Electronic Supplementary Material (ESI) for Chemical Communications.

SUPPORTING INFORMATION

Enhancement of long-lived luminescence in nanophosphors by surface defects passivation

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Experimental section

Materials. Zinc nitrate hexahydrate ($Zn(NO_3)_2·6H_2O$), Gallium oxide (Ga_2O_3, 99.99%), germanium oxide (GeO_2, 99.99%) and chromic nitrate ($Cr(NO_3)_3·9H_2O$) were obtained from Aladdin. Sodium hydroxide (NaOH), ammonium hydroxide ($NH_3·H_2O$), concentrated nitric acid (HNO_3), tetraethoxysilane (TEOS), rhodamine B were purchased from Sinopharm Chemical Reagent Co. (China). Na_2GeO_3 solution was prepared through dissolving GeO_2 powder in 2 mol/L NaOH solution to a final concentration of 400 mmol/L. Ga_2O_3 powder was dissolved in HNO_3 to obtain the $Ga(NO_3)_3$ solution. $Zn(NO_3)_2$ solution (2 mol/L), Na_2GeO_3 solution (400 mmol/L), and $Cr(NO_3)_2$ solution (80 mmol/L) were used as the precursor solutions in all the experiments.

Instruments. The transmission electron microscope (TEM) measurements and energy dispersive X-ray analysis were performed on a TEM (200 kV, JEOL, JEM-2100, Japan). The core-shell structure of the PLNPs was characterized using a high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM). The crystal structure of ZGGO:Cr, T-ZGGO:Cr, ZGGO:Cr@ZGO, ZGGO:Cr@SiO_2 PLNPs were carried out with a Bruker X-ray diffractometer with Cu-Kα radiation (λ = 1.5406 Å) (Bruker, D8 Advance, Germany). The photoluminescence curves of PLNPs were measured on a fluorescence spectrometer (Hitachi. Ltd., F-4600, Japan). Luminescence signal of the ZGGO:Cr, T-ZGGO:Cr, ZGGO:Cr@ZGO, ZGGO:Cr@SiO_2 PLNPs were captured by an IVIS imaging systems (Perkin-Elmer). Dynamic light scattering measurements and zeta potential measurements were tested using a Malvern Zetasizer Nano ZS system. The thermo-luminescence (TL) glow curves were carried out with a SL08-L meter (Guangzhou-radiation science and technology). The photoluminescence and persistent luminescence (PersL) images of PLNPs was captured using a digital single-lens reflex camera (Nikon, D7100, Japan). The surface coated ZGGO:Cr PLNPs ink was printed by an inject printer (HP Deskjet 1010).

Synthesis of $Zn_{1.2}Ga_{1.6}Ge_{0.2}O_4$: 0.5% Cr (ZGGO:Cr) PLNPs. The ZGGO:Cr nanoparticles were synthesized via a hydrothermal process.[1] In brief, 11 mL of solution containing 1.6 mmol of $Ga(NO_3)_3$, 0.2 mmol of Na_2GeO_3, 1.2 mmol of $Zn(NO_3)_2$, and 0.005 mmol of $Cr(NO_3)_3$ were prepared. To adjust the pH value to 8.5, $NH_3·H_2O$ (28 wt %) was added into the above solution. After keeping the mixture solution agitated for 1 h at room temperature, the mixture solution was added into a 20 mL Teflon-lined stainless autoclave and reacted for 10 h at 220 °C. Lastly, the suspension was centrifuged, and the prepared ZGGO:Cr PLNPs were collected and washed with DI water for several times.

Synthesis of thermal treated ZGGO:Cr (T-ZGGO:Cr) PLNPs. ZGGO:Cr PLNPs (0.15 g) were added to 11 mL DI water and were dispersed by sonication for 10 min. To regulate the pH value of mixed solution to 8.5, concentrated $NH_3 \cdot H_2O$ (28 wt %) was instantly added. The prepared mixture was stirred for 1 h under room atmosphere. After transferring into a 20 mL Teflon-lined stainless autoclave, the mixed solution then reacted for 10 h at 220 °C. Lastly, the obtained suspension was centrifuged, and the thermal treated ZGGO:Cr (T-ZGGO:Cr) PLNPs were collected and washed with DI water for several times.

Synthesis of core-shell structured ZGGO:Cr@ZGO PLNPs. ZGGO:Cr nanoparticles (0.1 g), $Ga(NO_3)_3$ (2 mmol) and $Zn(NO_3)_2$ (1 mmol) were added to 11 mL DI water. The pH value of the mixture was regulated to 8.5 by adding $NH_3 \cdot H_2O$ (28 wt %) under vigorous stirring. After keeping the prepared solution agitated under room atmosphere for 1 h, the mixture was further decanted into a 20 mL Teflon-lined stainless autoclave and reacted for another 10 h at 220 °C. After that, the acquired suspension was centrifuged to collect the ZGGO:Cr@ZGO PLNPs, followed by washing with DI water for several times.

Synthesis of core-shell structured ZGGO:Cr@SiO_2 PLNPs. ZGGO:Cr (0.15 g) PLNPs were added to a mixed solution of DI water (20 mL) and ethanol (80 mL). After the ZGGO:Cr PLNPs subjected to sonication, 1.4 mL $NH_3 \cdot H_2O$ (28 wt %) was added drop by drop into the resulting solution with vigorous stirring. The prepared solution was stirred for 15 min at 30 °C. After that, 1.1 mL TEOS was slowly added into the mixture solution and then stirred at 30 °C for 8 h. The suspension was centrifuged and washed with ethanol for three times.[2]

Measurement of the PersL of PLNPs. Briefly, ZGGO:Cr, T-ZGGO:Cr, ZGGO:Cr@ZGO, ZGGO:Cr@SiO_2 PLNPs (0.1 g) were put into a 48-plate well. The PLNPs were irradiated for 3 min by a commercial ZF-5 UV lamp (254 nm). After illumination, the 48-plate well was placed in IVIS imaging system to capture attenuation images. The exposure time was 3 s.

Autofluorescence-free bioimaging study. The healthy nude mice (4 weeks) weighing 18–21 g were obtained from Hunan SJA Laboratory Animal Co., Ltd (Changsha, China). The mice were randomized divided into two groups, including: (1) subcutaneous injection with rhodamine B (40 uL, 1 ug/mL), (2) subcutaneous injection with ZGGO:Cr PLNPs (40 uL, 3 mg/mL), T-ZGGO:Cr PLNPs (40 uL, 3 mg/mL), ZGGO:Cr@ZGO PLNPs (40 uL, 3 mg/mL) and ZGGO:Cr@SiO_2 PLNPs (40 uL, 3 mg/mL). The fluorescence image of the rhodamine B was captured with the IVIS imaging system (fluorescence mode). The PersL signals from the ZGGO:Cr, T-ZGGO:Cr, ZGGO:Cr@ZGO and ZGGO:Cr@SiO_2 PLNPs were captured in the bioluminescence mode.

Preparation of PLNPs ink and the information encryption study. Briefly, 100 mg ZGGO:Cr@ZGO were dispersed in 1 mL DI water by sonication for 30 min. The PLNPs ink was obtained by filtering through a pore filter with 220 nm pore size. The correct information (the number “202”) was first printed on office paper loaded with prepared ZGGO:Cr@ZGO ink with an HP Deskjet 1010 printer. The rest part of information was printed with commercial red color UV ink (cy5.5, Aladdin). Then, the images of the typed information on the office paper was captured on an IVIS imaging system. A portable UV lamp was used to charge the ZGGO:Cr@ZGO ink.

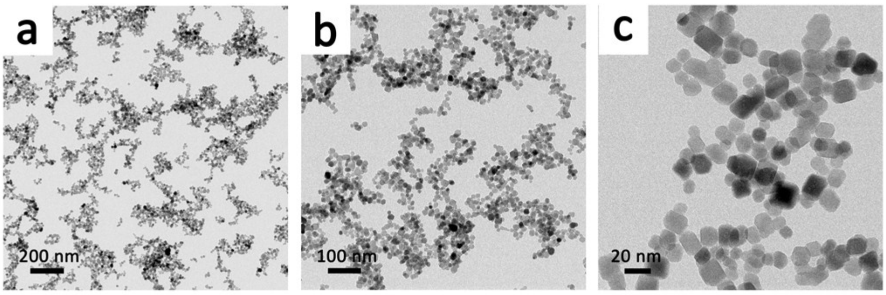

Figure S1. (a-c) TEM images of ZGGO:Cr PLNPs.

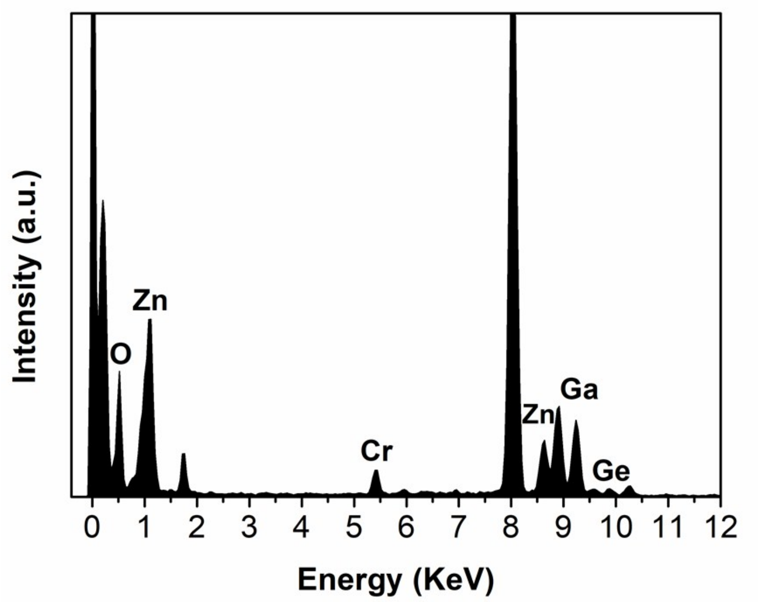

Figure S2. Energy-dispersive X-ray (EDX) analysis of the ZGGO:Cr PLNPs.

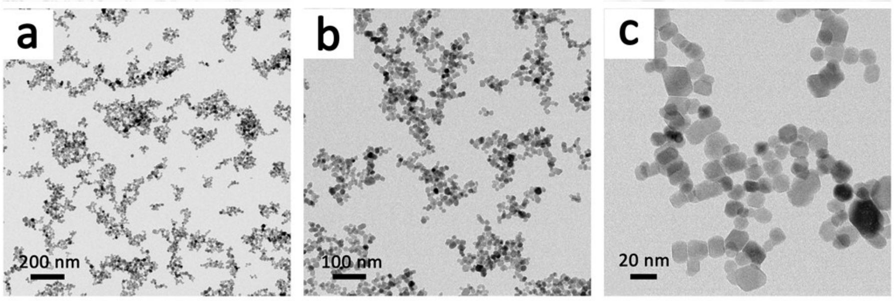

Figure S3. (a-c) TEM images of T-ZGGO:Cr PLNPs.

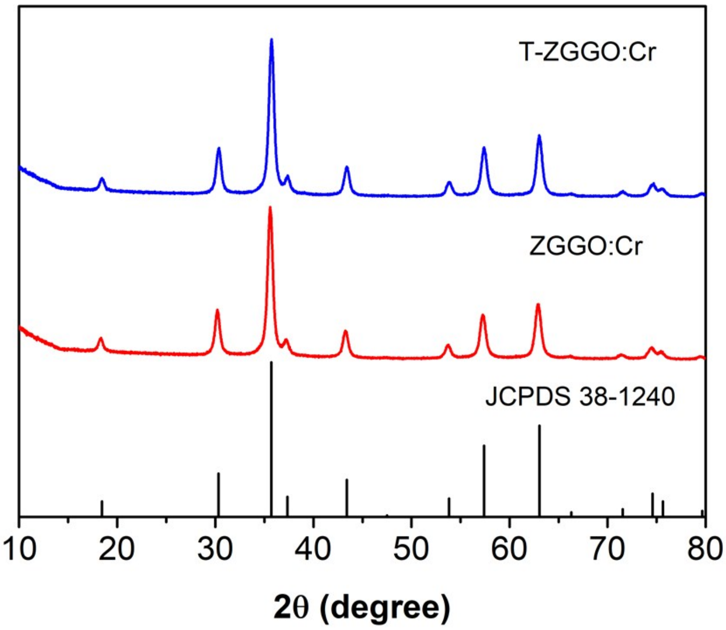

Figure S4. The X-ray diffraction (XRD) patterns of ZGGO:Cr and T-ZGGO:Cr PLNPs. The XRD patterns show their well-defined cubic spinel structure.

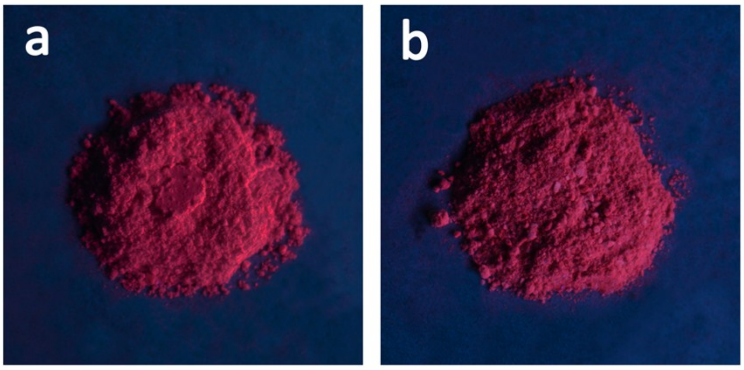

Figure S5. Photoluminescence images of ZGGO:Cr (a) and T-ZGGO:Cr (b) PLNPs.

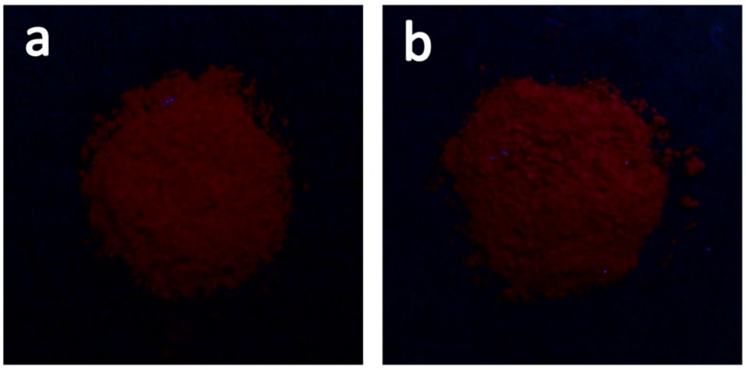

Figure S6. PersL images of ZGGO:Cr (a) and T-ZGGO:Cr (b) PLNPs.

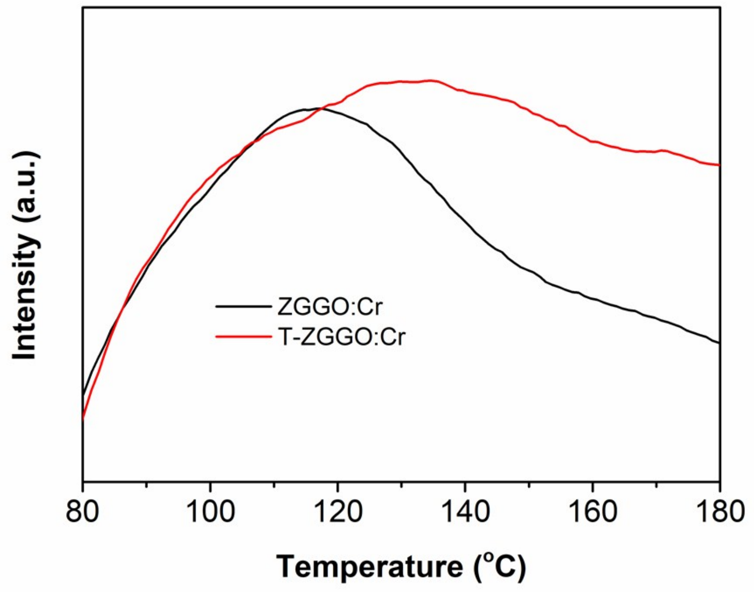

Figure S7. TL curves of ZGGO:Cr and T-ZGGO:Cr PLNPs.

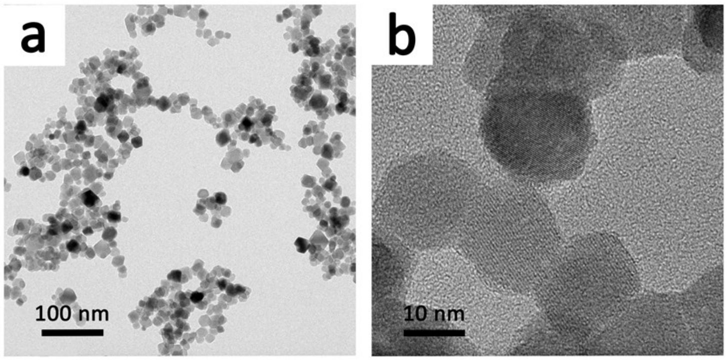

Figure S8. TEM images of ZGGO:Cr@ZGO PLNPs.

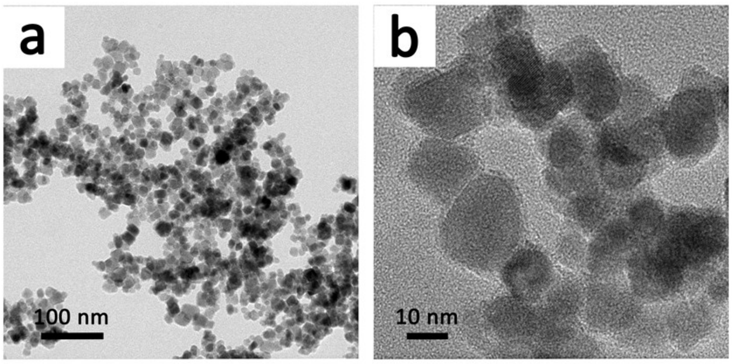

Figure S9. TEM images of ZGGO:Cr@SiO_2 PLNPs.

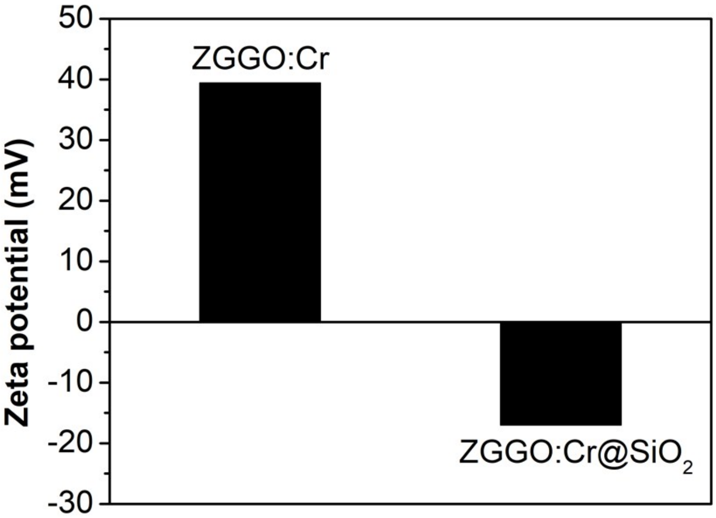

Figure S10. Zeta potentials of ZGGO:Cr and ZGGO:Cr@SiO_2 PLNPs.

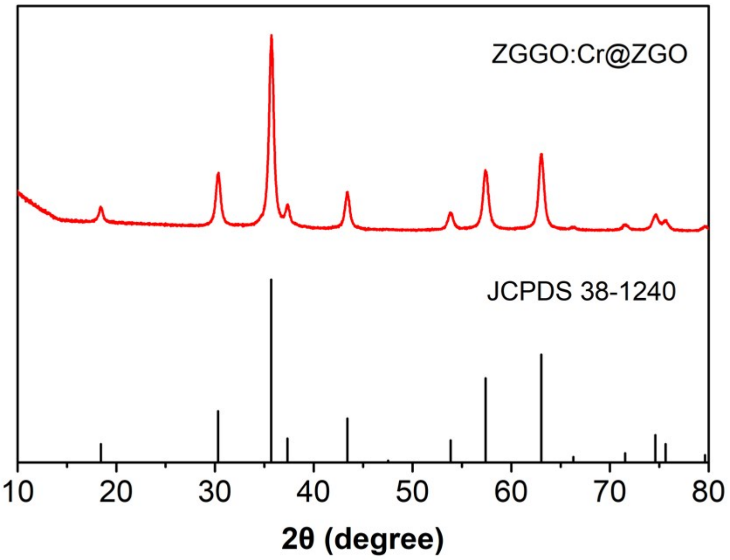

Figure S11. XRD pattern of ZGGO:Cr@ZGO PLNPs. The XRD pattern shows the well-defined cubic spinel structure of the ZGGO:Cr@ZGO PLNPs.

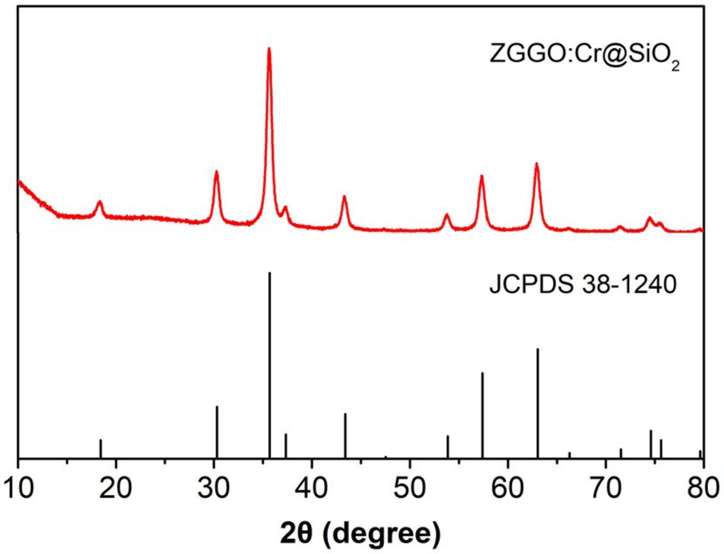

Figure S12. XRD pattern of ZGGO:Cr@SiO_2 PLNPs.

Table S1. The size and crystallinity of ZGGO:Cr, T-ZGGO:Cr, ZGGO:Cr@ZGO and ZGGO:Cr@SiO_2 PLNPs.

	ZGGO:Cr	T-ZGGO:Cr	ZGGO:Cr@ZGO	ZGGO:Cr@SiO_2
Size (nm)	13.7	13.7	15.5	14.0
Crystallinity (%)	89.50	94.02	92.83	72.83

The size of the PLNPs were calculated by Scherrer formula based on the XRD data, and the crystallinity of the PLNPs was analyzed by Jade software (Table S1). The ZGGO:Cr PLNPs are highly crystalized with a crystallinity value of about 89.50%. Thermal treatment can enhance the crystallinity of the ZGGO:Cr PLNPs. The ZGGO:Cr@SiO_2 shows increased particle size but decreased crystallinity compare to ZGGO:Cr PLNPs. The calculated decreased crystallinity is due to the amorphous SiO_2 shell.[3-5] The ZGGO:Cr@ZGO displays increased particle size and crystallinity as anticipated.

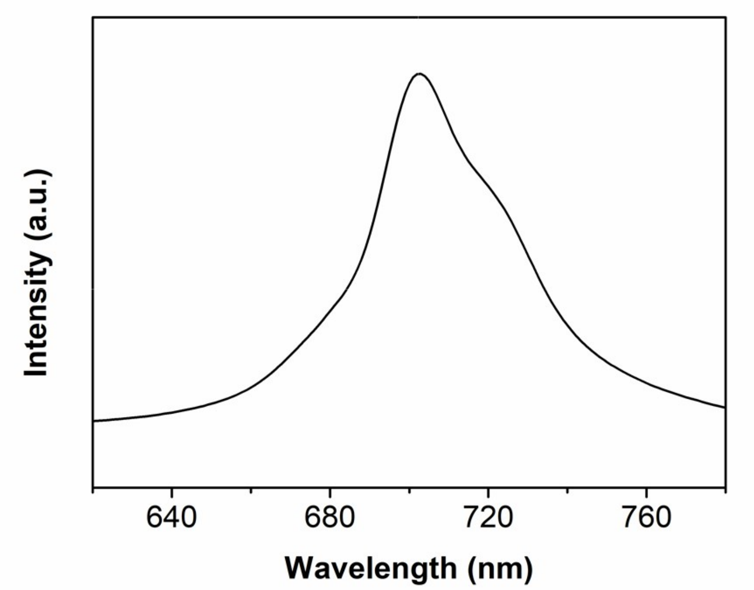

Figure S13. The photoluminescence spectrum of ZGGO:Cr@ZGO PLNPs.

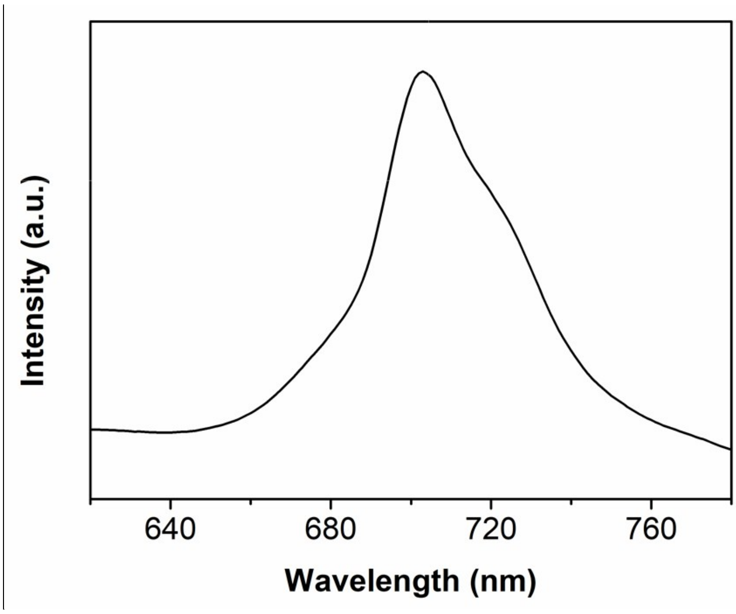

Figure S14. The photoluminescence spectrum of ZGGO:Cr@SiO_2 PLNPs.

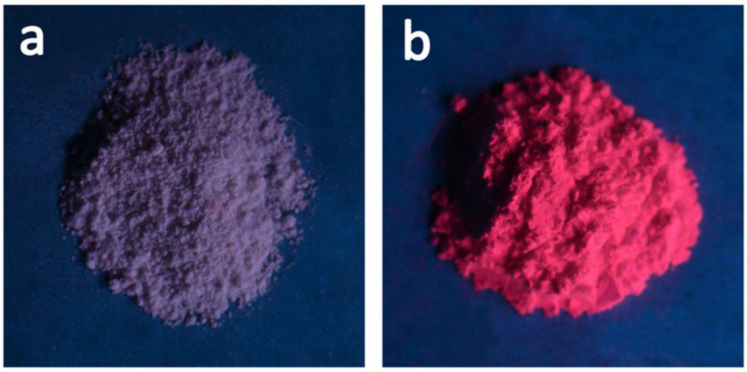

Figure S15. Photoluminescence images of ZGGO:Cr@ZGO (a) and ZGGO:Cr@SiO_2 (b) PLNPs.

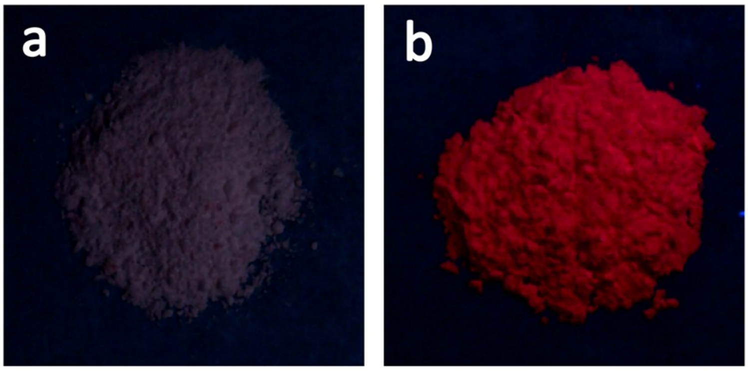

Figure S16. PersL images of ZGGO:Cr@ZGO (a) and ZGGO:Cr@SiO_2 (b) PLNPs.

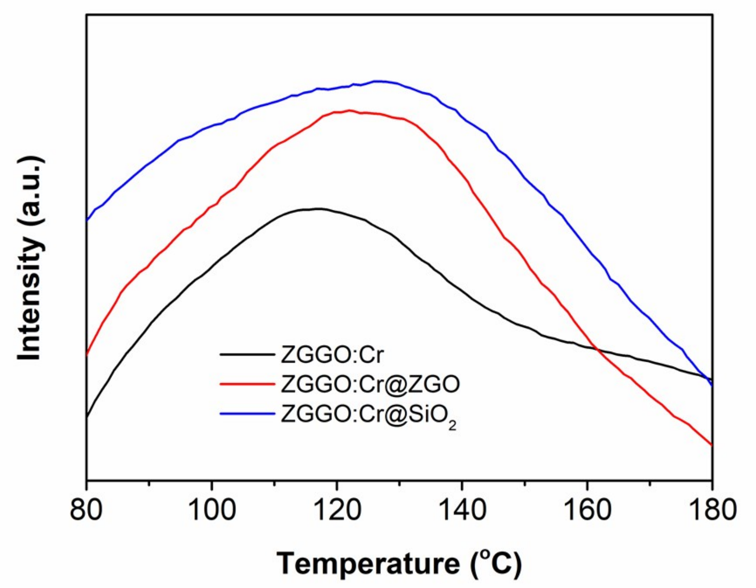

Figure S17. TL curves of ZGGO:Cr, ZGGO:Cr@ZGO and ZGGO:Cr@SiO_2 PLNPs. The TL curves show a stronger luminescence intensity at around 130 ^oC in ZGGO:Cr@ZGO and ZGGO:Cr@SiO_2 PLNPs compared with the ZGGO:Cr PLNPs, confirming that surface coating can enhance the PersL in PLNPs.

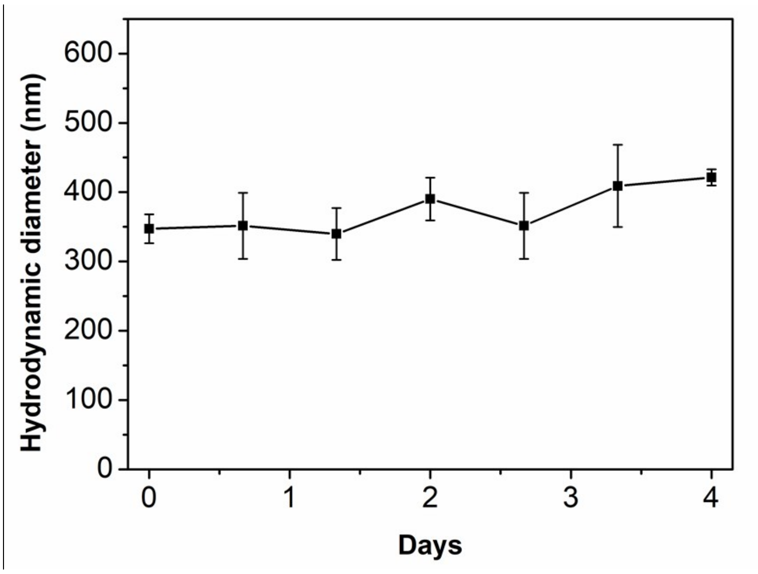

Figure S18. Colloidal storage stability of ZGGO:Cr@SiO_2 PLNPs in PBS.

Notes and reference

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