Electronic Supplementary Information

EDTA Etching: A Simple Way for Regulating the Traps, Size and
Aqueous-Dispersibility of Cr$^{3+}$-Doped Zinc Gallate

He-Fang Wang, *ab Xi Chen, a Fan Feng, a Xia Ji, a and Ye Zhang a

aResearch Center for Analytical Sciences, College of Chemistry, Nankai University, Tianjin Key Laboratory of Biosensing and Molecular Recognition, State Key Laboratory of Medicinal Chemical Biology, Tianjin, 300071, China
bCollaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin, 300071, China

*wanghefang@nankai.edu.cn
Regents

Ga₂O₃ (99.999%), Zn(NO₃)₂·6H₂O (99.99%), Cr(NO₃)₃·9H₂O (99.95%), and ethylenediaminetetraacetic acid disodium salt dehydrate (EDTA-Na₂·2H₂O) (99%) were all purchased from Aladdin (Shanghai, China). Tert-butylamine (TBA) was from TCI Development Co., Ltd. (Shanghai, China). Oleic acid and NaOH were purchased from Guangfu technology development co., Ltd (Tianjin, China). Toluene and ethanol were from Concord Chemical Research Institute (Tianjin, China). Ga(NO₃)₃ solution of 0.4 mol·L⁻¹ was prepared by dissolving Ga₂O₃ in 80% concentrated nitric acid. Zn(NO₃)₂·6H₂O and Cr(NO₃)₃·9H₂O were directly dissolved in ultrapure water to make solutions of 0.2 and 0.02 mol·L⁻¹ respectively.

Apparatus

The Fourier transform infrared (FT-IR) spectra were recorded on an MAGNA-IR 560 spectrometer (Nicolet, America). The X-ray powder diffraction (XRD) patterns were recorded on a Rigaku D/max-2500 X-ray diffractometer (Rigaku, Japan). The afterglow images were recorded on an IVIS Lumina II Imaging System (Xenogen, America) equipped with a CCD camera. The morphology and microstructure were characterized by high-resolution transmission electron micrograph (HRTEM) on a Tecnai G2 F20 field emission transmission electron microscope (FEI, America) operating at a 200 kV accelerating voltage. The hydrodynamic diameters were measured on a Zetasizer Nano ZS (Malvern Instruments Ltd., United Kingdom) equipped with a noninvasive back scattering (NIBS) device and polystyrene cell (1 cm × 1 cm). The PL, afterglow spectra and afterglow decay curves of the aqueous dispersions were measured on a PTI QM/TM/NIR spectrometer (Birmingham, NJ). The elemental analysis was recorded on Varian 725-ES inductively coupled plasma atomic emission spectrometer (ICP-AES) (Varian, America). The concentration of Ga, Zn and Cr was respectively measured at the wavelength of 294.363, 213.857 and 267.716 nm. The thermo-luminescent glow curves were measured on an OptistatDN-V2 TL meter (Oxford Instruments, UK) and FLS920 spectrometer (Edinburgh, UK). X-ray photoelectron spectra (XPS) were recorded on Axis Ultra DLD (Kratos Analytical Ltd., UK) X-ray photoelectron spectrometer. Electron paramagnetic resonance (EPR) spectra were recorded on an EMX-6/1 spectrometer (Bruker, Germany).

Preparation of ZGO

The ZGO was prepared via a modified procedure of the reference. Typically, Ga(NO₃)₃,
Zn(NO$_3$)$_2$ and Cr(NO$_3$)$_3$ solution were added into a round-bottom flask according to the stoichiometric of 2:1:0.004, and stirred throughout at room temperature, followed by the addition of Tert-butylamine until pH 8. One hour later, the mixture was transferred into a Teflon-lined autoclave, 2 mL of oleic acid and 15 mL toluene were added into the mixture before sealing. After being heated for 24 h at 160 °C, the autoclave was cooled to room temperature. The solid were collected via centrifugation, washed with ultrapure water and ethanol, and dried at 80 °C. Finally the powder was annealed in air at 1000 °C for 1 h.

**The Etching of ZGO by EDTA**

Typically, the ZGO powder (170 mg) and various amounts of EDTA-Na$_2$·2H$_2$O (1, 3, 5, 7 times of ZGO weight) were added into 17 mL ultrapure water under vigorously stirring. The pH of mixture was adjusted to 13 by addition of 1 M NaOH. One hour later, the mixture was transferred into a 25 mL Teflon-lined stainless steel autoclave and heated at 220 °C for 18 h. For the treatments by EDTA at room temperature (RT), 850 mg of EDTA was used and pH was adjusted to 13, and the mixture was stirred at RT for 19 h. For the etching at other pHs, the amount of EDTA was 850 mg, and pH was adjusted to 4, 7 and 10 respectively. The controls were done in parallel using pure water, HNO$_3$-pH 4 and NaOH-pH 13 for the same treatments of 220 °C. After fully cooling, the resultant mixtures were centrifuged and the supernatants were collected for ICP-AES analysis. Three duplicates were done for every case of treatment. The solid of the three duplicates was merged and washed with ultrapure water for three times, then dispersed in 40 mL ultrapure water. After 10 minutes of natural settlement, the solid in suspensions (marked as ZGO-nEDTA-S) and sediments (marked as ZGO-nEDTA-B) were collected respectively and dried at 80 °C (n was the equivalent weight of EDTA over ZGO, n = 1, 3, 5, 7). The solid from water treatment at 220 °C and EDTA treatment at RT were marked as ZGO-water-S (or B) and ZGO-5EDTA-RT-S (or B), respectively. For comparison, the products of ZGO-S (in suspension) and ZGO-B (in sediment) from the traditional grinding were also prepared. All the dried powder was weighed and the yields were calculated.

**Evaluation of the Aqueous-Dispersibility**

The aqueous dispersions (1 g L$^{-1}$) of ZGO, ZGO-B, ZGO-S and ZGO-nEDTA (both B and S, n= 1, 3, 5, 7) were freshly made respectively. After ultrasonication for 5 min, 2 mL dispersion was transferred into the cuvette (10 mm × 10 mm) individually and then settled in ZF-8 UV (Jiapeng Technology, Shanghai, China) holder (without any disturbs since settled). The digital photos under
daylight or irradiation of 254 nm UV light were taken respectively at 5 min, 1 h, 8 h, 24 h, 48 h and 72 h. S and B series were evaluated separately and then the photos are merged. The even distribution of white suspensions (daylight) and the red luminescence (254 nm UV) suggested the fine aqueous dispersibility.

**Measurement of photoluminescence (PL) and the Afterglow Spectra**

All spectra were recorded by PTI spectrometer. The aqueous dispersions (1 g L\(^{-1}\)) of ZGO, ZGO-B, ZGO-S and ZGO-nEDTA (both B and S, n\(=\) 1, 3, 5, 7) were freshly made respectively. For PL, the dispersion was ultrasonicated for 2 min and then measured under the in-situ excitation of 254 nm (by 70 W Xe light), with both slit of 2 nm. For afterglow spectrum, the dispersion was ultrasonicated individually before excitation by 254 nm UV light (6 W) for 2 min, after stoppage the excitation for 15 s, the afterglow spectrum was recorded with EM slit of 10 nm. The time schedule for each measurement was the same.

**Measurement of the Afterglow Decays**

For the afterglow decays of solid ZGO, ZGO-B, ZGO-S and ZGO-nEDTA (both B and S, n\(=\) 1, 3, 5, 7), 3 mg powders in ELISA plate strips (one powder in one plate) were irradiated with a 254 nm UV lamp for 5 min. Then the samples were wrapped in tin foil paper and put in a closed drawer during storage. When taking afterglow images, we first turned off the ceiling light. With the dim light far away from the IVIS Lumina II Imaging System, we put the wrapped samples into that instrument, and opened the wrapped paper, and then took images. The samples were wrapped again as soon as the process of taking images was completed. The afterglow images were recorded by the CCD camera on different days (the 1, 3, 5, 9, 15, 21, 30, 42 and 51 day) without any illumination, and the corresponding afterglow intensity of each image was measured and plotted against the settled time (in days).

For the aqueous dispersions of ZGO, ZGO-B, ZGO-S and ZGO-nEDTA (both B and S, n\(=\) 1, 3, 5, 7), 2 g L\(^{-1}\) dispersions were freshly made and ultrasonicated for 5 min respectively, then 3 mL dispersions were transferred into the cuvette (10 mm \(\times\) 10 mm) and pre-irradiated by a 254 nm UV lamp (6 W) for 5 min, and then the afterglow intensity at 695 nm were recorded immediately by PTI fluorescence spectrophotometer without any further excitation. The dispersion was measured individually with the same time schedule.
**Tumor Cell Culture and Animal Model**

Human breast carcinoma cell lines (MCF-7 cell) were cultured in DMEM medium, supplemented with 10% fetal bovine serum (FBS) and streptomycin–penicillin (100 U mL$^{-1}$) under a humidified atmosphere containing 5% CO$_2$ at 37 °C. All animal experiments were carried out following the Tianjin Committee of Use and Care of Laboratory Animals. The Balb/c nude mice (5–6 weeks old, female) were purchased from HFK Bioscience Co., Ltd (Beijing, China). MCF-7 tumor-bearing mice were obtained by subcutaneously injecting MCF-7 tumor cells ($5 \times 10^6$) into the normal nude mice and used for optical imaging a week later.

**Afterglow Imaging in vivo**

All the mice were anesthetized with 100 μL pentobarbital sodium (1% in 10 mM PBS solution) by intraperitoneal injection. The ZGO and ZGO-5EDTA (1 g L$^{-1}$) were dispersed in 10 mM PBS solution and pre-irradiated for 5 min by a UV lamp (254 nm, 6 W). Immediately, 100 μL of the above two dispersions were intravenously injected into the mice via tail vein. The afterglow images were recorded directly (without any excitation) at different durations of 15 min, 30 min, 1 h, 3 h and 6 h. After 24 h, the mice were activated in vivo by a 650 nm LED for 1 min, and then the afterglow images were recorded by a CCD camera without external illumination. Finally, the mice were sacrificed and the major organs were collected. The afterglow images of isolated organs were obtained by pre-irradiated by a 254 nm UV lamp (6 W) for 1 min, and then the biodistributions of ZGO and ZGO-5EDTA nanoparticles were evaluated by the ex vivo afterglow images of the organs and the digital afterglow intensity in individual organ recorded by the CCD camera.

**Information Storage**

The ZGO or ZGO-5EDTA powders (600 mg) were suspended in 2 mL of ethylene glycol and ethyl alcohol (1:1), and then the suspensions were spread on a glass dish and gradually dried via heating; finally the flat layers of ZGO or ZGO-5EDTA were acquired. The flat layers were covered with photomasks of heart shape and N. K. letters, and exposed to 254 nm UV light for 2 min to record the specific patterns on the flat layers. After removing the UV light and the photomask, the luminous patterns were read out by a CCD camera at room temperature or 220 °C. For 220 °C readout, the flat layers were heated at 95 °C for 1 h to release the electron in mediate traps, and at 220 °C for 1 min to read out the specific patterns stored in the deep traps.
Table S1. The concentration (Conc., mean ± SD) and corresponding erosion percentage (P, mean ± SD) of the metals existed in the supernatants from the treatments of ZGO by 5EDTA (at different pH and Temperature), HNO₃-pH4 and NaOH-pH13

| Entry          | Ga Conc. (mg L⁻¹)ᵃ | Ga P (%)ᵇ | Zn Conc. (mg L⁻¹)ᵃ | Zn P (%)ᵇ | Cr Conc. (mg L⁻¹)ᵃ | Cr P (%)ᵇ |
|----------------|-------------------|-----------|-------------------|-----------|-------------------|-----------|
| 5EDTA-pH4      | 3473 ± 492        | 67.0 ± 9.5| 1129 ± 175        | 46.4 ± 7.2| 3.99 ± 0.49       | 51.7 ± 6.3|
| 5EDTA-pH7      | 2807 ± 124        | 54.2 ± 2.4| 848 ± 42          | 34.9 ± 1.7| 2.82 ± 0.09       | 36.5 ± 1.2|
| 5EDTA-pH10     | 995 ± 56          | 19.2 ± 1.1| 165 ± 11          | 6.8 ± 0.4 | 0.49 ± 0.02       | 6.3 ± 0.2 |
| 5EDTA-pH13     | 2233 ± 143        | 43.1 ± 2.8| 714 ± 42          | 29.4 ± 1.7| 0.030 ± 0.016     | 0.30 ± 0.16|
| NaOH-pH13      | 1702 ± 102        | 32.8 ± 2.0| 172.4 ± 12        | 7.09 ± 0.50| 2.81 ± 0.10      | 36.3 ± 1.3 |
| HNO₃-pH4       | 1.89 ± 0.07       | < 0.05    | 2.32 ± 0.01       | 0.11 ± 0.00| < 0.004          | < 0.05    |
| 5EDTA-pH13-RT  | 75.0 ± 1.9        | 1.45 ± 0.04| 8.24 ± 0.10      | 0.34 ± 0.00| 0.032 ± 0.001    | 0.32 ± 0.02|

ᵃ The concentration of each metal is detected by ICP-AES.
ᵇ The erosion percentage is calculated by \[ \frac{c \times V}{m \times M_{m} \times n} \times 100\% \], where c is the concentration of individual metal in the supernatant; V is the volume of the supernatant; m is the mass of raw ZGO; Mm is the molar mass of the individual metal; n is the number of the individual metal in nominal formula of ZGO; and M is the molar mass of ZGO calculated from the nominal formula.

Table S2. The weight and corresponding yields of ZGO-nEDTA harvested from EDTA hydrothermal-treatment of 510 mg raw ZGO

| n*  | ZGO-nEDTA-S Weight (mg) | Yield (%) | ZGO-nEDTA-B Weight (mg) | Yield (%) |
|-----|-------------------------|-----------|-------------------------|-----------|
| 0   | 24                      | 4.7       | 459                     | 90.0      |
| 1   | 27                      | 5.3       | 313                     | 61.4      |
| 3   | 99                      | 19.4      | 225                     | 44.1      |
| 5   | 204                     | 40.0      | 119                     | 23.3      |
| 7   | 179                     | 35.1      | 175                     | 34.3      |

ⁿ The is the mass multiples of EDTA over ZGO (n = 0 means ZGO-S and ZGO-B from traditional grinding, where no EDTA is used).

Table S3. The hydrodynamic diameter (HD) of ZGO, ZGO-S, ZGO-B and ZGO-nEDTA (both S and B, n = 1, 3, 5, 7) from DLS

|        | HD (nm) | PDI  |        | HD (nm) | PDI  |
|--------|---------|------|--------|---------|------|
| ZGO    | 34.40   | 0.233| ZGO    | 34.40   | 0.228|
| ZGO-S  | 8.82    | 0.219| ZGO-B  | 30.04   | 0.239|
| ZGO-1EDTA-S | 8.07   | 0.199| ZGO-1EDTA-B | 25.52 | 0.271|
| ZGO-3EDTA-S | 7.44   | 0.192| ZGO-3EDTA-B | 21.93 | 0.292|
| ZGO-5EDTA-S | 6.18   | 0.191| ZGO-5EDTA-B | 26.05 | 0.284|
| ZGO-7EDTA-S | 8.46    | 0.286| ZGO-7EDTA-B |       |      |
Fig. S1. (a)(b) Excitation (at the emission of 695 nm) spectra, (c)(d) emission (at the excitation of 254 nm) spectra and (e)(f) the afterglow spectra of the aqueous dispersions (1 g L$^{-1}$) of ZGO, ZGO-B, ZGO-S and ZGO-nEDTA (both S and B, n= 1, 3, 5, 7). The spectra were recorded by PTI spectrometer, both slit was set at 2 nm for PL (a-d), and EM slit was 10 nm for afterglow spectra (e and f). The detailed operation was stated in above “Measurement of photoluminescence (PL) and the Afterglow Spectra” part.
Fig. S2. The photos of the aqueous dispersions (1 g L$^{-1}$, 2 mL) of (1) ZGO, (2) ZGO-B, (3) ZGO-1EDTA-B, (4) ZGO-3EDTA-B, (5) ZGO-5EDTA-B, (6) ZGO-7EDTA-B, (7) ZGO-S, (8) ZGO-1EDTA-S, (9) ZGO-3EDTA-S, (10) ZGO-5EDTA-S, (11) ZGO-7EDTA-S taken under daylight and the excitation of 254 nm with a UV lamp (6 W). The even distribution of white suspensions (daylight) and the red luminescence (254 nm UV) suggested the fine aqueous dispersibility. At 5 min, ZGO showed obvious sedimentation, ZGO-B showed part sedimentation, and ZGO-S showed slight sedimentation, but all ZGO-nEDTA (n= 1, 3, 5, 7) displayed fine suspensions at least at 8 h. The ZGO-nEDTA-S displayed better suspension than the corresponding ZGO-nEDTA-B.
Fig. S3. High-resolution TEM images of ZGO (upper), ZGO-5EDTA-S (middle) and ZGO-5EDTA-B (lower), all bars are 5 nm.
Fig. S4. FT-IR spectra of the ZGO and ZGO-nEDTA (both S and B, n= 1, 3, 5, 7). 3 mg ZGO or ZGO-nEDTA powder was grinded respectively with 100 mg dry KBr and then made as KBr pellet for FT-IR measurements.
**Fig. S5.** TL peak-differentiating and imitating of solid (a) ZGO, (b) ZGO-B, (c) ZGO-1EDTA-B, (d) ZGO-3EDTA-B, (e) ZGO-5EDTA-B, (f) ZGO-7EDTA-B, (g) ZGO-3EDTA-S, (h) ZGO-5EDTA-S and (i) ZGO-7EDTA-S. 60 mg of solid was irradiated at 0 °C by a 254 nm UV lamp for 5 min. Two minutes later, the solid sample was heated to 237 °C at 10 °C min⁻¹ and the afterglow at 695 nm was synchronously recorded by FLS920 fluorescence spectrophotometer.
Fig. S6. (a) TL of solid ZGO-water-B and ZGO-5EDTA-RT-B; TL peak-differentiating and imitating of solid (b) ZGO-5EDTA-RT-B and (c) ZGO-water-B; and (d) the afterglow decays of solid ZGO-water-B and ZGO-5EDTA-RT-B. For (a), 60 mg of solid was irradiated at 0 °C by a 254 nm UV lamp for 5 min. Two minutes later, the solid sample was heated to 237 °C at 10 °C min\(^{-1}\) and the afterglow at 695 nm was synchronously recorded by FLS920 fluorescence spectrophotometer. For (d), 3 mg of solid was irradiated by a 254 nm UV lamp (6 W) for 5 min, and the afterglow images and intensity were recorded by the CCD camera at different durations after stoppage of irradiation.
Fig. S7. Afterglow images of the ZGO, ZGO-B, ZGO-S and ZGO-nEDTA (both B and S, n= 1, 3, 5, 7) recorded by CCD camera of IVIS Lumina II Imaging System. 3 mg powders in ELISA plate strips (one powder in one plate) were irradiated with a 254 nm UV lamp for 5 min, and then were settled in dark. The afterglow images were recorded on different days (the 1, 3, 5, 9, 15, 21, 30, 42 and 51 day) without any illumination. The detailed operation was stated in above “Measurement of the Afterglow Decays” part.
Fig. S8 The decay time-dependent TL curves of ZGO-7EDTA-B. 60 mg of solid was irradiated at 0 °C by a 254 nm UV lamp for 5 min. 2, 30 or 60 min later, the solid sample was heated to 237 °C at 10 °C min⁻¹ and the afterglow at 695 nm was synchronously recorded by FLS920 fluorescence spectrophotometer. With the increase of decay time, the TL intensities are decreased and the peaks are shifted to the higher temperature, indicating that the electrons in the mediate traps are emptied faster than those in deep traps.

Fig. S9. The XRD patterns of the ZGO, ZGO-5EDTA-S and ZGO-5EDTA-B.
Fig. S10. (a) Afterglow images of the normal mice after intravenous injection of ZGO and ZGO-5EDTA (0.1 mg, 5 min irradiation with a 254 nm UV lamp before injection); (b) Representative afterglow images of isolated organs from the normal mice in panel a: (1) liver, (2) spleen, (3) stomach, (4) intestine, (5) kidney, (6) heart, (7) lung; and (c) Mean afterglow intensity of the organs in panel b.

References
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