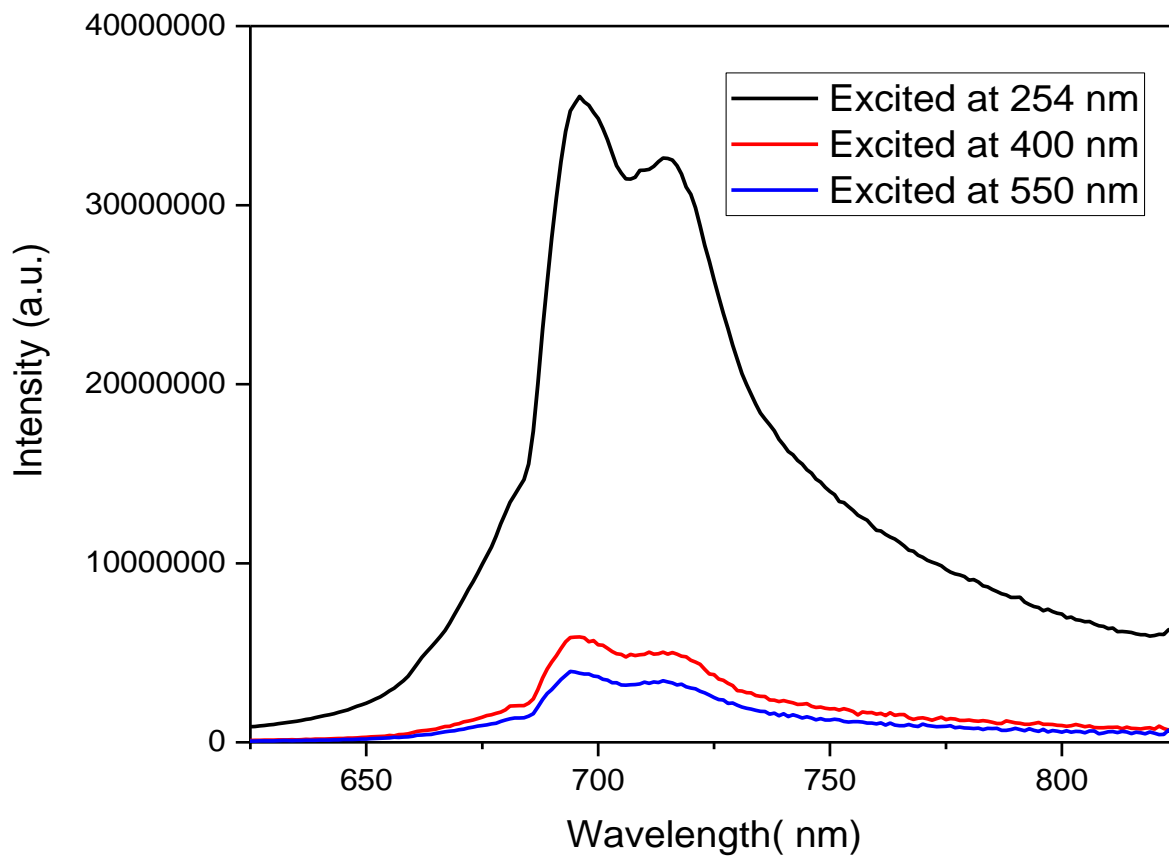


Figure S2. Photoluminescence spectra of the as-synthesized Cr:ZnGa₂O₄ NPs using tert-butylamine as the base after dispersed in hexane and excited at different wavelengths: black curve by 254 nm, red curve by 400 nm, and blue curve by 550 nm, respectively. These results confirm that changing the excitation wavelengths changes only the emission intensity (highest intensity from 254 nm excitation) but the spectral nature remains the same. Moreover, it confirms that these NPs can be excited with a wide range of excitation sources to give similar spectral nature.

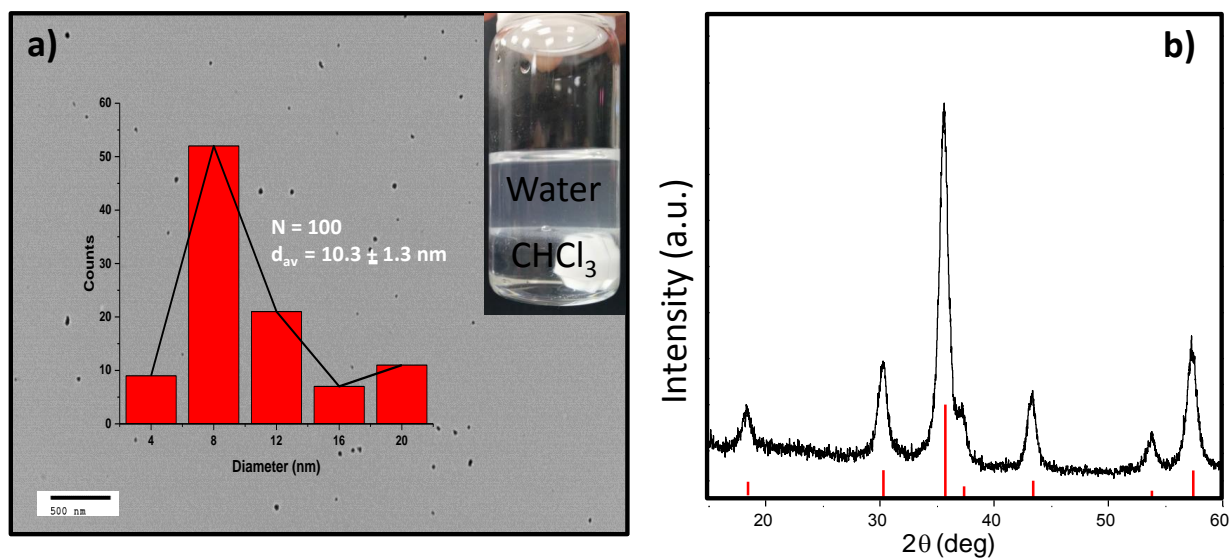


Figure S3. (a) Low resolution TEM of the high temperature annealed Cr:ZnGa₂O₄ NPs dispersed in water after surface modification. The sample was prepared by dispersing the NPs in water using surface modification procedure from reference 10 of the main text. A histogram represents particle size distribution with average particle size 10.3 ± 1.3 nm. Inset shows high temperature annealed Cr:ZnGa₂O₄ NPs after phase transfer to water media as evident from all NPs being transferred to water phase with no NPs in chloroform (CHCl₃) giving clear chloroform phase. (b) XRD pattern of the annealed Cr doped ZnGa₂O₄ NPs at 750 °C for 1 hour (black curve) matches with the diffraction pattern of corresponding spinel ZnGa₂O₄ (red lines, JCPDS No. 38-1240).

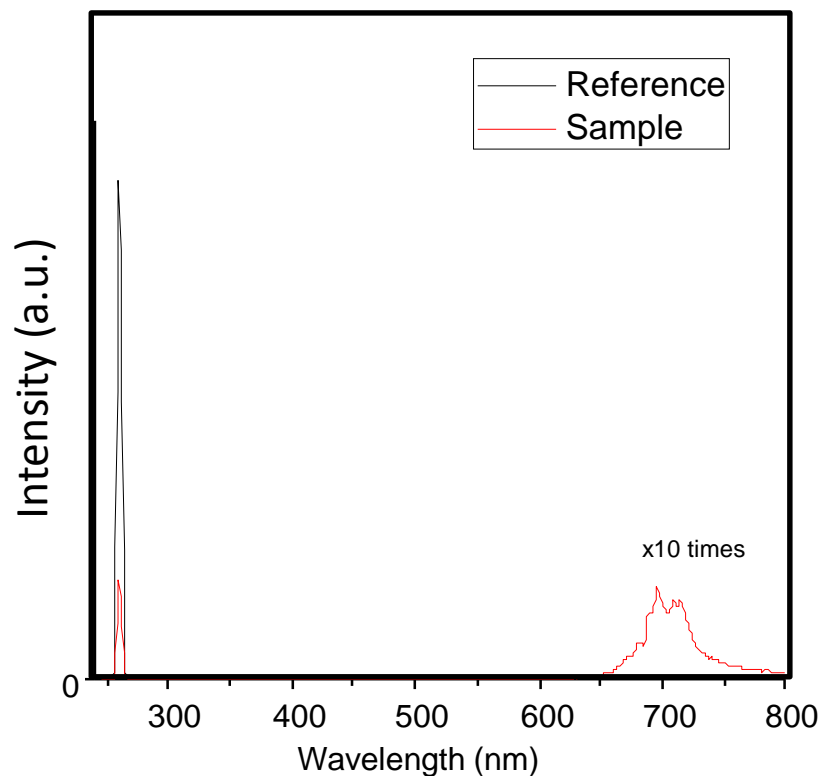


Figure S4. Excitation and emission spectra collected after the diffuse reflectance from the high temperature (750 °C) annealed Cr:ZnGa₂O₄ NPs and the reference. Emission spectra were multiplied 10 times for better visibility.

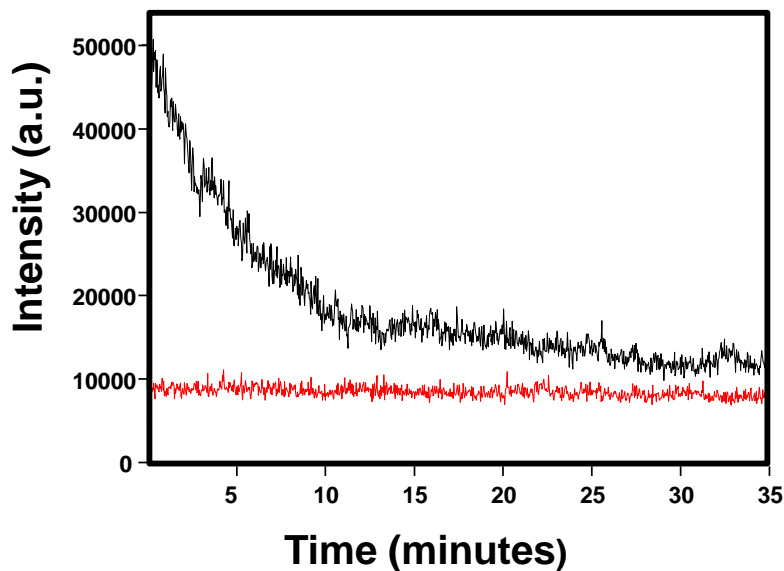


Figure S5. Afterglow decay of high temperature annealed Cr:ZnGa₂O₄ NPs in water after 5 min irradiation with a 254 nm UV lamp (black curve), which clearly illustrate these NPs shows efficient persistent emission in water phase up to 10 minutes. The red curve shows the background of the instrument without any sample under identical instrument condition.

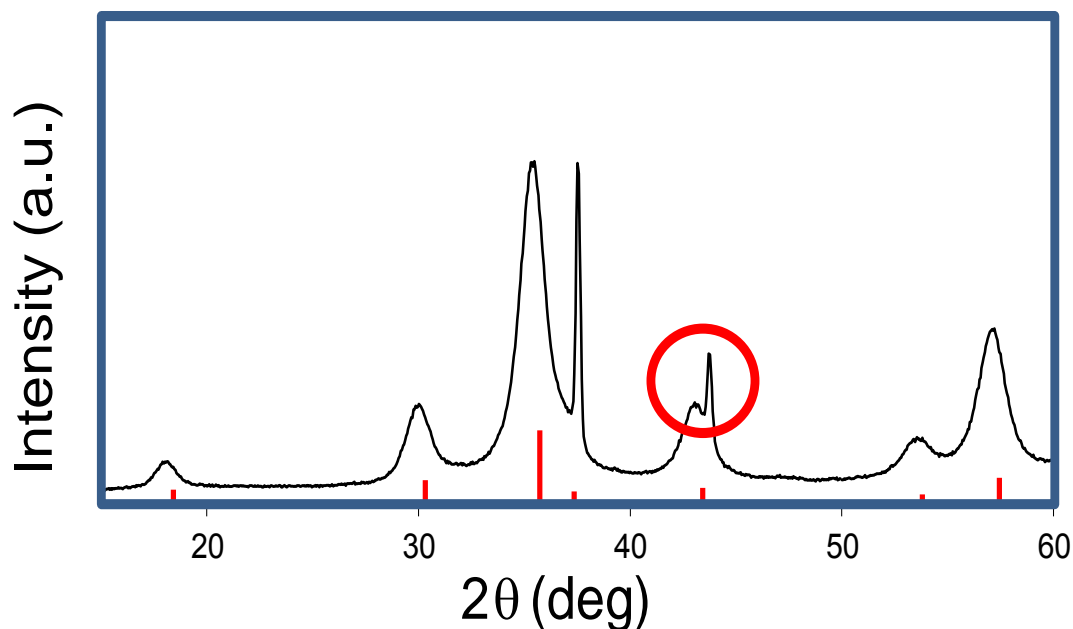


Figure S6. XRD of the Cr doped ZnGa_2O_4 NPs synthesized at pH 3 (black curve) matching with the diffraction pattern of corresponding spinel ZnGa_2O_4 (red lines, JCPDS No. 38-1240) with some impurity (red circle) of Ga_2O_3 phase (standard XRD pattern of Ga_2O_3 not shown here).

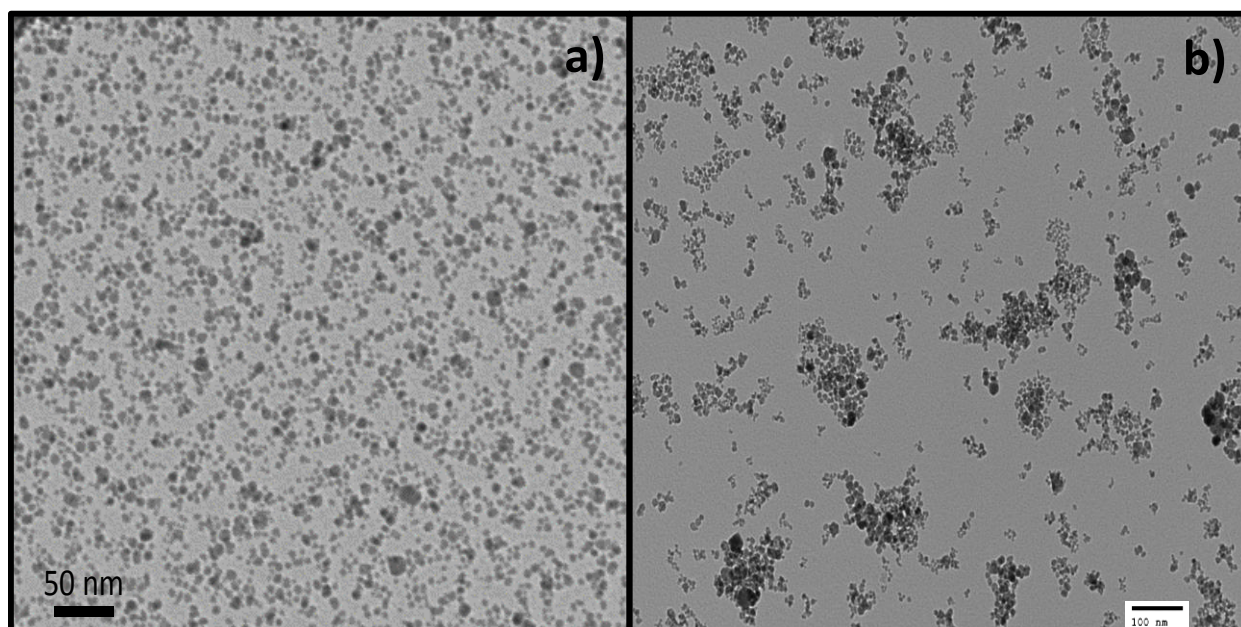


Figure S7. (a) Low resolution TEM of the Cr: ZnGa_2O_4 NPs synthesized using ammonium hydroxide as the base with average particle size of 5.2 ± 1.1 nm. (b) Low resolution TEM of Cr: ZnGa_2O_4 NPs synthesized using triethylamine as the base. The NPs synthesized under these conditions are nonspherical but are still sub-10-nm with some degrees of agglomeration is observed.

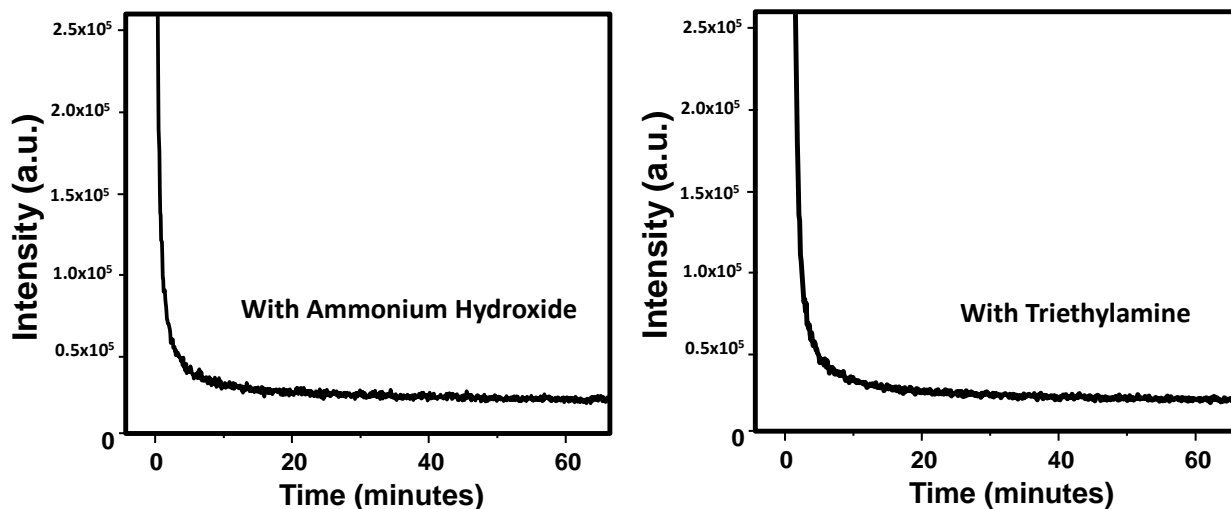


Figure S8. Afterglow decay of the Cr:ZnGa₂O₄ NPs (annealed at 750 °C for 1 hour) powder after 5 min irradiation with a 254 nm UV lamp (left panel corresponding to NPs synthesized with ammonium hydroxide and right panel to NPs synthesized with trimethylamine). Both plot shows relatively fast decay at the first ten minutes, and then levels off.

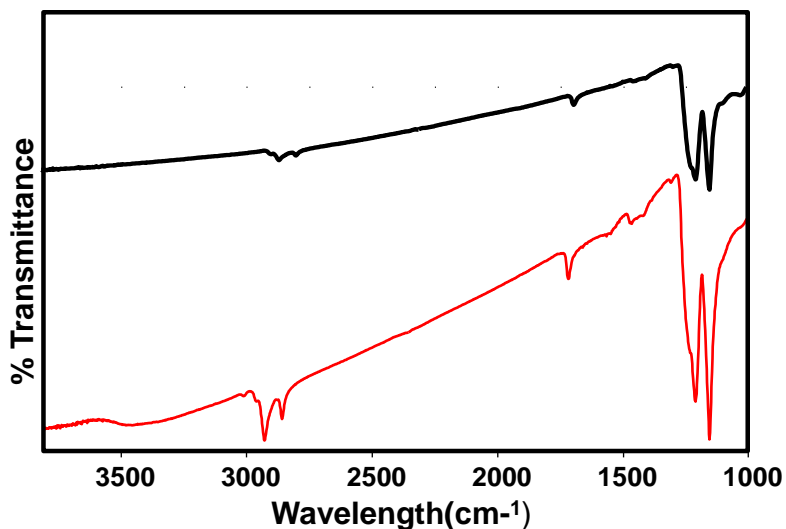


Figure S9. FT-IR spectra of the as-prepared Cr:ZnGa₂O₄ NPs synthesized biphasic hydrothermally at 150 °C with different bases: ammonium hydroxide (black curve) and triethylamine (red curve) and dispersed in hexane at pH 8. Presence of oleic acid on the surface of these NPs endows them dispersible in organic solvents, and is confirmed by the 1710 cm⁻¹ C=O peak (stretching mode) and 2840 cm⁻¹ and 2922 cm⁻¹ peaks of alkyl CH stretching mode.

Reference

- (1) J. C. de Mello, H. F. Wittmann, R. H. Friend, *Adv. Mater.*, 1997, **9**, 230.
- (2) M. Pokhrel, A. K. Gangadharan, and D. K. Sardar, *Materials Letters*, 2013, **99**, 86.