Supporting Information

Nanogaps inducted thermo-plasmonic nano-heaters for amplified photo-triggered tumor ablation at a low laser power density

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This file contains 17 figures (Figure S1-S17), and one table (Table S1).

Experimental details

1. General

All chemical reagents were purchased from Sigma-Aldrich (St. Louis, MO, USA) and used as received without further purification. Transmission electron microscopy (TEM, H-7650, Hitachi, Japan) was used for the nanoparticles analysis. Extinction spectra were obtained with a UV spectrometer (SCINCO, South Korea). Structural analyses were performed using X-ray diffraction (Rigaku D/MAX 2500Tokyo, Japan). A near-infrared (NIR) laser (OCLA Laser, Passive Cooled InGaAs diode laser, LaserLab® South Korea, 808 nm, output power = 0.5 – 15 W) was used. A solar simulator (Newport) with a power density of 0.23 W/cm^2 was used.

2. Experimental Methods

2.1 Preparation of GNSSs. The synthesis of GNSSs was carried out by following previously reported method [1]. In a typical experiment, 20 mL of HEPES (100 mM, pH 7.4) solution was mixed with 30 mL of deionized water, followed by the addition of 500 µL of $HAuCl_4$ (20 mM) solution. The resulting mixture was kept undisturbed for 30 min, the color of solution changed from light yellow to slightly purple and finally to greenish blue.

2.2 Preparation of CTAB modified GNRs. Cetyltrimethylammonium bromide (CTAB) mediated growth method was used to prepare GNRs (λ_{max} = 735 nm).[2] $HAuCl_4$ (0.25 mL, 0.01 M) was mixed with a CTAB aqueous solution (9.75 mL, 0.1 M) to make seed solution. The solution color changed from yellow to pale-brown while ice-cold solution of $NaBH_4$ (600 µL, 0.01 M) was quickly added with vigorous stirring. Then this seed solution was stored in a water bath for 3 h at 28 °C. Growth solution was prepared by mixing CTAB (475 mL, 0.1 M) with $HAuCl_4$ (20 mL, 0.01 M), $AgNO_3$ (3.0 mL, 0.01 M), and ascorbic acid (3.2 mL, 0.1 M) in slow stirring. With the

addition of ascorbic acid, the yellow-colored solution became colorless. At last, the seed solution (3.6 mL) was quickly added to the growth solution and mixed with brief shaking for 5 s, and then the resulting solution was kept undisturbed in a water bath at 28 °C for 12 h.

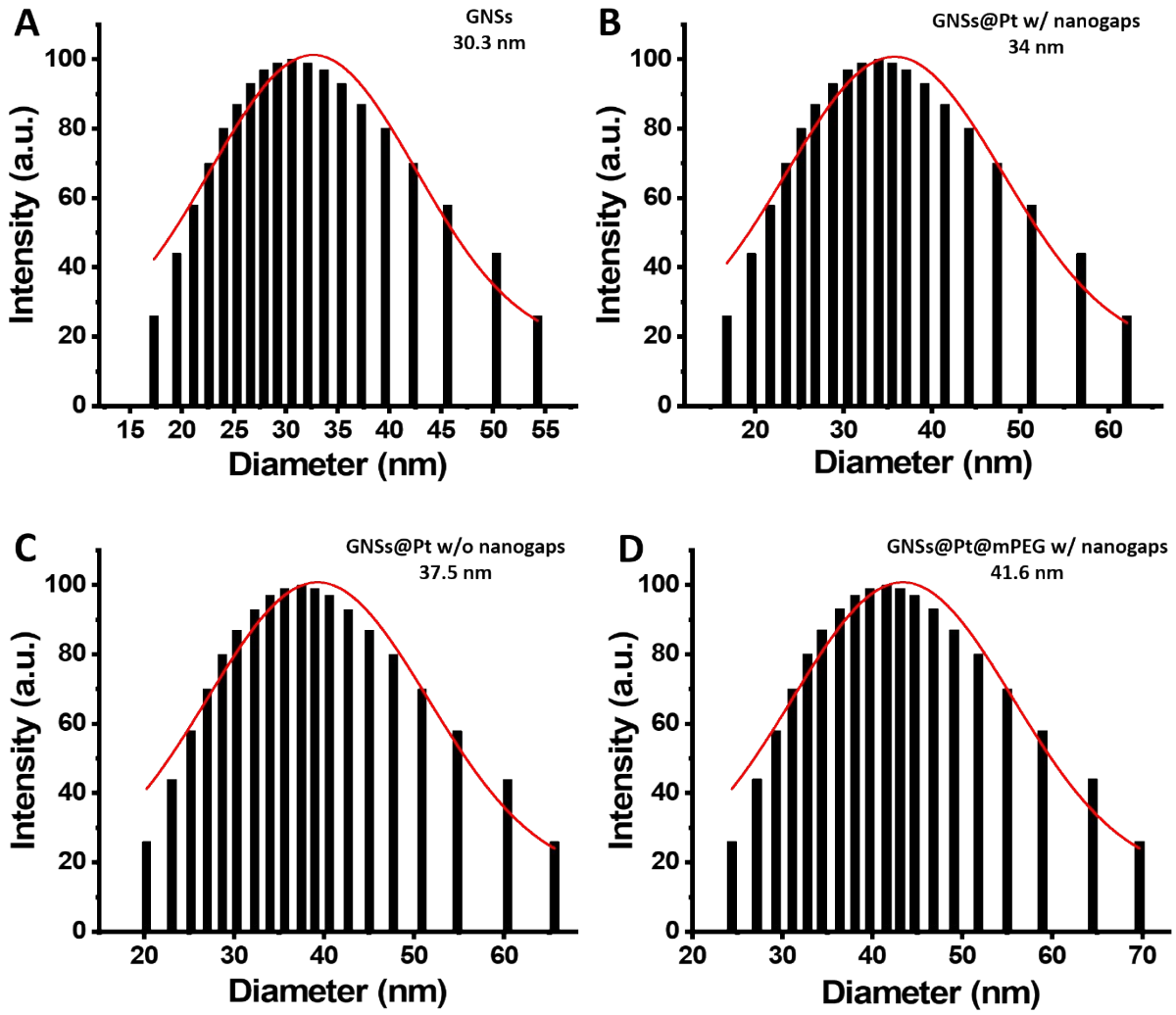

Fig. S1. Particle size distribution (DLS) analysis of **(B)** GNSs, **(C)** GNSs@Pt with nanogaps, **(D)** GNSs@Pt without nanogaps, and **(E)** GNSs@Pt@mPEG.

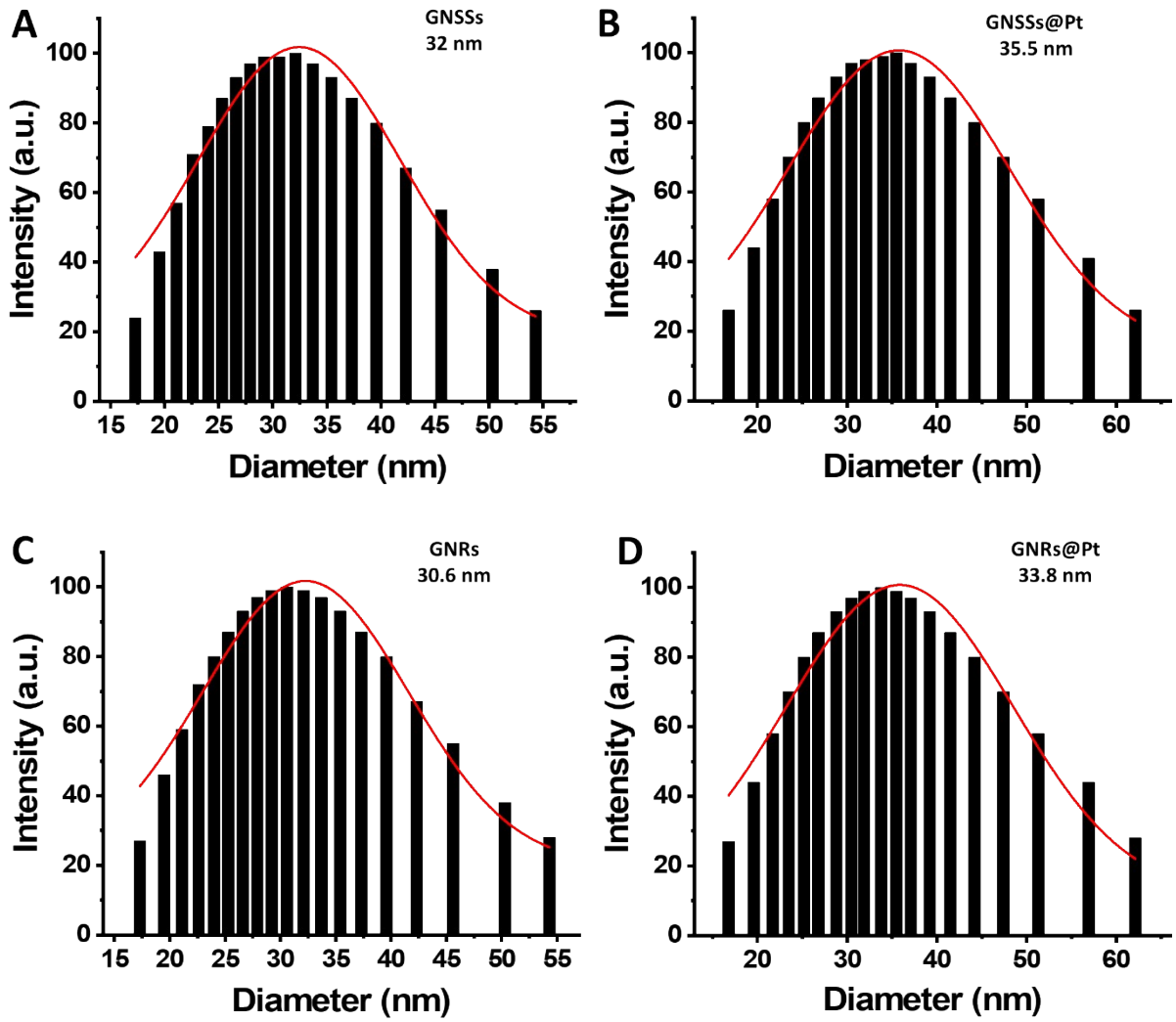

Fig. S2. Particle size distribution (DLS) analysis of **(B)** GNSSs, **(C)** GNSSs@Pt, **(D)** GNRs, and **(E)** GNRs@Pt nanomaterials.

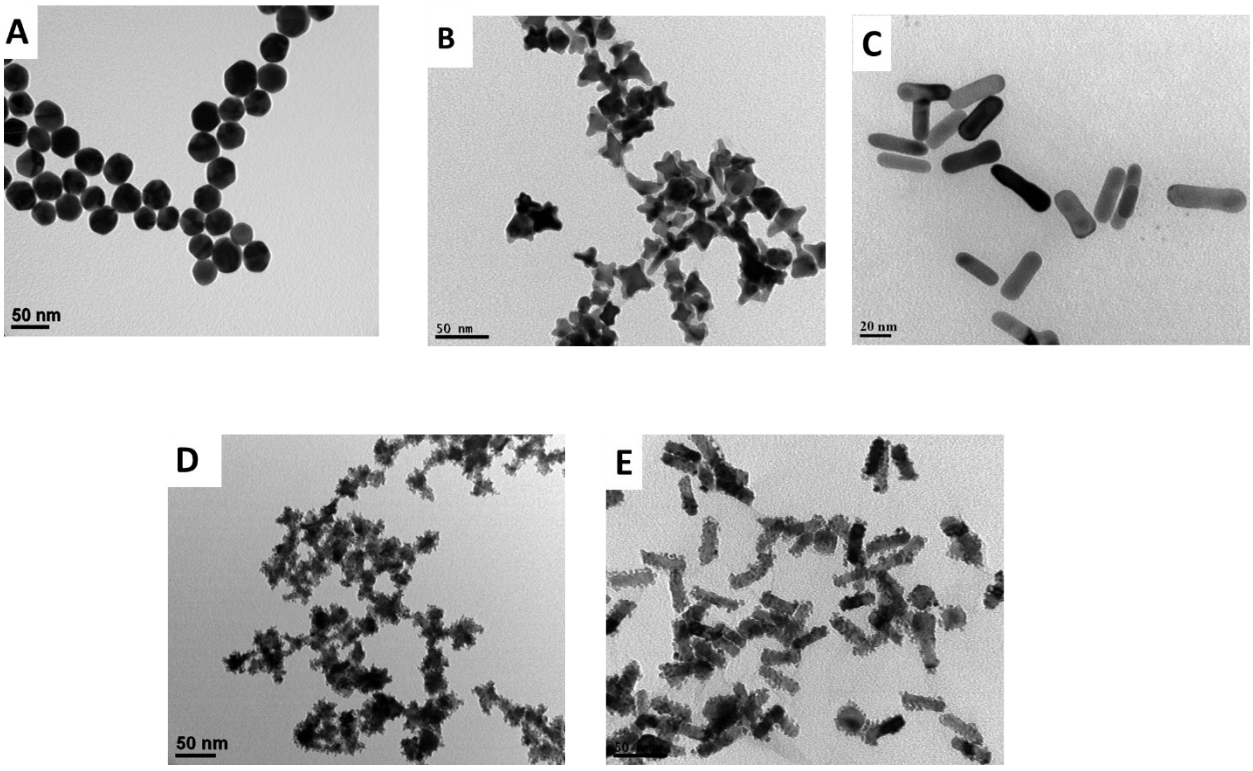

Fig. S3. TEM images of **(A)** GNSs, **(B)** GNSSs, **(C)** GNRs, **(D)** GNSSs@Pt and **(E)** GNRs@Pt nanostructures.

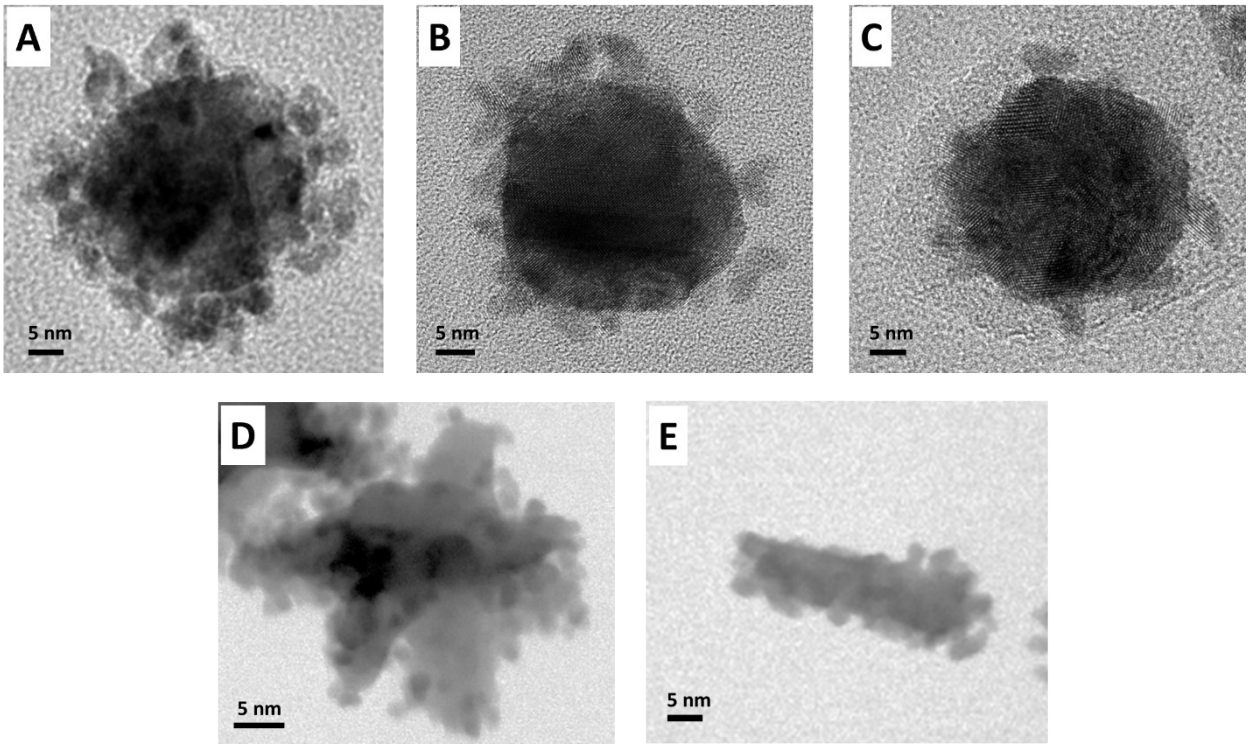

Fig. S4. The HRTEM images of **(A)** GNSs@Pt-w/o nanogaps, **(B)** GNSs@Pt-w/ nanogaps, (C) GNS@Pt@mPEG-w/ nanogaps, GNSSs@Pt, and GNRs@Pt nanoparticles.

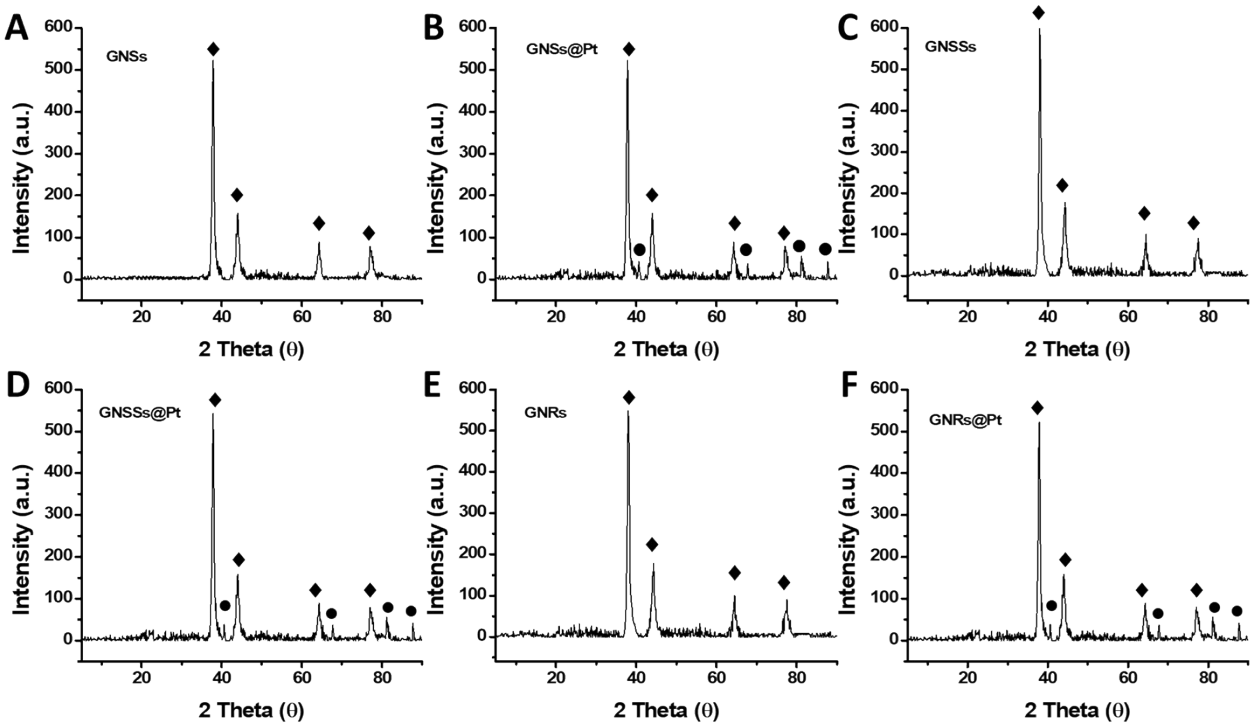

Fig. S5. XRD spectrum of **(A)** GNSs, **(B)** GNSs@Pt, **(C)** GNSSs, **(D)** GNSSs@Pt, **(E)** GNRs, and **(F)** GNRs@Pt nanoparticles, respectively.

Table S1. BET surface area of GNSs and GNSs@Pt (with controlled and high Pt coating) and comparative weight percent of Pt and Au in GNSs@Pt.

Nanomaterials	**BET surface area (m^2/g)**	**ICP-MS analysis**	
		Au (wt%)	**Pt (wt%)**
GNSs	3.85	100	0
GNSs@Pt (with 1-2 nm nanogaps)	5.26	67.13	32.87
GNSs@Pt (withoout nanogaps)	5.84	51.27	48.73

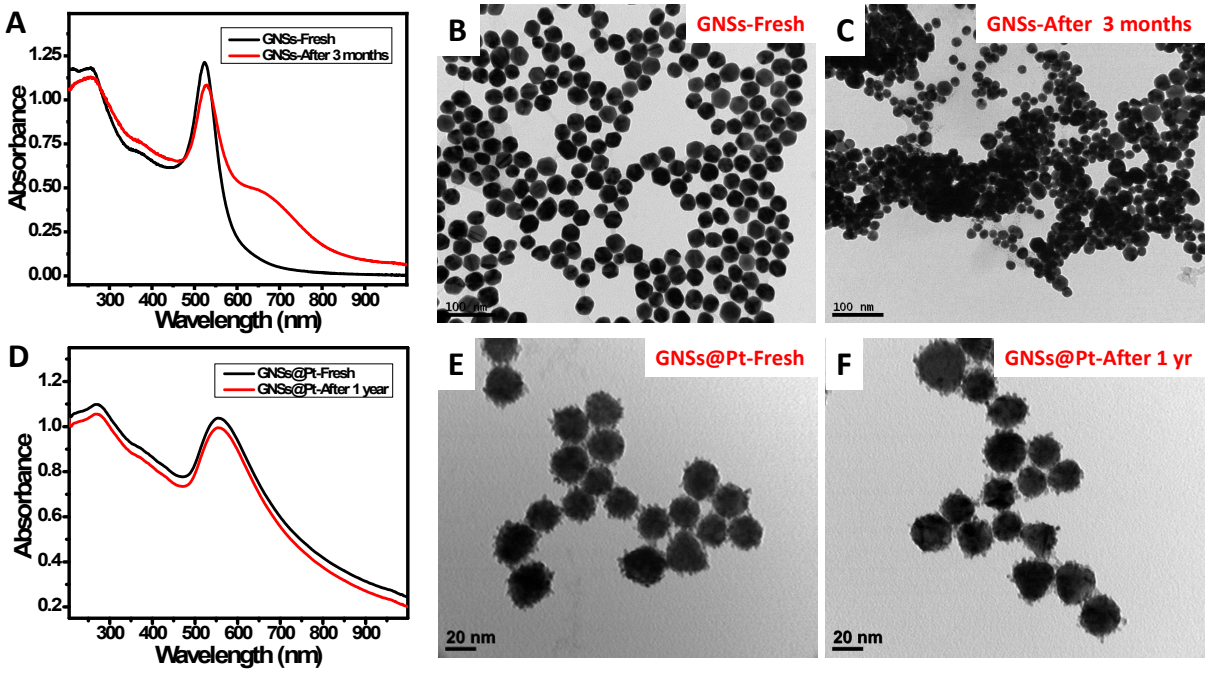

Fig. S6. UV-Visible spectrum of **(A)** GNSs fresh & after 3 months and **(D)** GNSs@Pt fresh & after 1 year. TEM images of GNSs **(B)** Fresh, **(C)** after 3 months. TEM images of GNSs@Pt **(E)** Fresh, **(F)** after 1 year.

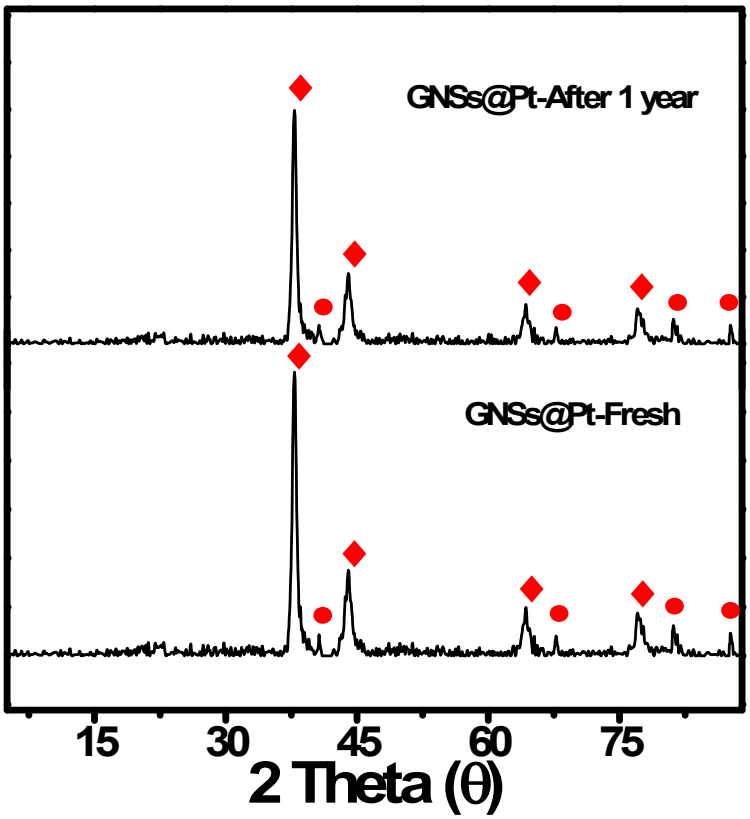

Fig. S7. XRD spectrum of GNSs@Pt fresh and GNSs@Pt after 1 year.

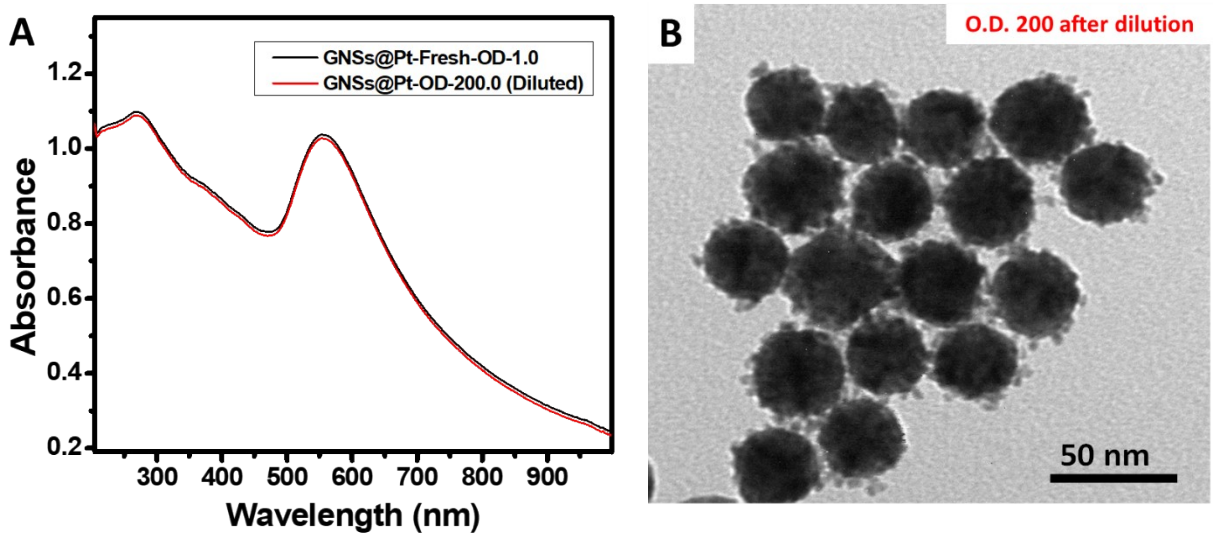

Fig. S8. (A) UV-Visible spectrum of GNSs@Pt with O.D. = 1.0 & O.D. = 200.0 and **(B)** TEM image of GNSs@Pt with O.D. 200.

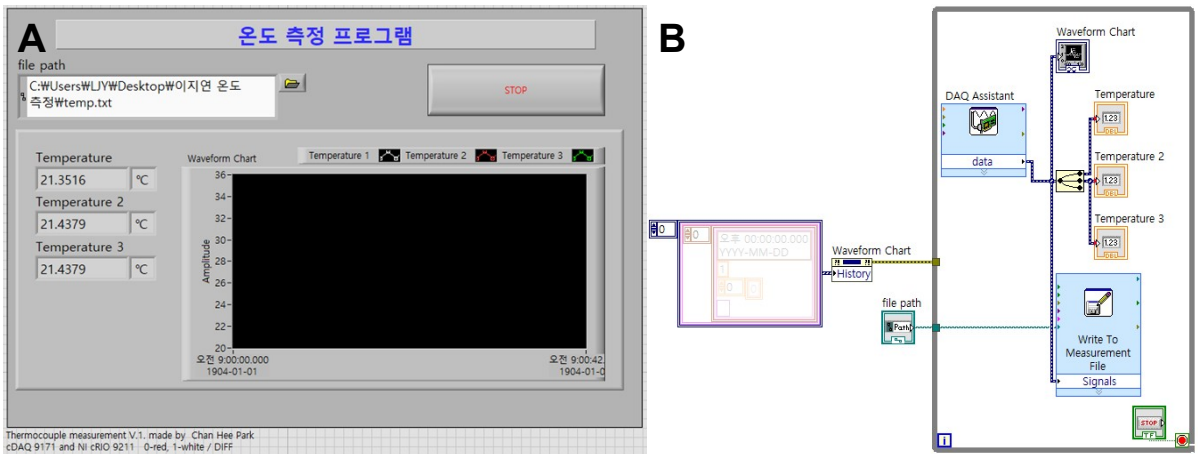

Fig. S9. (A) The front panel and **(B)** block diagram of temperature measurement program using LabVIEW software provided from National Instruments Corporation.

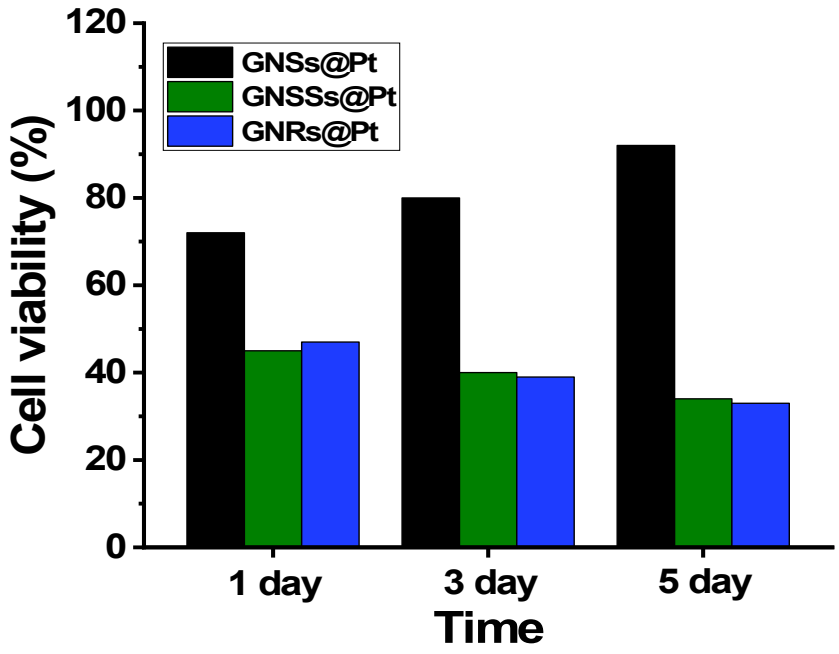

Fig. S10. Cell viabilities of NIH3T3 cells after incubation with 0.075 mg/mL of GNSs@Pt, GNSSs@Pt, and GNRs@Pt nanoparticles after 1, 3, and 5 days.

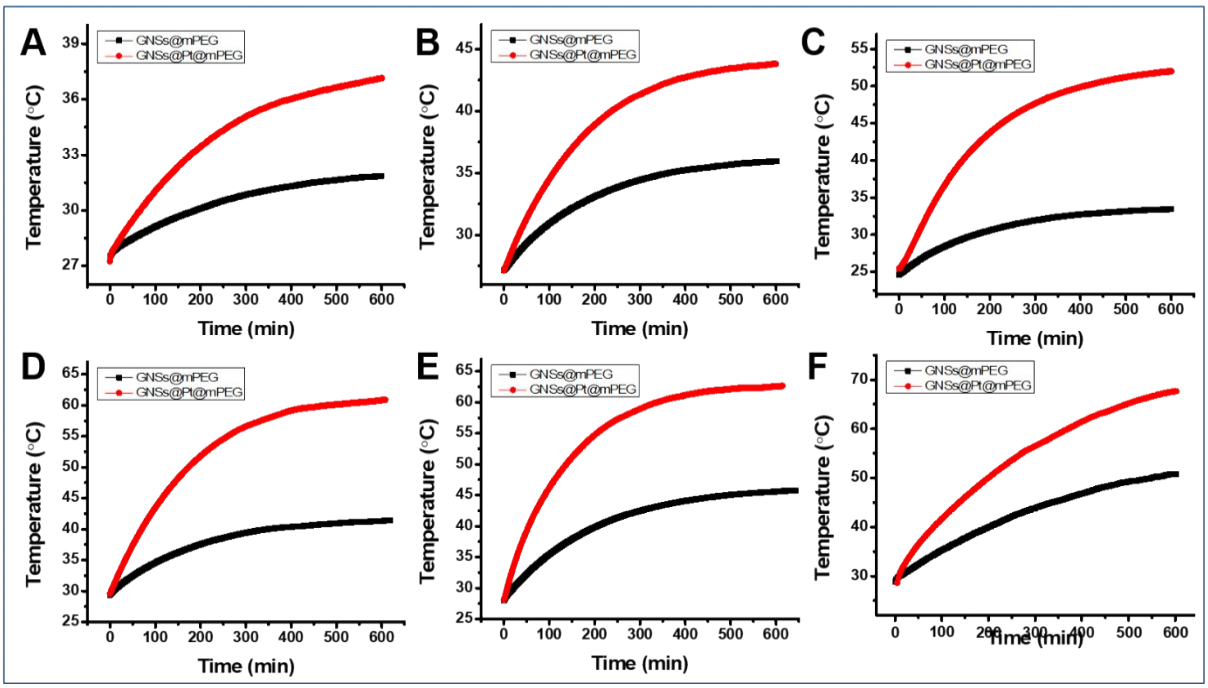

Fig. S11. The change in temperature curves of GNSs@mPEG and GNSs@Pt@mPEG with 0.075 mg/mL concentration after NIR light irradiation at **(A)** 0.18, **(B)** 0.36, **(C)** 0.72, **(D)** 1.44, **(E)** 2.5, and **(F)** 3.0 W/cm^2 of laser power density, respectively, at room temperature for 10 min.

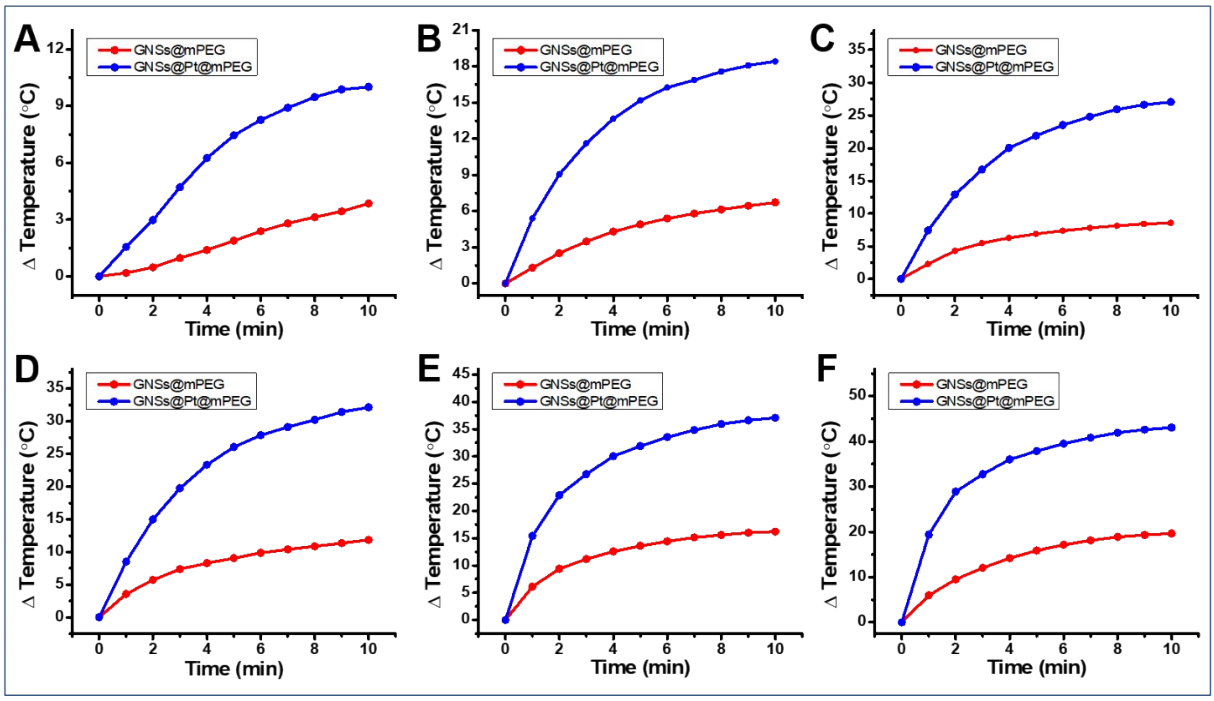

Fig. S12. The 808 nm laser-induced temperature change of GNSs@mPEG and GNSs@Pt@mPEG at **(A)** 0.18, **(B)** 0.36, **(C)** 0.72, **(D)** 1.44, **(E)** 2.5, and **(F)** 3.0 W/cm^2 of laser power density, respectively, respectively, at room temperature for 10 min.

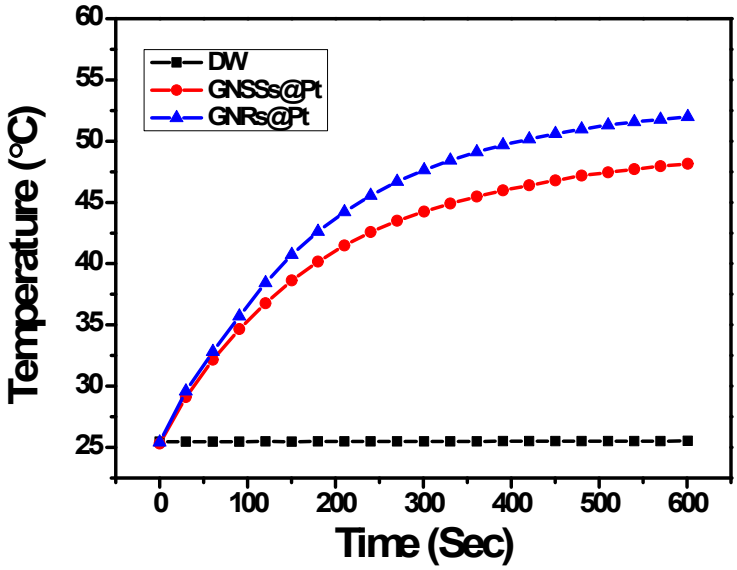

Fig. S13. The change in temperature curves of GNSSs@Pt and GNRs@Pt with 0.075 mg/mL concentration after NIR light irradiation at 0.36 W/cm^2 of laser power density at room temperature for 10 min.

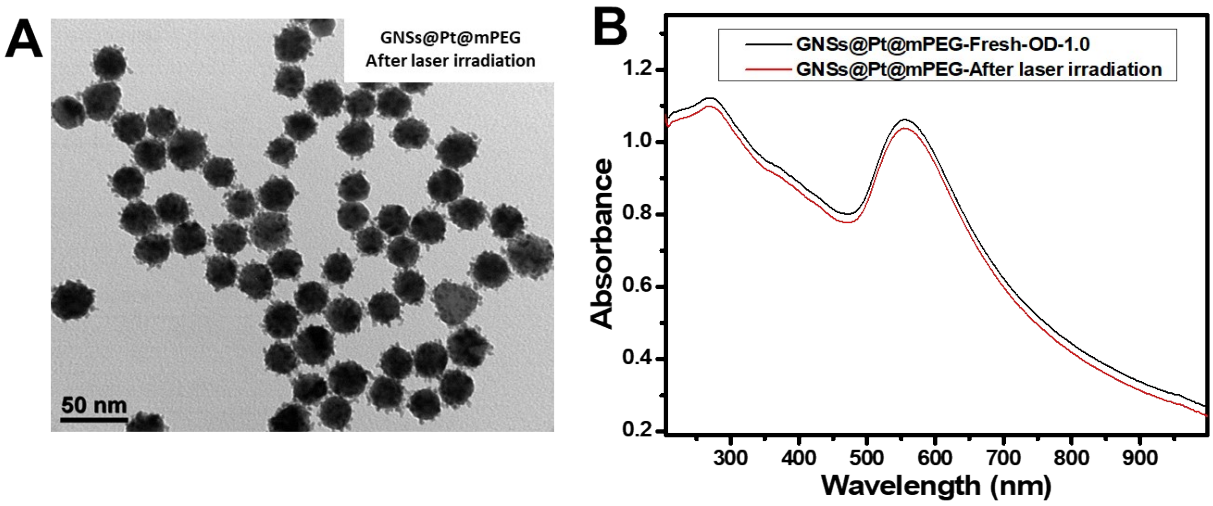

Fig. S14. (A) UV-Visible spectrum and **(B)** TEM image of GNSs@Pt@mPEG fresh & after laser irradiation.

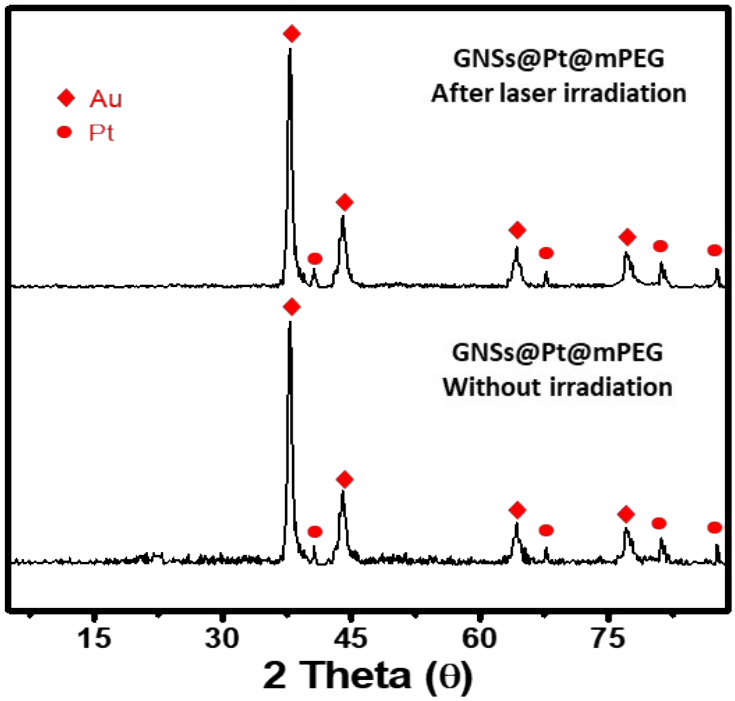

Fig. S15. XRD spectrum of GNSs@Pt@mPEG fresh & after laser irradiation, resepctively.

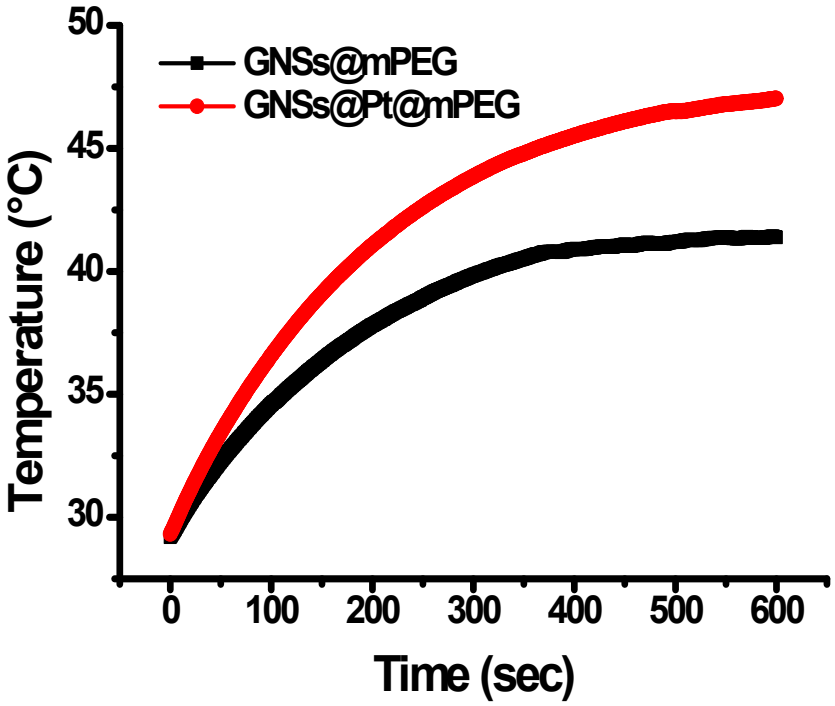

Fig. S16. Temperature curves of the cells treated in GNSs and GNSs@Pt.

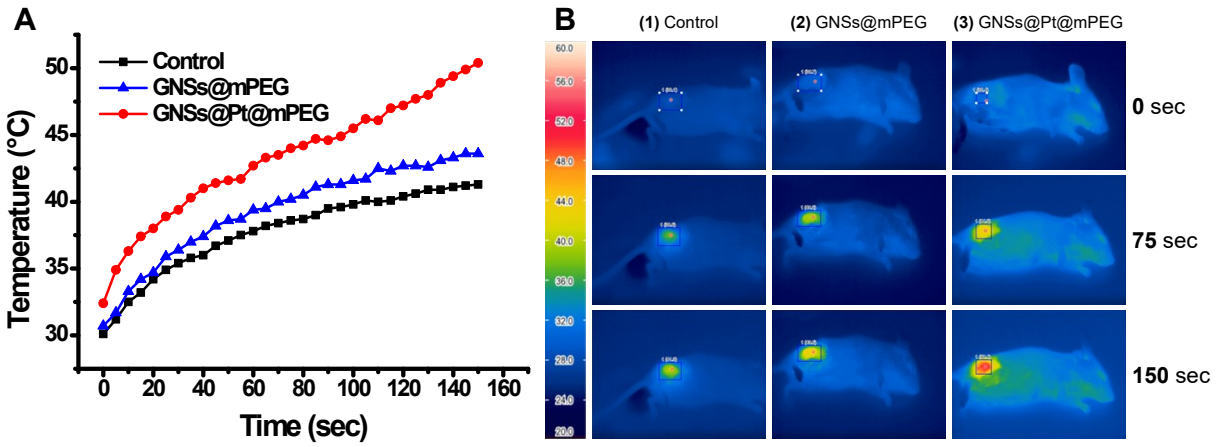

Fig. S17. (A) The temperature evolution on tumors of mice with different groups (control, GNSs@mPEG, and GNSs@Pt@mPEG) injection under the same laser power irradiation. **(B)** IR thermal images of tumor-bearing mice with different groups (control, GNSs@mPEG, and GNSs@Pt@mPEG) injection exposed to the NIR laser under the same power density recorded at different time intervals. As the control, IR thermal images of mice with intravenous injection with equivalent PBS exposed to the NIR laser at the power of 0.36 W/cm^2 were taken.

References

[1] J. Xie, J.Y. Lee, D.I.C. Wang, Seedless, Surfactantless, High-Yield Synthesis of Branched Gold Nanocrystals in HEPES Buffer Solution, Chemistry of Materials, 19 (2007) 2823-2830.

[2] Z. Ban, Y.A. Barnakov, F. Li, V.O. Golub, C.J. O'Connor, The synthesis of core-shell iron@gold nanoparticles and their characterization, Journal of Materials Chemistry, 15 (2005) 4660-4662.