Supporting Information

Tunable Plasmonic Gallium Nano Liquid Metal from Facile and Controllable Synthesis

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Experimental Procedures

1. Materials

All materials used in this work are commercially available. Zinc (Zn, 99.9 %, ZH-Zn50 nm) power was purchased from Hefei ZhongHang Nanometer Technology Development Co., Ltd. Gallium chloride (GaCl₃, 99.999 %) and 1,4-dioxane (Diox, 99.7 %, Extra Dry, with molecular sieves, stabilized with BHT, Water \leq 50 ppm (by K.F.), EnergySeal) were purchased from Saan Chemical Technology (Shanghai) Co., Ltd. Gallium (Ga, melting point at 29.8 °C) was purchased from Shenyang Jiabei commercial trading company. Zn foil (99.99 %, thickness: 30 µm) was purchased from Fengtengjinshu. Magnesium (Mg, 99.9 %), acetonitrile (AN, AR), N,N-dimethylformamide (DMF, AR) and ethanol (EtOH, AR) were all purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd.

2. Methods

2.1 Preparation of Ga nano LM (117.8 \pm 9.2 nm) by GRR with the feed ratio of GaCl₃/Zn@2:1: Ga nanodroplets were prepared in a schlenk flask by firstly dispersing 0.093 g Zn powder in 3 mL AN via sonication for 5 minutes. Then, 0.5 g GaCl₃ was dissolved in another 3 mL AN, which were added to another flask upon sonication for 5 minutes and the

solution was slowly transferred to the schlenk flask. The mixed solution was sonicated for additional 5 min with the 30 minutes protection of nitrogen gas. The mixture was magnetically stirred and reacted in an ice-water bath for 6 hours. After the reaction, the solution was centrifuged and rinsed with EtOH (30 mL) for three times to remove the metal salts (ZnCl₂ and GaCl₃). Due to the excessive amount of GaCl₃, the Ga nanodroplets (0.066 g) was calculated according to the fully reacted Zn powder. Finally, nano Ga was dispersed in 6 mL EtOH and the EtOH solution of nano Ga (0.011 g/mL) was obtained.

2.2 Preparation of bulk Ga LM by GRR with the feed ratio of GaCl₃/Zn@2:1: Bulk Ga was prepared in a schlenk flask. Zn powder (0.093 g) dispersed in 3 mL AN and GaCl₃ (0.5 g) dispersed in 3 mL AN were mixed and sonicated for 5 minutes. After the 30 minutes protection of nitrogen gas, the mixture was magnetically stirred and reacted 6 hours under 35 °C. After the reaction, the solution was rinsed with EtOH (30 mL) for three times to remove the metal salts (ZnCl₂ and GaCl₃) and stored 6 mL EtOH.

2.3 Preparation of sonicated Ga NPs (259.5 \pm 12.7 nm) by sonication: In order to ensure the validity of the control experiment, the quality of commercial Ga was the same as that of the Ga nano LM produced (0.066 g). The solution containing AN (6 mL) and commercial Ga (0.066 g) was sonicated for 1 hour (power at 60%). After the ultrasonication, the solution was centrifuged and rinsed with EtOH (30 mL) for three times. Finally, the sonicated Ga NPs was dispersed in 6 mL EtOH and the EtOH solution of sonicated Ga NPs (0.011 g/mL) was obtained.

2.4 Preparation of GaZn binary blends by GRR with the feed ratio of GaCl₃/Zn@2:2: Zn powder (0.186 g) dispersed in 3 mL AN and GaCl₃ (0.5 g) dispersed in 3 mL AN were mixed and sonicated for 5 minutes. After the 30 minutes protection of nitrogen gas, the mixture was magnetically stirred and reacted 6 hours in an ice-water bath (NPs blend) and 35 °C (bulk blend). After the reaction, the solution was rinsed with EtOH (30 mL) for three times to remove the metal salts (ZnCl₂ and GaCl₃) and stored 6 mL EtOH.

2.5 Preparation of GaZn binary blends by GRR with the feed ratio of GaCl₃/Zn@2:3:

Zn powder (0.278 g) dispersed in 3 mL AN and GaCl₃ (0.5 g) dispersed in 3 mL AN were mixed and sonicated for 5 minutes. After the 30 minutes protection of nitrogen gas, the mixture was magnetically stirred and reacted 6 hours in an ice-water bath (NPs blend) and 35 °C (bulk blend). After the reaction, the solution was rinsed with EtOH (30 mL) for three times to remove the metal salts (ZnCl₂ and GaCl₃) and stored 6 mL EtOH.

2.6 Preparation of GaMg binary blends by GRR with the feed ratio of GaCl₃/Mg@2:1:

GaCl₃ (0.5 g) was dispersed in 6 mL degassed AN. Mg (0.0345 g) was then added in the schlenk flask under the protection of nitrogen. After fully degassing, the mixture was magnetically stirred and reacted for 6 hours under 35 °C. After the reaction, the solution was centrifuged and rinsed with EtOH (30 mL) for three times to remove the metal salts (MgCl₂ and GaCl₃). The product was dried at 70 °C before DSC measurement.

2.7 Preparation of Ga nano LM (73.2 \pm 7.9 nm) by GRR with the feed ratio of GaCl₃/Zn@2:1: Zn powder (0.093 g) dispersed in 1.5 mL AN and GaCl₃ (0.5 g) dispersed in 1.5 mL AN were mixed and sonicated for 5 minutes. After the 30 minutes protection of nitrogen gas, the mixture was magnetically stirred and reacted 6 hours under 35 °C. After the reaction, the solution was centrifuged and rinsed with EtOH (30 mL) for three times to remove the metal salts (ZnCl₂ and GaCl₃). Due to the excessive amount of GaCl₃, the Ga nanodroplets (0.066 g) was calculated according to the fully reacted Zn powder. Finally, nano Ga was dispersed in 6 mL EtOH and the EtOH solution of nano Ga (0.011 g/mL) was obtained.

2.8 Preparation of Ga nano LM (152.8 \pm 12.7 nm) by GRR with the feed ratio of GaCl₃/Zn@2:1: Zn powder (0.093 g) dispersed in 6 mL AN and GaCl₃ (0.5 g) dispersed in 6 mL AN were mixed and sonicated for 5 minutes. After the 30 minutes protection of nitrogen gas, the mixture was magnetically stirred and reacted 6 hours under 35 °C. After the reaction, the solution was centrifuged and rinsed with EtOH (30 mL) for three times to remove the metal salts (ZnCl₂ and GaCl₃). Due to the excessive amount of GaCl₃, the Ga nanodroplets (0.066 g) was calculated according to the fully reacted Zn powder. Finally, nano Ga was dispersed in 6 mL EtOH and the EtOH solution of nano Ga (0.011 g/mL) was obtained.

2.9 Preparation of SERS substrates: 20 μ L of the as-prepared samples with concentration of 0.011 mg/mL were mixed with 180 μ L of R6G EtOH solution (10⁻³ M, 10⁻⁴ M, 10⁻⁵ M and 10⁻⁶ M), and then ultrasonicated for 30 min in ice-water bath to prevent overheated. Subsequently, the mixtures were drop-casted on the silicon substrate and dried naturally.

3. Instruments and Characterization

3.1 Dynamic light scattering (DLS): The Omni, instrument (Brookhaven, USA) was used to determine the average size of commercial Zn NPs, the nano Ga from GRR and the sonicated Ga NPs from ultrasonication. The EtOH solution of nano Ga (50 μ L, 0.011 g/mL) and 3 mL EtOH were mixed, sonicated (5 min) and transferred into the glass sample cell. The angle and cell type were selected as 90 degree and BI-SCGO, respectively. Wavelength was 640 nm and solvent was set as ethanol. The temperature was set at 25 °C, and the measurement was carried out when the sample cell temperature was stable at 25 °C.

3.2 Differential scanning calorimetry (DSC): The TA DSC25 was used to determine thermal transitions. The samples (5~10 mg) were loaded into DSC pans, then quenched to -20 °C and subsequently heated to 375 °C at a rate of 10 °C/min. The melting points and enthalpy were determined under nitrogen atmosphere.

3.3 Scanning electron microscope (SEM): FEI Nova Nano SEM 450 was used to record SEM images and energy-dispersive X-ray (EDX) spectroscopy. The EtOH solution (0.5 mL, 0.011 g/mL) of nano Ga was dispersed in 4.5 mL EtOH. The diluted solution (50 μ L, 1.1 mg/mL) was drop-casted on the silicon wafer (1.5 × 1.5 cm) and dried naturally. After sprayed gold three times for 50 seconds, the sample was measured under room temperature.

3.4 Ultrasonic Crashing: Commercial Ga (0.066 g) was sonicated and dispersed in AN (6 mL) for 1 hour by using Biosafer 150-96 ultrasonic crasher (power at 60%).

3.5 Transmission electron microscopy (TEM): FEI Tecnai G2 T20 was used to record TEM images and selected area electron diffraction (SAED). The EtOH solution (0.5 mL, 0.011 g/mL) of nano Ga (117.8 \pm 9.2 nm) was dispersed in 4.5 mL EtOH. Similarly, sonicated Ga NPs (259.5 \pm 12.7 nm) was also dispersed in 4.5 mL EtOH. The diluted solution (50 μ L, 1.1 mg/mL) was drop-casted on the silicon wafer (1.5 \times 1.5 cm) and dried naturally. After sprayed three times for 50 seconds, the sample was measured under room temperature.

3.6 X-ray diffraction (XRD): XRD patterns were measured with Ultima IV. The samples were centrifuged and vacuumed (50 °C, 8 h) to remove the EtOH solvent. The scanning speed was 10° min⁻¹ from 5° to 80°. The characterization was proceeded under 35 °C and below 0 °C (treated with liquid nitrogen).

3.7 Optical microscope: Optical microscope (Teelen XTL-16B) was used to characterize the microscopy images of Zn foil before and after the 6 hours reaction in Ga^{3+} solution in the air. The reacted Zn foil was rinsed with EtOH three times to completely remove excess salts (ZnCl₂ and GaCl₃). After the EtOH was dried, the surface morphology of the reacted Zn foil was observed.

3.8 X-ray photoelectron spectroscopy (XPS): XPS peaks were recorded by Thermo ESCALAB 250XI (American Thermo Fisher Scientific). Before the measurement, the reacted Zn foil was rinsed by EtOH three times to completely remove excess salts (GaCl₃ and ZnCl₂). The elements (Ga, Zn, O, C) on the surface of reacted Zn foil were recorded by XPS.

3.9 Electrical conductivity and solubility: Electrical conductivity meter (DDS-307A) was utilized to determine the electrical conductivity and solubility values of GaCl₃ (0.02 g) in different solvents (AN, DMF, EtOH and Diox) (2.4 mL). Before the measurement, the above solvents were all sonicated 10 minutes.

3.10 pH measurements: GaCl₃ (0.5 g) was added to water (6 mL) and the solution was fully dissolved by ultrasonication for 10 minutes. pH paper was used to measure the acid-base property. And pH value was measured by digital table acidity meter (FE-standard, METTLER TOLEDO).

3.11 Raman measurements: The Raman measurements were performed at room temperature on a Jobin Yvon Lab RAM HR 800 micro-Raman spectrometer with a 633 nm excitation laser. The laser power density was about 7.65×10^6 mW cm⁻². The standard Raman dye Rhodamine 6G (R6G) was selected as probe molecule owing to its well-studied Raman properties. The EtOH solution of nano Ga (20 µL, 0.011 g/mL) and the EtOH solution of R6G (180 µL, 10⁻³ $M \sim 10^{-6}$ M) were thoroughly mixed by ultrasonication and incubated for 30 minutes. Then, the mixture (5 µL) was drop-casted on the silicon wafer (1 × 1 cm) and dried naturally. For other control samples (sonicated Ga NPs (20 µL, 0.011 g/mL) and (Zn powder (20 µL, 0.011 g/mL)), the sample preparation method is the same.

3.12 UV-vis absorption spectra: UV-vis spectra of nano Ga (GRR) synthesized under different GaCl₃ concentration (166.6 mg/mL, 83.3 mg/mL and 41.7 mg/mL) were obtained from Cary 100 (Agilent, Singapore). The EtOH solution of nano Ga (200 µL, 0.011 g/mL)

was dispersed in 4.8 mL EtOH. The diluted solution was sonicated (10 minutes) and transferred into sample cell.

3.13 Ultraviolet photoelectron spectrum (UPS): The Fermi level of nano Ga was estimated by measuring UPS with Thermo ESCALAB 250Xi. The EtOH solution of nano Ga (80 μ L, 0.011 g/mL) was drop-casted on silicon substrate and dried naturally. The work function of nano Ga was measured after the sample was cleaned with an ion source to remove the contamination of surface adsorption.

3.14 Finite-difference time-domain (FDTD) Simulations: The model was constructed according to the TEM image shown in **Figure 2g**. The Plasmonic modes were excited by a plane wave source with incident wave vector perpendicular to the x-y plane. The incident wavelength was set as 633 nm, and its electric field intensity E_0 was set as 1 V/m. The optical constants of nano Ga were set as $\epsilon^{-1}=-10$ and $\epsilon^{-1}=7$. The enhanced electric fields were observed at the junctions between adjacent nano Ga. The maximum electric field intensity E_{loc} was approximately 22.5 V/m. The corresponding EF could be simplified as the fourth power of maximum electric intensity: $EF = (E_{loc}/E_0)^4$. The calculated EF in FDTD simulation reached at 2.56 × 10⁵, in agreement with the experiment results. The simulated result indicated the dominant contribution of electromagnetic mechanism to the overall Raman intensity.

Results and Discussion

This Supplemental Information contains the following sections.

-Supplemental Discussion I: Preparation of bulk Ga (GRR) and nano Ga (GRR).

-Supplemental Discussion II: Preparation of products (GRR) under different GaCl₃/Zn feed atomic ratios.

-Supplemental Discussion III: Effects of oxygen and solvents for the GRR.

-Supplemental Discussion IV: SERS performance of commercial Zn NPs, sonicated Ga NPs and nano Ga (GRR).

Supplemental Discussion I: Preparation of bulk Ga (GRR) and nano Ga (GRR).

Calculation of ΔG under 0 °C and 35 °C:

The GRR is realized by the redox reaction between solid metal Zn NPs and GaCl₃ solution, and proceeds as following:

$$3 \operatorname{Zn}(s) + 2 \operatorname{Ga}^{3+}(\alpha_{\operatorname{Ga}}^{3+}) \to 3 \operatorname{Zn}^{2+}(\alpha_{\operatorname{Zn}}^{2+}) + 2 \operatorname{Ga}(s)$$
 (Equation S1)

The detailed calculation of the Gibbs free energy (ΔG) is as following:

 $\Delta G = -nFE$

T=273.15 K

$$E = \psi Ga^{3+} | Ga - \psi Zn^{2+} | Zn$$

$$= (\psi^{\theta} \operatorname{Ga}^{3+} | \operatorname{Ga} - \frac{\operatorname{RT}}{\operatorname{nF}} \ln \frac{1}{(\alpha \operatorname{Ga}^{3+})^2} - (\psi^{\theta} \operatorname{Zn}^{2+} | \operatorname{Zn} - \frac{\operatorname{RT}}{\operatorname{nF}} \ln \frac{1}{(\alpha \operatorname{Zn}^{2+})^3})$$

$$= (\psi^{\theta} \operatorname{Ga}^{3+} | \operatorname{Ga} - \psi^{\theta} \operatorname{Zn}^{2+} | \operatorname{Zn}) - \frac{\operatorname{RT}_{nF} \ln (\alpha \operatorname{Zn}^{2+})^{3}}{(\alpha \operatorname{Ga}^{3+})^{2}}$$

 $= (0.53 - 0.7618) - \frac{8.314 \times 273.15}{6 \times 96485} \ln \frac{(0.0002371)3}{(0.00047237)2}$ $= 0.2318 - 0.0039228362 \times (-9.73)$ = 0.26997 V $\therefore \Delta G = -nFE$ $= -6 \times 96485 \times 0.27$

= -156306

 $= -1.56 \times 10^5 \text{ J} < 0$

T=308.15 K

$$E = (-0.53 - 0.7618) - \frac{8.314 \times 308.15}{6 \times 96485} \ln \frac{[0.0002371]3}{[0.00047237]2)}$$
$$= 0.2318 - [0.00442549 \times (-9.73)]$$
$$= 0.27486 \text{ V}$$

$$\therefore \Delta G = -nFE = -6 \times 96485 \times 0.27486 = -159119 = -1.6 \times 10^5 J < 0$$

The ΔG of the reaction are less than zero (-1.56 × 10⁵ and -1.6 × 10⁵ J/mol), indicating the spontaneously GRR under 0 °C and 35 °C.



Figure S1. DLS of commercial Zn NPs. It could be seen that the average size of commercial Zn NPs was ca. 277.6 ± 88.1 nm, evaluated by dynamic light scattering (DLS).



Figure S2. DSC curves of commercial Ga, bulk Ga (GRR) and nano Ga (GRR). The melting points of bulk Ga (GRR) and nano Ga (GRR) were respectively 28.4 °C and 27.5 °C, consistent with the melting points of commercial Ga (29.1 °C), which indicated that no matter what temperatures of the GRR, the products of the GRR were Ga metals.



Figure S3. Schematic illustration for the GRR under different time at 35 °C. Zn powder (0.093 g) dispersed in 3 mL AN and GaCl₃ (0.5 g) dispersed in 3 mL AN were mixed and sonicated for 5 minutes. After the 30 minutes protection of nitrogen gas, the mixture was magnetically stirred and reacted 6 hours under 35 °C. During the 6 hours, the opaque suspension gradually became transparent and liquid metal (bulk Ga) was formed because that Ga³⁺ was gradually replaced by Zn atoms to form liquid Ga nanodroplets, which can easily aggregate into large droplets since the reaction temperature was higher than the melting point of Ga (29.1 °C).



Figure S4. (a1-b1) SEM and (a2-b2) EDX images for GRR products after different reaction time (0 h and 1 h) (red: Zn, green: Ga, yellow: O, cyan: Cl).



Figure S5. EDS spectrum of pure Zn NPs from Figure 2a2.



Figure S6. DLS of smaller Zn NPs. It could be seen that the average size of smaller Zn NPs was ca. 99.6 ± 17.8 nm, evaluated by dynamic light scattering (DLS).



Figure S7. DLS size distribution of smaller nano Ga from GRR with smaller Zn NPs ($D = 88.6 \pm 9.7$ nm).



Figure S8. XRD patterns of nano Ga (GRR), commercial Ga and sonicated Ga NPs (ultrasonication 1hour and 2 hours) (all samples were characterized below 0 °C. The green and red symbols represented the diffraction peaks of Ga and Ga_2O_3 , respectively.

Supplemental Discussion II: Preparation of products (GRR) under different GaCl₃/Zn feed atomic ratios.



Figure S9. Ga-Zn binary phase diagram, L: liquid phase; S: solid phase. The binary phase diagram of Ga-Zn is divided into five regions, including one liquid region (L(Ga + Zn)), two solid phase regions (S(Zn) + S(Ga) and S(Zn)), and two solid-liquid biphasic regions (L + S(Ga) and L + S(Zn)). The inset shows schematic diagrams of binary blends with different Ga-Zn atomic ratios (Ga_{0.49}Zn_{0.51} and Ga_{0.33}Zn_{0.67}). The dotted lines indicate that the liquidus temperature of the blends at Zn content of 51% and 67% are 249 °C and 299 °C, respectively, which are consistent with the 254.7 °C and 309.1 °C from DSC measurement.

Table S1 Detailed information of differential scanning calorimetry (DSC) curves (**Figure S2 and Figure 2j**) for commercial Ga and GRR products synthesis at different feed atomic ratios of GaCl₃/Zn under 35 °C, including melting point and enthalpy.

Samples	Melting point (Tm _{Ga} / °C)	Enthalpy (ΔH _{Ga} / J·g⁻¹)	Melting point (Tm _{Zn} / °C)	Enthalpy (ΔH _{zn} / J·g⁻¹)
Commercial Ga	29.1	81.4	/	/
Ga (GaCl₃/Zn@2:1)	28.4	83.4	1	/
Ga _{0.49} Zn _{0.51} (GaCl ₃ /Zn@2:2)	27.2	41.5	254.7	56.3
Ga _{0.33} Zn _{0.67} (GaCl ₃ /Zn@2:3)	26.3	32.0	309.1	85.6

The melting enthalpy of the two peaks is utilized to calculate the molar fraction of the products. For example, the melting enthalpy of the two peaks at 27.2 °C and 254.7 °C in the product of $GaCl_3/Zn@2:2$ is 41.5 and 56.3 J/g, corresponding to the melting of Ga and the dissolution of Zn in Ga, respectively. According to the standard melting enthalpy of Ga (80.3 J/g) and Zn (112.0 J/g), the molar fraction of Ga in the products (Zn-Ga blends) can be calculated as 49%. Therefore, the blend is defined as $Ga_{0.49}Zn_{0.51}$.



Figure S10. DSC graphs of the products from GRR under 0 °C at the feed ratios of GaCl₃/Zn@2:2 and 2:3. The product of GaCl₃/Zn@2:2 had two peaks (26.8 °C and 251.4 °C, respectively), consistent with of the solidus and liquidus at the atomic ratio of Ga to Zn $(Ga_{0.49}Zn_{0.51})$ are 24.7 °C and 249 °C. And the product of GaCl₃/Zn@2:3 had two peaks (25.7

°C and 306.2 °C, respectively), basically consistent with the solidus and liquidus (24.7 °C and 298 °C) at the atomic ratio of $Ga_{0.34}Zn_{0.66}$.

Table S2 Detailed information of differential scanning calorimetry (DSC) curves (**Figures S2** and **S10**) for GRR products synthesis at different feed atomic ratios of GaCl₃/Zn under 0 °C, including melting point and enthalpy.

Samples	Melting point (Tm _{Ga} / °C)	Enthalpy (ΔH _{Ga} / J·g⁻¹)	Melting point (Tm _{Zn} / °C)	Enthalpy (ΔH _{zn} / J·g⁻¹)
Ga (GaCl₃/Zn@2:1)	27.5	83.4	/	/
Ga _{0.49} Zn _{0.51} (GaCl ₃ /Zn@2:2)	26.8	41.0	251.4	55.2
Ga _{0.33} Zn _{0.67} (GaCl ₃ /Zn@2:3)	25.7	32.0	306.2	81.6

The melting enthalpy of the two peaks is utilized to calculate the molar fraction of the products. For example, the melting enthalpy of the two peaks at 26.8 °C and 251.4 °C in the product of $GaCl_3/Zn@2:2$ is 41.0 and 55.2 J/g, corresponding to the melting of Ga and the dissolution of Zn in Ga, respectively. According to the standard melting enthalpy of Ga (80.3 J/g) and Zn (112.0 J/g), the molar fraction of Ga in the products (Zn-Ga blend) can be calculated as 49%. Therefore, the blend is defined as $Ga_{0.49}Zn_{0.51}$.



Figure S11. XRD patterns of commercial Ga under different temperatures (35 °C and below 0 °C). Commercial Ga exhibited diffraction peaks at low temperature (below 0 °C) and the

peaks disappear since Ga melted into liquid under 35 °C (higher than the melting point of Ga, 29.1 °C). The phenomenon could also be observed in the product of $GaCl_3/Zn@2:1$, indicating the successful synthesis of pure Ga at the feed atomic ratio $GaCl_3/Zn@2:1$.



Figure S12. XRD patterns of $Ga_{0.49}Zn_{0.51}$ under different temperatures (35 °C and below 0 °C). $Ga_{0.49}Zn_{0.51}$ simultaneously exhibited the diffraction peaks of both Ga and Zn at low temperature (below 0 °C) and the peaks disappeared since Ga melted into liquid under 35 °C (higher than the melting point of Ga, 29.1 °C). The green and red symbols represented the diffraction peaks of Ga and Zn, respectively.



Figure S13. XRD patterns of $Ga_{0.33}Zn_{0.67}$ under different temperatures (35 °C and below 0 °C). $Ga_{0.33}Zn_{0.67}$ simultaneously exhibited the diffraction peaks of both Ga and Zn at low temperature (below 0 °C) and the peaks disappeared since Ga melted into liquid under 35 °C (higher than the melting point of Ga, 29.1 °C). The green and red symbols represented the diffraction peaks of Ga and Zn, respectively.

Supplemental Discussion III: Effects of oxygen and solvents for the GRR.



Figure S14. DSC curves of the sample synthesized in the presence of oxygen. Insets were the photos of solution before and after 6 hours reaction in the air. After 6 hours stirring of GaCl₃ and Zn in AN solution in the air, no obvious phenomenon was observed. After fully rinsed with EtOH, the solids in the suspension were collected by centrifugation for DSC measurement. No peak was observed in the DSC curve near 30 °C, indicating that Ga³⁺ was not reduced by Zn in the air. Thus, oxygen in the air showed critical effect towards the GRR between Ga³⁺ and Zn.



Figure S15. XPS wide survey spectra for the surface of the reacted Zn foil from **Figure 3b**. Before the XPS characterization, the reacted Zn foil were rinsed with EtOH for three times to completely remove excess salts (GaCl₃ and ZnCl₂). Peaks at 17.4 eV and 20.6 eV were ascribed to Ga⁰ 3*d* and Ga^{III} 3*d*, indicating the existence of Ga₂O₃. Meanwhile, peaks at binding energy of 1021.7 eV and 1044.8 eV belonged to Zn $2p_{3/2}$ and Zn $2p_{1/2}$ of the Zn²⁺ species indicating Zn was also oxidized.



Figure S16. Photos of the products obtained from the GRR reaction in different solvents (AN, DMF, EtOH, Diox). Specifically, under the protection of nitrogen, different solvents (AN, DMF, EtOH, Diox) were used for the GRR reaction and different phenomena were observed in different solvents (AN, DMF, EtOH, Diox). After the reaction, the solution in AN become completely transparent. The solution in DMF was slightly nontransparent and that in EtOH and Diox were still suspension, indicating different reactions occurred in different solvents.

After 6 hours reaction, solids in these solutions were collected for further DSC characterization.



Figure S17. Solubility and conductivity of the solution (0.02 g GaCl₃ in 2.4 mL H₂O or AN). The solubility of GaCl₃ in H₂O is as high as 7.80 g/L, higher than that in AN (1.06 g/L).



Figure S18. Photos of gray porous solids from the GRR in water. Once $GaCl_3$ was mixed with Zn, gray porous solids would be immediately formed with the generation of bubbles, strongly indicating the side reactions in water. Subsequently, under the protection of nitrogen, the system continued to react. After 6 hours, the gray solid sank into the bottom. Bubbles could be observed during the reaction (**Figure 3g**). The solid was rinsed with EtOH and collected for later DSC and XRD measurement.



Figure S19. XRD patterns of gray solids from the GRR in water. The diffraction peaks of Ga and Zn were observed, indicating that the product obtained in water was a mixture. The green and red symbols represented the diffraction peaks of Ga and Zn, respectively.

$$Ga^{3+} + 3 H_2O \rightarrow Ga(OH)_3 + 3 H^+$$
 (Equation S2)

Once GaCl₃ was mixed with Zn, gray porous solids would be immediately formed with the generation of bubbles, strongly indicating the side reactions in water. Subsequently, the pH of the solution was measured and showed acidity.



Figure S20. Photos of pH measurement of GaCl₃ aqueous solution (8.33 g/L) with pH at 1.68. When Ga³⁺ was mixed with H₂O, protons were generated immediately, making the solution acidic (**Equation S2**).



Figure S21. DSC curve of the product from the GRR between Mg and Ga³⁺.

Supplemental Discussion IV: SERS performance of commercial Zn NPs, sonicated Ga NPs and nano Ga (GRR).

Calculations of the enhancement factor (EF)

The EF is calculated according to the following formula:

$$EF = \left(\frac{I_{SERS}}{N_{SERS}}\right) / \left(\frac{I_{bulk}}{N_{bulk}}\right)$$
Equation S3

$$N_{SERS} = \frac{CVN_A A_{Raman}}{A_{Sub}}$$
 Equation S4

$$N_{bulk} = \frac{\rho h A_{Raman} N_A}{M}$$
 Equation S5

 I_{SERS} and I_{bulk} are the intensities of the selected Raman peak in the SERS and non-SERS spectra, and N_{SERS} and N_{bulk} are the average number of molecules in scattering area for SERS and non-SERS measurement. The data of bulk R6G is used as non-SERS-active reference substance. Specifically, the intensity is obtained by taking average from measurements of 10 spots, and the number of analyte molecules is estimated by **Equation S4** on the assumption that the analyte molecules were distributed uniformly on the substrates.

C is the molar concentration of R6G solution and *V* is the volume of the droplet (20µL). N_A is Avogadro constant. A_{Raman} is the laser spot area. A_{Sub} is the effective area of the substrate, which is approximately 1 cm^2 . The confocal depth *h* of the laser beam is 21 µm. The molecular weight *M* of R6G is 479 g mol⁻¹ and density ρ of bulk R6G is 1.15 g cm⁻³. The normal Raman measurement of R6G molecules is acquired on silicon substrate. R6G EtOH solution with concentration of 10E-2 M is drop-casted on Si substrate and dried naturally.

The calculated average EF (R6G concentration of 10^{-6} M) is 1.3×10^{5} .



Figure S22. SERS spectra of R6G with different concentrations acquired on sonicated Ga NPs. It could be noticed that the sonicated Ga NPs obtained via ultrasonication only exhibited weak Raman-enhancing capability. Its EF was calculated to be ~ 1.40×10^4 (R6G concentration of 10^{-5} M) due to its relatively broader size distribution and larger average size (**Figure S23**). The EF was calculated according to the characteristic peak 612 cm⁻¹.



Figure S23. SEM images for sonicated Ga NPs obtained by ultrasonication. Sonicated Ga NPs exhibited broader size distribution and larger average size ($D = 259.5 \pm 12.7$ nm) than

nano Ga from GRR (D = 117.8 ± 9.2 nm) (Figures 2d and 2f) since ultrasonication was uncontrollable.



Figure S24. The SERS intensity of R6G from the SERS substrate (nano Ga (GRR)) at different time (R6G concentration of 10^{-5} M). Only slightly decay was observed over 60 days, indicating the excellent stability for SERS.



Figure S25. Ultraviolet photoelectron spectroscopy (UPS) spectrum of nano Ga (GRR). The work function was measured to be 3.84 eV.



Figure S26. SERS spectra of R6G with different concentrations for commercial Zn NPs. There was no obvious Raman-enhancing phenomenon for commercial Zn NPs.