Supporting Information

EXPERIMENTAL SECTION

Materials: ZnO, GeO_2, Tb_4O_7, Bi_2O_3, $Zn(NO_3)_2·6H_2O$, $Tb(NO_3)_3·6H_2O$, $Bi(NO_3)_3·5H_2O$, Sodium hydroxide, Nitric acid, trimethyl benzoyl diphenylphosphine oxide (TPO) and hydroxyethyl methacrylate (HEMA) were purchased from Aladdin (China) without further purification. Aliphatic urethane acrylate oligomer (CN9010 NS), polyethylene glycol 200 diacrylate (SR259), pentaerythritol triacrylate (SR444NS) were purchased from Sartomer (China). Poly(dimethylsiloxane) (PDMS) was obtained from Dow Corning Company (USA). ATTO 425 NHS ester was provided by Sigma-Aldrich (USA). Sulfhydryl-functionalized MUC1 aptamer and its part cDNA modified with ATTO425 (cDNA-ATTO425) was purchased from Shanghai Sangon Biological Science & Technology (China). Their sequences are as follow:

MUC1 aptamer: 5'-SH-GCAGTTGATCCTTTGGATACCCTGG-3'

Complementary strand (cDNA): 5'-CCAGGGTATCCAAAGGATCAACTGC-ATTO425-3'

Apparatus: XRD patterns were obtained by Miniflex 600 (Rigaku Co., Ltd., Japan). Elements mapping and EDS spectrum were acquired by Apreo S LoVac (Thermo Fisher Co., Ltd., USA). PL spectra and PersL spectra and PersL decay curves were recorded by FluoroMax-4 (Horiba Instruments Inc, USA). Thermoluminescence curves were measured by DSC600 temperature-controlled stage (Linkam, UK). The optical images were taken by mobile phone (Huawei P40 pro, China). TEM image, element mapping and corresponding EDS spectrum were acquired by Talos F200X unit (Thermo Fisher Co., Ltd., USA) with 200 kV accelerating voltage. Zeta potential and hydrodynamic diameter of samples were measured by Brookhaven Omni (Nano Brook Omni, Brookhaven Instruments Corporation, USA).

Synthesis of Zn_2GeO_4: Tb^{3+}/Bi^{3+} luminescent materials: ZGO: Tb^{3+}/Bi^{3+} materials were synthesized by solid-state method. Briefly, ZnO, GeO_2, Tb_4O_7 and Bi_2O_3 in their stoichiometric ratios, were mixed homogeneously by grinding with ethanol. Then the mixture was sintered at 1200 ℃ in the air for 4 h with heating rate at 5 ℃/min. Finally, the samples were grinded in agate mortar after natural cooling to room temperature.

Preparation of the anti-counterfeiting patterns: A mixture of 40 wt% of aliphatic urethane acrylate oligomer, 20 wt% of HEMA, 20 wt% of polyethylene glycol 200 diacrylate, 15 wt% of pentaerythritol triacrylate, and 5 wt% of TPO was used as photo-curable resin for 3D printing. The 3D structures were fabricated by a LCD printing apparatus (S100, Doumi, China). The light intensity of the LCD printer was set as 1.0 mW/cm^2. The thickness of each slicing layer was controlled as 0.05 mm. The 3D printing exposure time for all layers was similar with an optimal value of 15 s/layer. After printing, the stamps were washed with ethanol to remove residual liquid resin. The PLP was mixed with PDMS (with a curing agent in a 10:1 weight ratio) in a weight ration of 1:1 to form ink slurry.

Synthesis of nZGO: nZGO was synthesized by hydrothermal method. Briefly, 11 mL of water, 2 mmol of $Zn(NO_3)_2$, 1.1 mmol of Na_2GeO_3, 0.01 mmol of $Bi(NO_3)_2$, 0.05 mmol of $Tb(NO_3)_3$ and 300 uL of nitric acid were homogenously mixed. The pH value of the mixture was adjusted to 8.5 by ammonium hydroxide. After stirring for 1 h, the mixture was transferred to autoclave and kept at 220 ℃ for 12 h. The nZGO was obtained by centrifugation and washed three times with water.

Amino modification of nZGO: 50 mg of nZGO was dispersed in 30 mL of DMF and stirred at 80 ℃. Then 200 uL of APTES was added under violently stirring for 12 h. nZGO-NH_2 was collected by centrifugation and wash three times with water.

Preparation of nZGO-ATTO425: 2 mg of nZGO-NH_2 and 0.6 mg of Sulfo-SMCC were dispersed in HEPES buffer (10 mM, Ph 7.2) and gently stirred for 1 h. The maleimide-functionalized nZGO was collected by centrifugation and wash three times with Tris-HCl buffer (10 nM, pH 7.2), followed by redispersed in 2 mL Tris buffer. 4 nmmol of

MUC1 aptamer was added into the above mixture and coincubated under gently shaking for 12 h. nZGO-apt was obtained by centrifugation, wash three times with Tris buffer and redispersed in 2 mL of Tris buffer. After that, 4 nmmol of cDNA-ATTO425 was added into nZGO-apt dispersion under shaking at 37 ℃ for 12 h. The nZGO-ATTO425 was finally obtained by centrifugation, washed three times with Tris buffer and redispersed in 1 mL of Tris buffer for further use.

Detection of MUC1: 100 uL of nZGO-ATTO425 solution and samples were homogenously mixed and made up to 400 uL by Tris buffer. The system was incubated at 37 ℃ for 1 h. The intensity of persistent luminescence at 455 nm and 540 nm was recorded by fluorescence spectrometer.

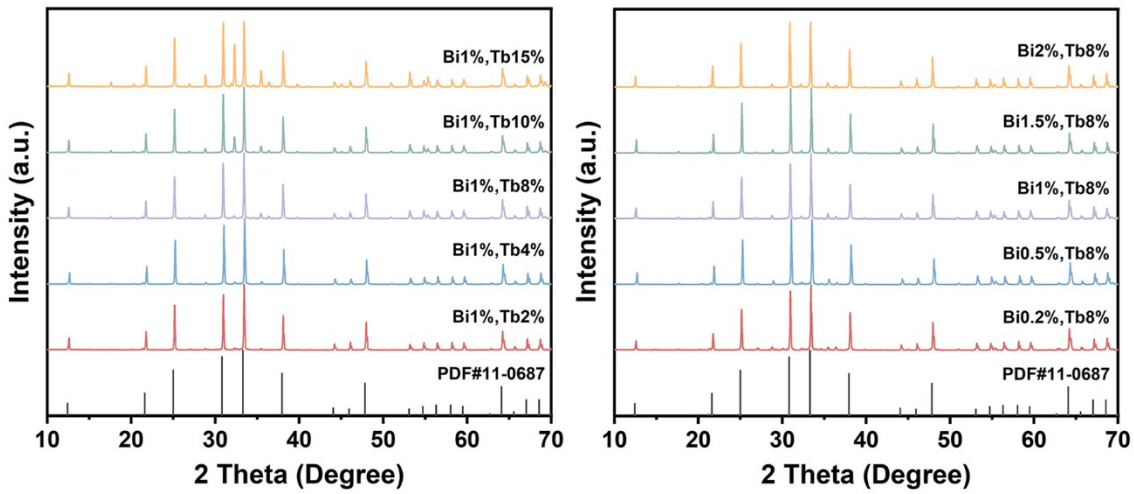

Figure S1. XRD patterns of Zn_2GeO_4: x% Tb^{3+}/y% Bi^{3+}.

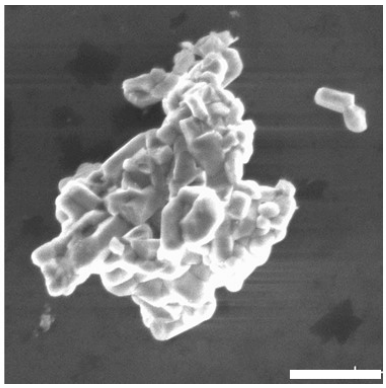

Figure S2. The SEM image of sample synthesized by high temperature solid state method. Scale bar 10 μm

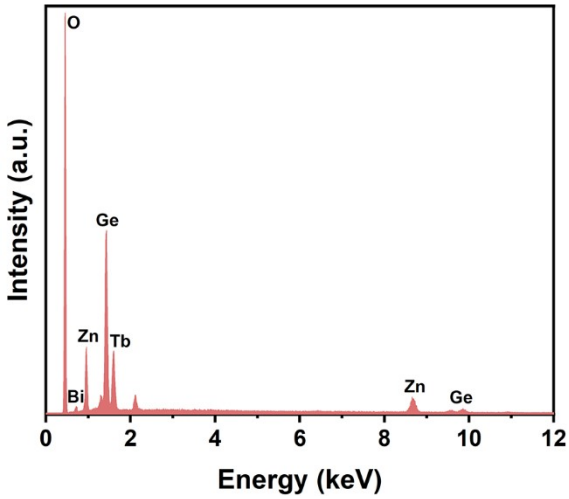

Figure S3. The EDS spectrum of sample synthesized by high temperature solid state method.

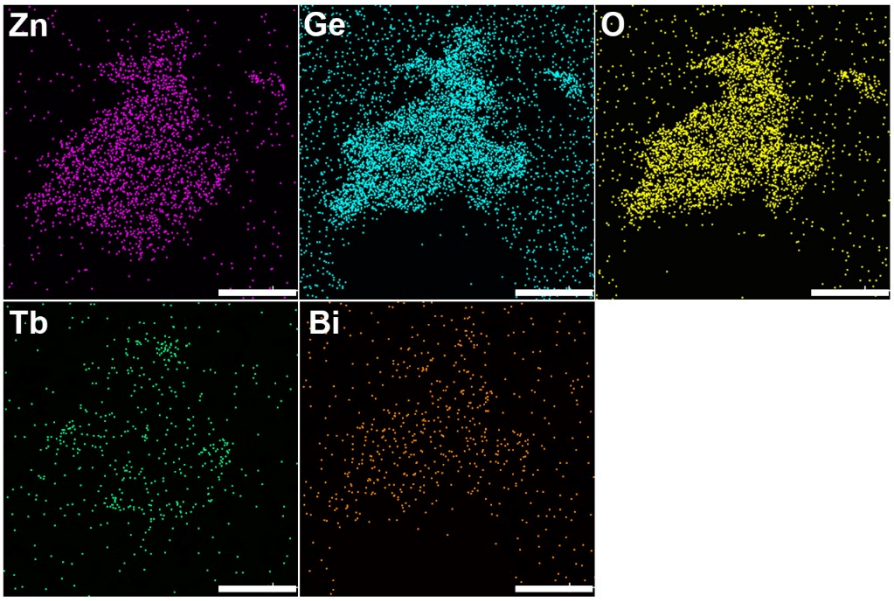

Figure S4. Element mapping images of sample synthesized by high temperature solid state method. Scale bar 10 μm

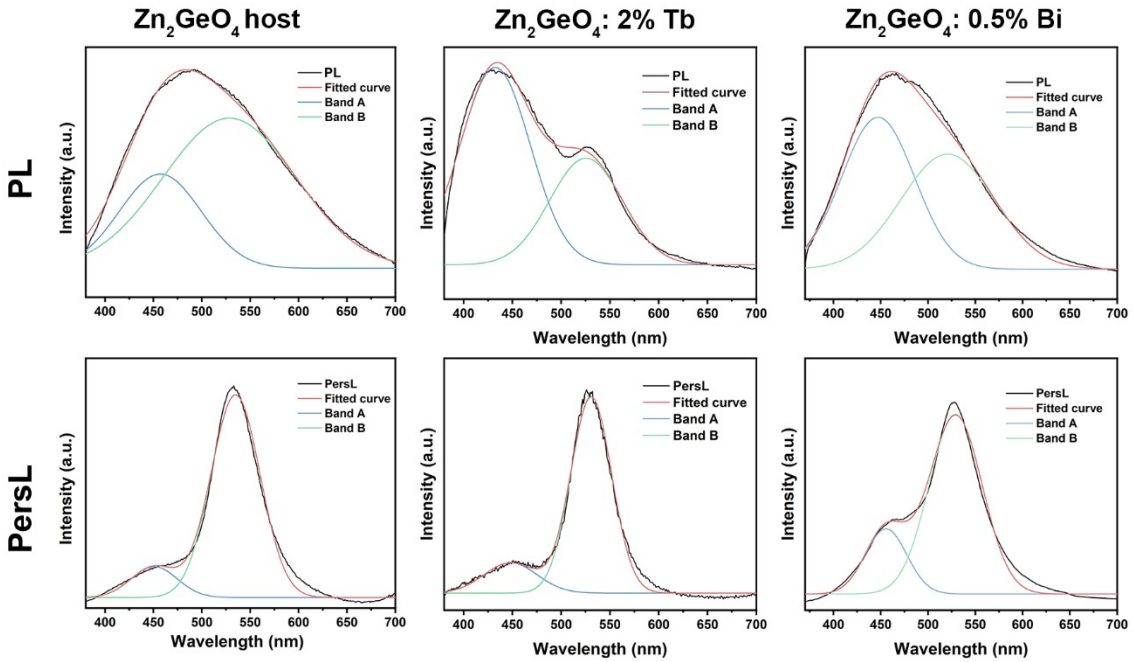

Figure S5. PL spectra and PersL spectra of Zn_2GeO_4 host, Zn_2GeO_4: 2% Tb and Zn_2GeO_4: 0.5% Bi, respectively.

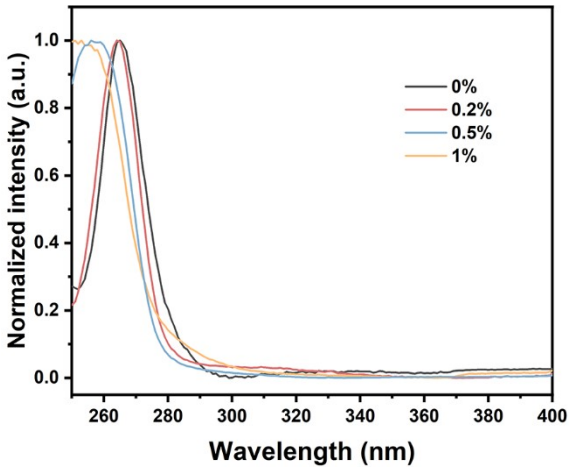

Figure S6. Excitation spectrum with different Bi^{3+} doping concentration.

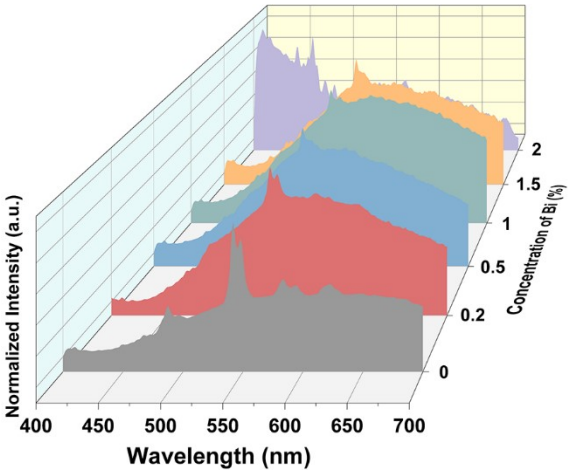

Figure S7. PL spectra with different Bi^{3+} concentration under 365 nm UV excitation.

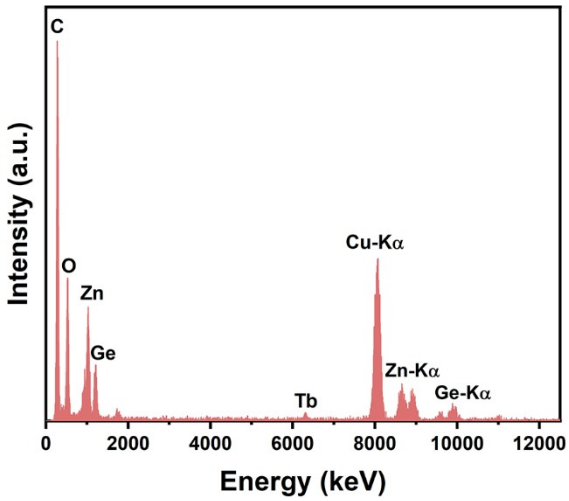

Figure S8. EDS spectrum of nZGO.

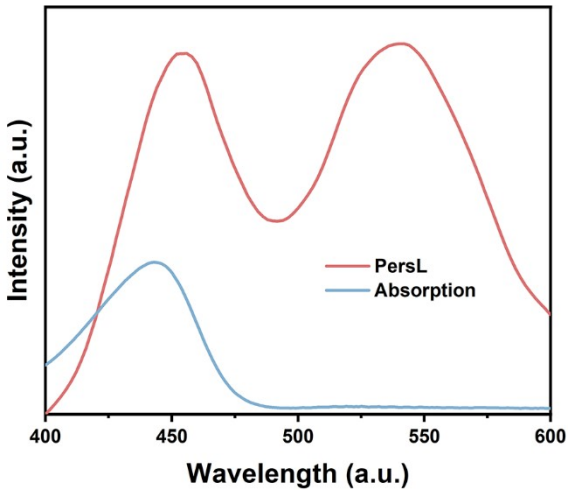

Figure S9. PersL spectrum of nZGO and absorption spectrum of ATTO425.

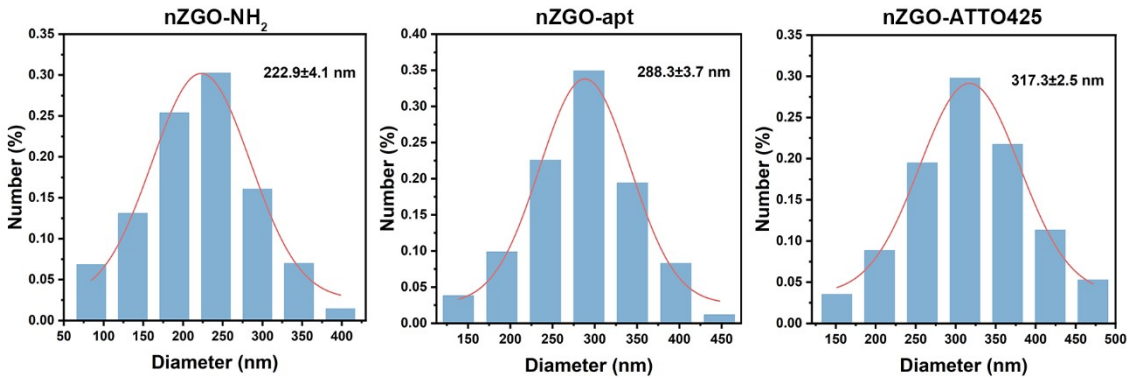

Figure S10. Hydrodynamic diameter of samples with different modification.

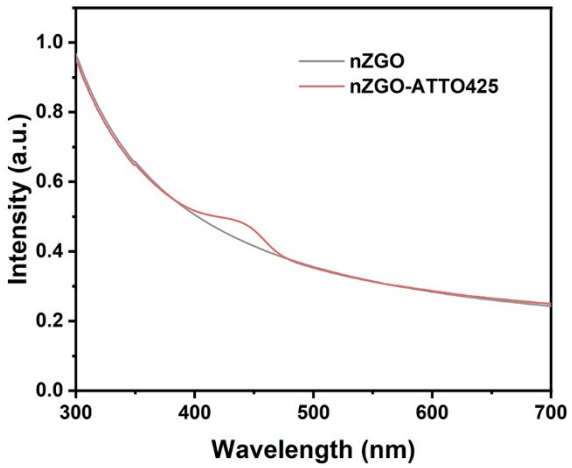

Figure S11. Absorption spectra of nZGO and nZGO-ATTO425.

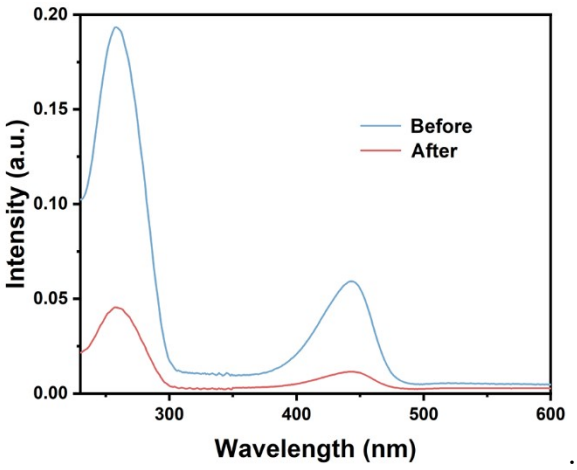

Figure S12. The absorbance spectra of the initial cDNA-ATTO425 solution and the supernatant

obtained after nZGO-ATTO425 preparation.

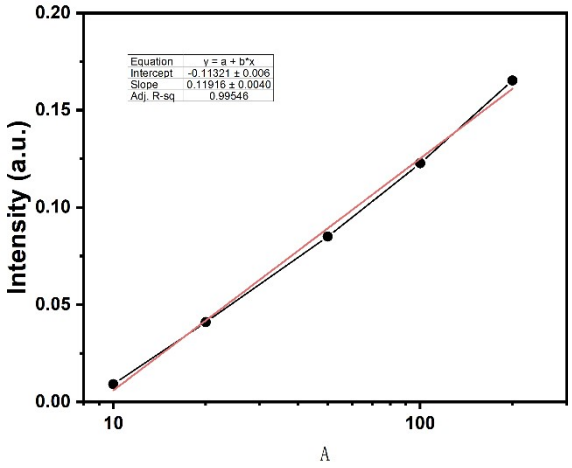

Figure S13. Standard curve for ATTO425 solution monitored at the wavelength of 443 nm.