Electronic Supplementary Information

Enhanced Type I photoreaction of indocyanine green *via* electrostatic-force-driven aggregation

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Experimental Procedures

1. Materials

Chloroauric acid ($HAuCl_4 \bullet 3H_2O$), cetyltrimethylammonium bromide (CTAB), L-ascorbic acid (AA) and poly (sodium 4-styrenesulfonate) (PSS) were purchased from Alfa Aesar. (3-Aminopropyl) triethoxysilane (APTES) and propidium iodide (PI) were purchased from Solarbio life science. Sodium ascorbate (NaA), dimethyl sulfoxide (DMSO), Poly dimethyl diallyl ammonium chloride (PDDAC), 2,2,6,6-tetramethyl-4-piperidine (TEMP), superoxide dismutase (SOD), poly(acrylic acid) (PAA, Mw 100,000), 9,10-anthracenediyl-bis(methylene) dimalonic acid (ABDA) and indocyanine green (ICG) were purchased from Sigma-Aldrich. Sodium dodecyl sulfate（SDS）was purchased from Sinopharm chemical reagent corporation. 3'- (p-amino phenyl) fluorescein (APF) was purchased from Life technologies corporation. Poly (allylamine hydrochloride) (PAH, Mw 15,000) was purchased from Macklin. 5-tert-Butoxycarbonyl-5-methyl-1-pyrroline N-oxide (BMPO) and WST-1 was purchased from Dojindo molecular technologies. 3,3',5,5'-Tetramethylbenzidine dihydrochloride hydrate (TMB) was purchased from Lablead. O-phenylenediamine (OPD) and tetraethyl orthosilicate (TEOS) were purchased from Aladdin. Calcein-AM was purchased by Biotium. CM-H_2DCFDA was purchased from Introgen. Milli-Q water (18 $M\Omega \bullet cm^{-1}$) was used for preparation of all solutions.

2. Calculating the molar concentration of nanoparticles

The molar concentration of AuNSs and AuNRs in the suspension was estimated using extinction spectra and TEM result. The molar concentration of Au atom was determined by the extinction value at 400 nm ($Ext_{400\ nm}$) of nanoparticles suspension via $C_{Au} = Ext_{400\ nm}/(l*\varepsilon_{400\ nm})$, where l and $\varepsilon_{400\ nm}$ are optical path length (cm) and molar extinction coefficient of Au atom at 400 nm ($2.02*10^3\ M^{-1}\ cm^{-1}$), respectively.[1] TEM was used to determine the mean size (diameter and length) of nanoparticles. Then, by assuming AuNSs as a sphere and AuNR as a cylindrical shape with two half-sphere endcaps, we could obtain

the volume of single nanoparticle (V_{rod} in cm^3). Through formula $C_{rod} = V_{Au}*C_{Au}/(A*V_{rod})$, where V_{Au} and A are molar volume of Au (10.2 cm^3/mol) and Avogadro's constant, we could obtaine the molar concentration of AuNSs and AuNRs in the suspension.

3. Detection of absorption and fluorescence spectra

The reductant or ROS probe was added to the ICG mixed solution (containing CTAB or other molecules, nanoparticles) and transferred to the quartz cuvette. The solution was irradiated with an 808 nm continuous-wave diode laser (Daheng Science & Technology, China) for various time and recorded the spectra in Varian Cary 50® UV–Vis spectrophotometer (Agilent Technologies, USA) or Horiba Fluoro-Max4 spectrometer (HORIBA Ltd., Japan).

4. Transient absorption measurement

Femtosecond transient absorption spectroscopy measurements were performed using a commercial fs-TAS system, i.e., HELIOS (Ultrafast Systems). The 800 nm pulse from a Coherent Astrella regenerative amplifier (100 fs, 1 kHz, 2.5 mJ/pulse), seeded by a Coherent Vitara-s oscillator (35 fs, 80 MHz), was used to pump an optical parameters amplifier (Coherent, OperA Solo) to generate the excitation pulse at 610 nm for the excitation of ICG. A small fraction of the 800 nm output from the Astrella was fed to a sapphire crystal in the HELIOS for generating the white light continuum (WLC). The focused pump and probe spot sizes were 150 and 100 μm, respectively. A 750 nm SPF was placed in the probe path before the sample to filter out the residual 800 nm in the WLC. The system has an ultimate temporal resolution of ~130 fs.

5. Cell culture and cytotoxicity experiment

Human hepatocytes (LO2) cells were incubated at 10^4 cells per well in 96-well plates at 37 °C for 24 h. Then, the medium was replaced by fresh medium containing different materials (ICG, 2 μM; AuNR@SiO_2-NH_2, 0.04 nM) and irradiated with an 808 nm laser for 1 min. Cell Counting Kit-8 (CCK-8) assay was used to determine the cell viability.

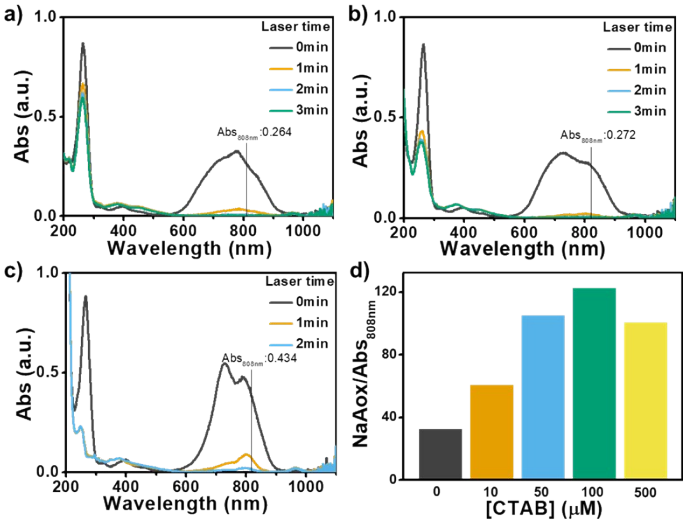

Figure S1. Photo-oxidation of NaA (50 μM) by ICG (5 μM) in the mixtures of ICG and CTAB with CTAB concentration of (a) 10 μM, (b) 50 μM and (c) 500 μM, respectively. Effect of CTAB amount after normalized by the absorbance at 808 nm (d). All experiments were conducted using 4 W/cm^2 808 nm laser.

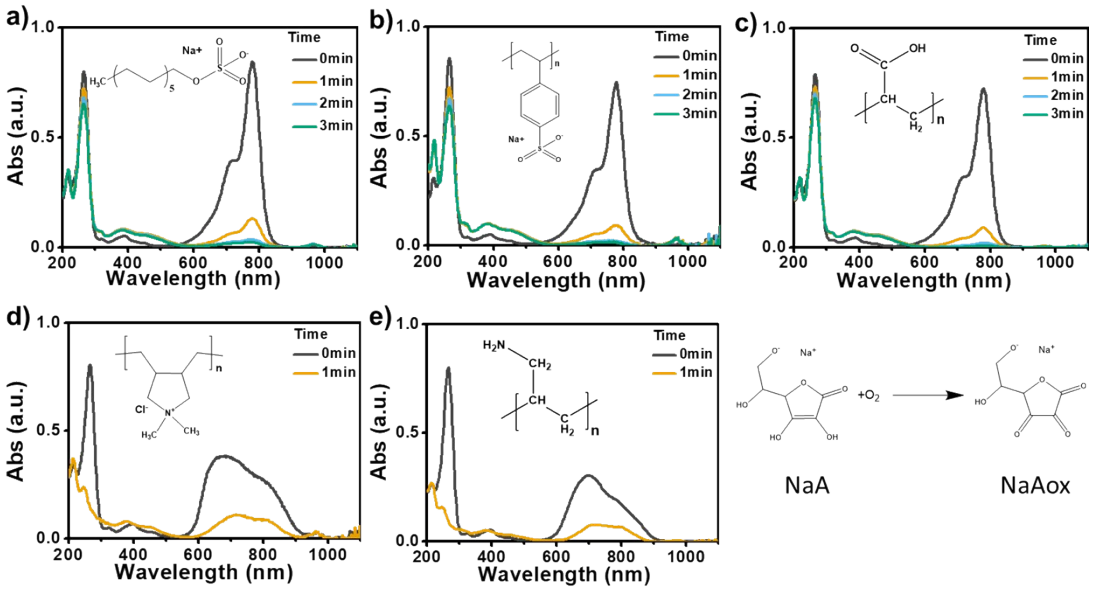

Figure S2. Photo-oxidation of NaA (50 μM) by ICG (5 μM) in the mixtures of ICG with different molecules monitored by absorption spectra. (a) SDS, (b) PSS, (c)PAA, (d) PDDAC and (e) PAH. SDS, 500 μM; PSS, PDDAC, PAA, PAH, 1mg/L. All experiments were conducted using 4 W/cm^2 808 nm laser.

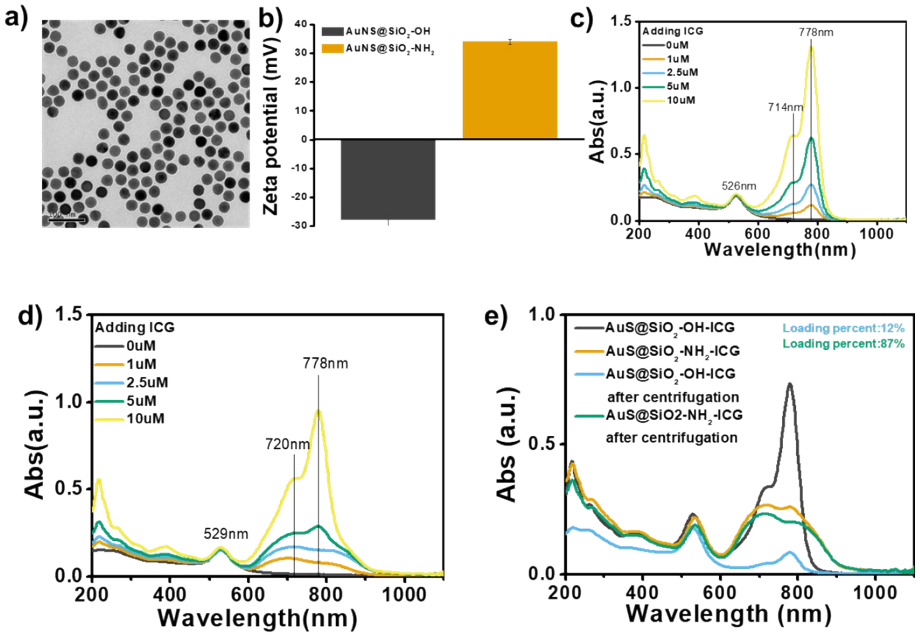

Figure S3. (a) Representative TEM image of AuNSs with a mean diameter of 32.1 ± 1.1 nm as measured using Image Pro Plus. (b) Zeta potentials of negatively charged AuNS@SiO_2-OH and positively charged AuNS@SiO_2-NH_2. Electrostatic interactions of AuNS@SiO_2-OH (c) and AuNS@SiO_2-NH_2 (d) with ICG monitored by absorption spectra and calculation of ICG (5 μM) loading precentage (e). AuNS@SiO_2-OH, AuNS@SiO_2-NH_2, 0.1 nM.

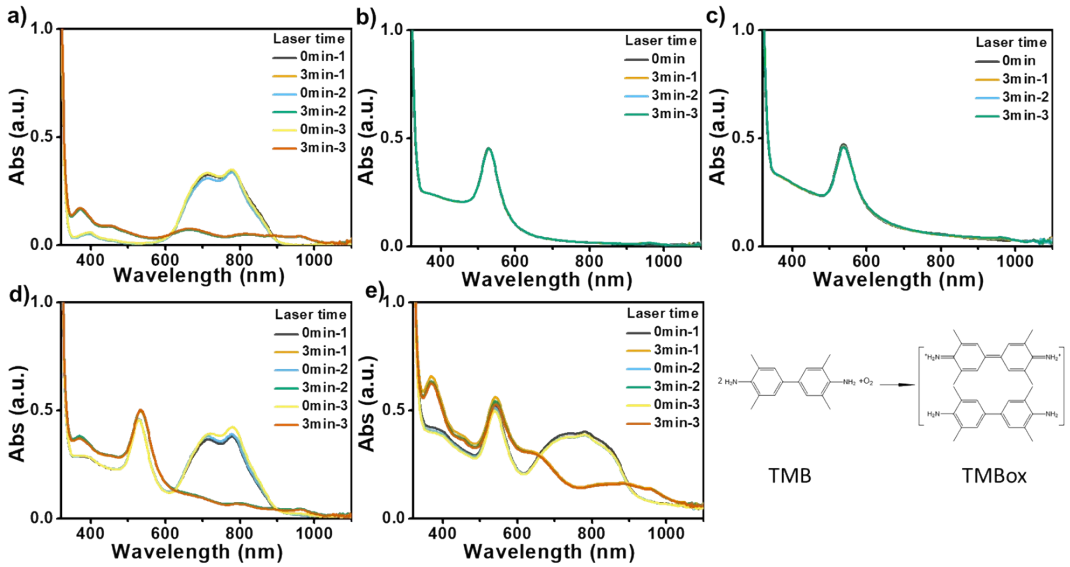

Figure S4. TMB (500 μM) photo-oxidation by (a) ICG (5 μM), (b) 0.1 nM AuNS@SiO_2-OH, (c) AuNS@SiO_2-NH_2, (d) AuNS@SiO_2-OH-ICG (0.1 nM/5 μM), and (e) AuNS@SiO_2-NH_2-ICG (0.1 nM/5 μM), respectively. All experiments were conducted using 4 W/cm^2 808 nm laser.

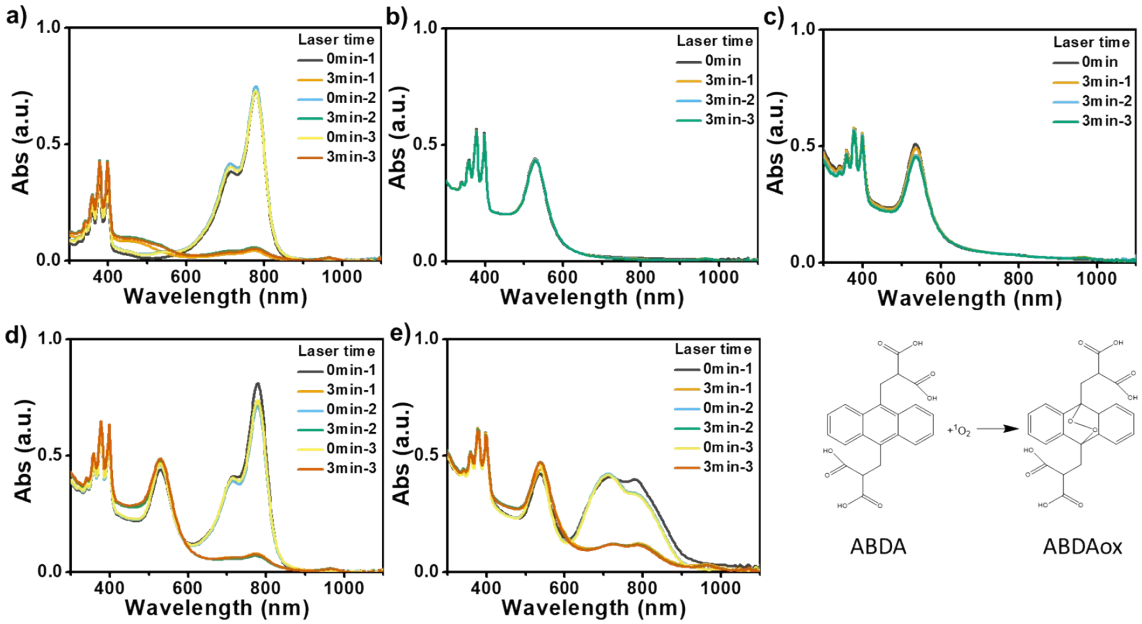

Figure S5. ABDA (100 μM) photo-oxidation by (a) ICG (5 μM), (b) 0.1 nM AuNS@SiO_2-OH, (c) AuNS@SiO_2-NH_2, (d) AuNS@SiO_2-OH-ICG (0.1nM/5 μM), and (e) AuNS@SiO_2-NH_2-ICG (0.1 nM/5 μM), respectively. All experiments were conducted using 4 W/cm^2 808 nm laser.

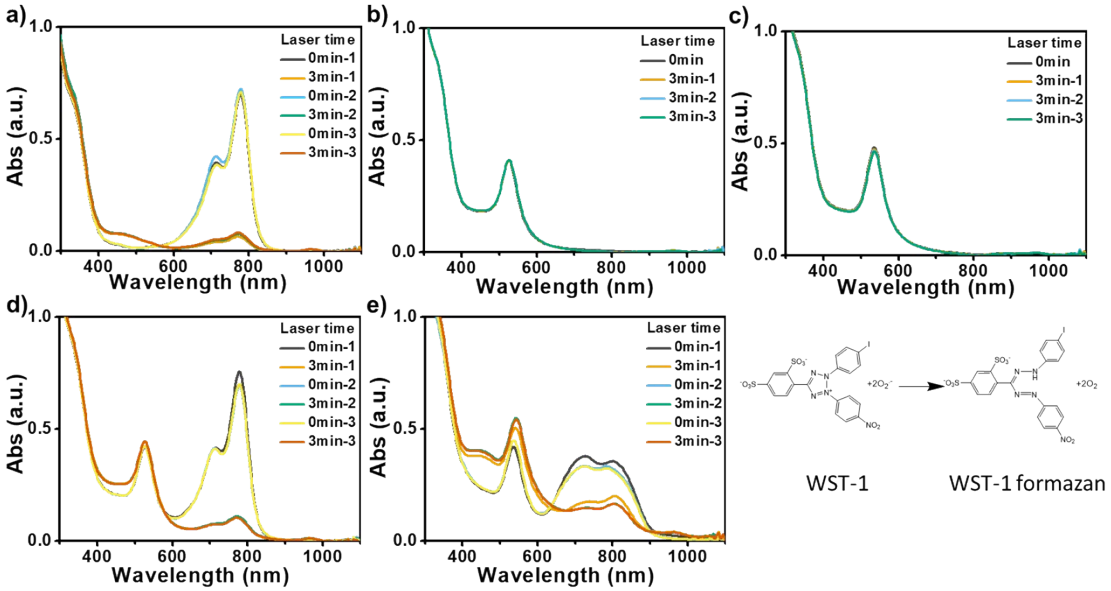

Figure S6. WST-1 (100 μM) photo-reduction by (a) ICG (5 μM), (b) 0.1 nM AuNS@SiO_2-OH, (c) AuNS@SiO_2-NH_2, (d) AuNS@SiO_2-OH-ICG (0.1nM/5 μM), and (e) AuNS@SiO_2-NH_2-ICG (0.1 nM/5 μM), respectively. All experiments were conducted using 4 W/cm^2 808 nm laser.

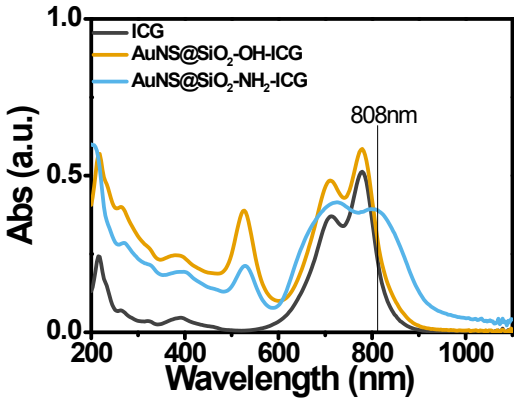

Figure S7. Absorption spectra of ICG (50 μM) before and after mixing with AuNS@SiO_2 (1 nM).

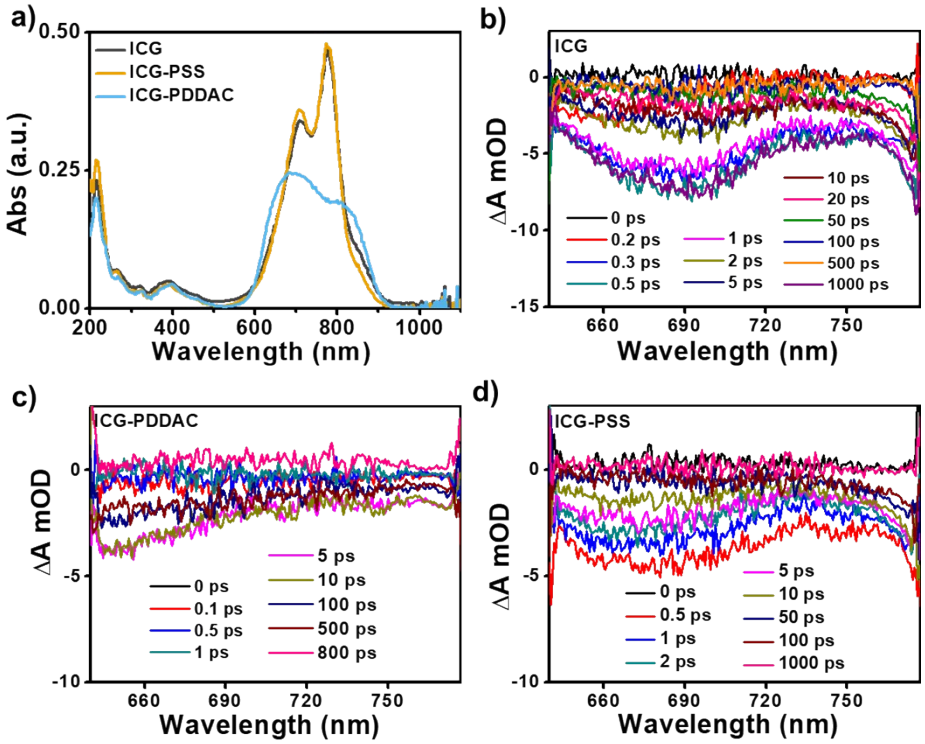

Figure S8. Absorption (a) and fs TA spectra (b-d) monitored at indicated wavelength for ICG itself and its mixtures with PDDAC or PSS.

Table S1. Decay times obtained by using bi-exponential decay fitting.

	~ 680 nm		~ 770 nm	
λ_{exe}=610nm	T_1(ps)	T_2(ps)	T_1(ps)	T_2(ps)
ICG	62.8 ± 11.2 (33%)	4.2 ± 0.5 (67%)	131.4 ±11.1 (67%)	3.1 ± 0.7 (33%)
ICG-PDDAC	74.9 ± 22.9 (21%)	5.9 ±0.7 (79%)	66.4 ± 16.1 (23%)	4.9 ± 0.5 (77%)
ICG-PSS	50.5 ± 13.2 (28%)	4.2 ± 0.7 (72%)	114.4 ± 15.6 (49%)	2.8 ± 0.5 (51%)

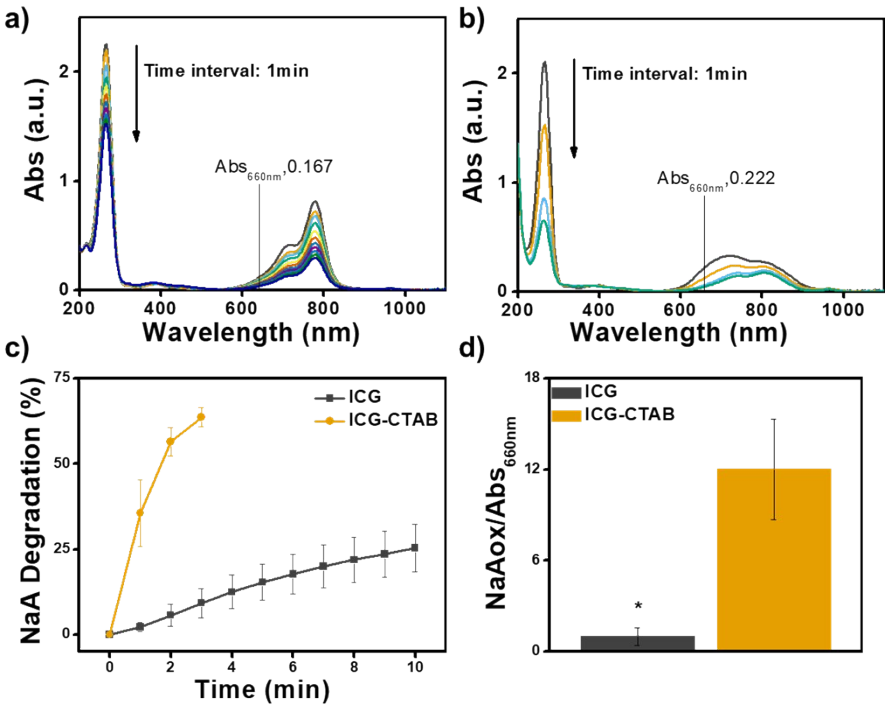

Figure S9. NaA (150 μM) photo-oxidation by ICG upon 660 nm laser irradiation (200 mW). (a, b) Spectral evolutions of NaA upon laser irradiation in the aqueous solution of 5 μM ICG (a) and that containing 5 μM ICG and 100 μM CTAB (b), respectively. (c) NaA photo-oxidation percentage vs irradiation time. (d) Comparison of 1 min laser irradiation after normalized the absorbance of 660 nm.

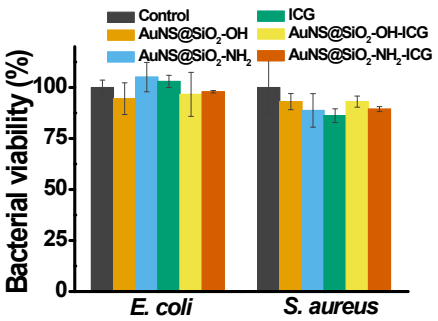

Figure S10. *E. coli* and *S. aureus* viability upon sample exposure in dark.

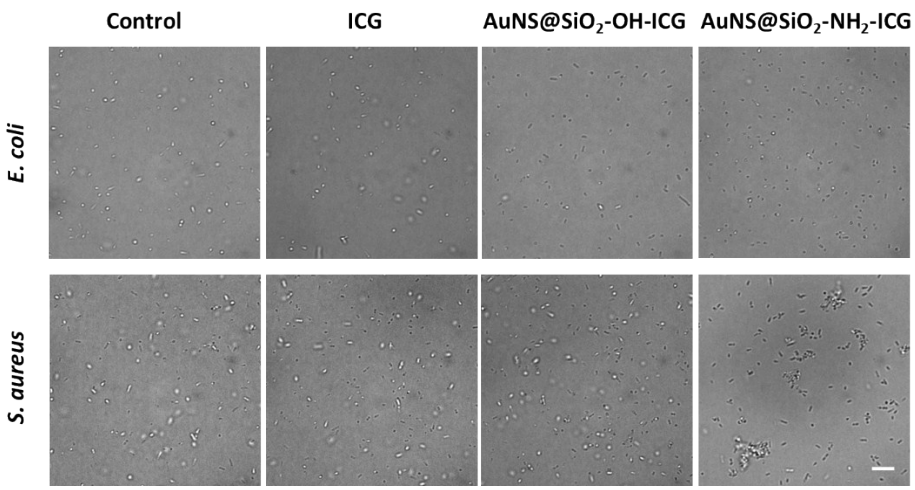

Figure S11. Brightfield images of ROS detection in bacteria (Figure 4c) incubated with different samples. Scale bar, 10 μm.

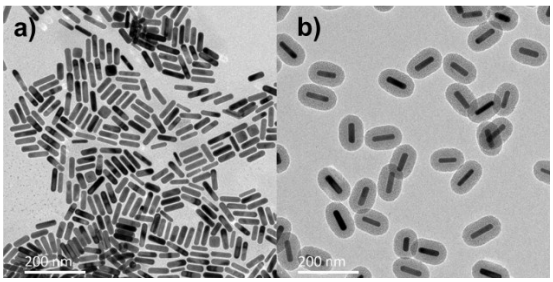

Figure S12. (a) Representative TEM image of AuNRs with a mean rod length and width of 66.4 ± 3.5 nm and 18.9 ± 2.0 nm, respectively, as measured using Image Pro Plus and (b) that of AuNR@SiO_2-NH_2.

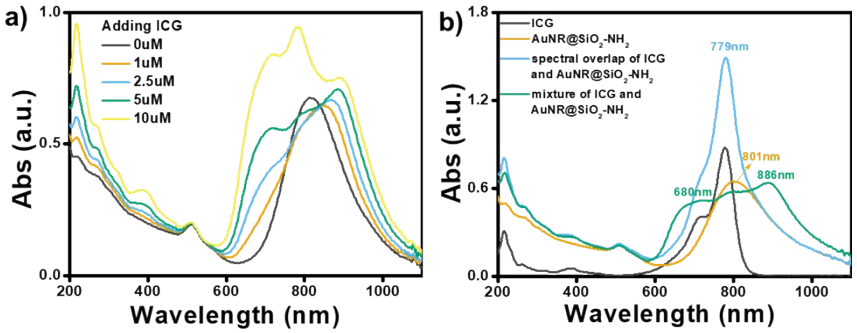

Figure S13. (a) Electrostatic interactions of positively charged 0.1 nM AuNR@SiO_2-NH_2 with ICG monitored by absorption spectra. (b) Absorption spectra of ICG (5 μM) before and after mixing with 0.1 nM AuNR@SiO_2-NH_2. The extinction spectrum of AuNR@SiO_2-NH_2 and the spectral overlap of AuNR@SiO_2-NH_2 and ICG are shown to indicate the formation of ICG aggegrates by mixing ICG and AuNR@SiO_2-NH_2 together.

From Figure S13a, the optimzied loading ratio of ICG to AuNR@SiO_2-NH_2 is roughly 5 μM ICG/0.1 nM AuNR@SiO_2-NH_2.

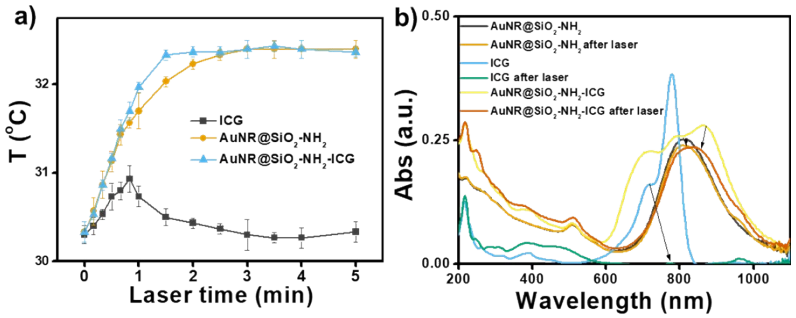

Figure S14. (a) Temperature-rising curves of 2 μM ICG, 0.04 nM AuNR@SiO_2-NH_2, and AuNR@SiO_2-NH_2–ICG (0.04 nM/2 μM) upon laser illumination at a power density of 1 W/cm^2. (b) Absorption spectra of three samples before and after laser illumination.

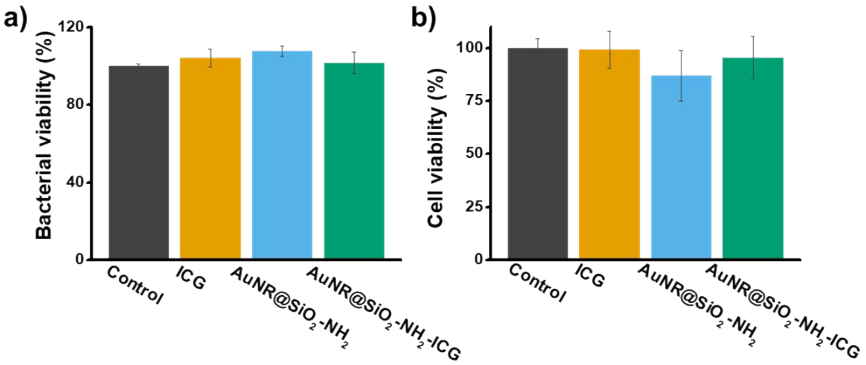

Figure S15. The toxicity of samples to bacteria and cells in dark. (a) Viability of *S. aureus*. (b) Viability of LO2.

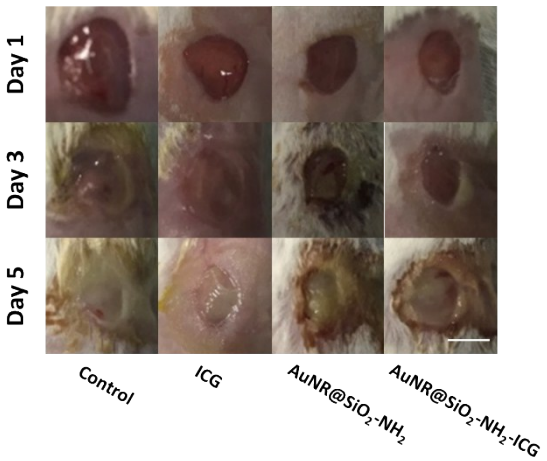

Figure S16. Typical photographs of the wounds at day 1, 3 and 5 after different treatments in dark.

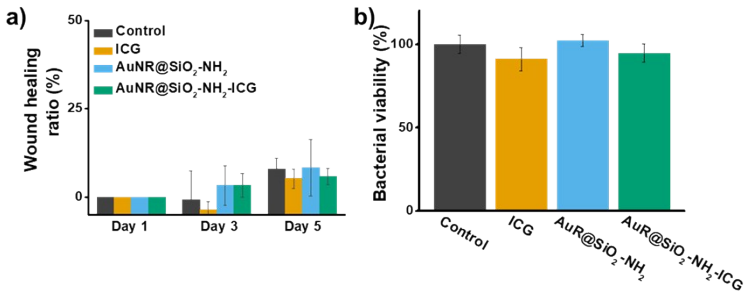

Figure S17. (a) Wound healing ratio on day 1, day 3 and day 5 and (b) bacterial viability at infected wounds treated by different particles in dark on the day 5.

References

1. Z. Hu, S. Hou, Y. Ji, T. Wen, W. Liu, H. Zhang, X. Shi, J. Yan and X. Wu, *AIP Adv.* 2014, **4**, 117137.