Aqueous green synthesis of organic/inorganic nanohybrids with an unprecedented synergistic mechanism for enhanced near-infrared photothermal performance

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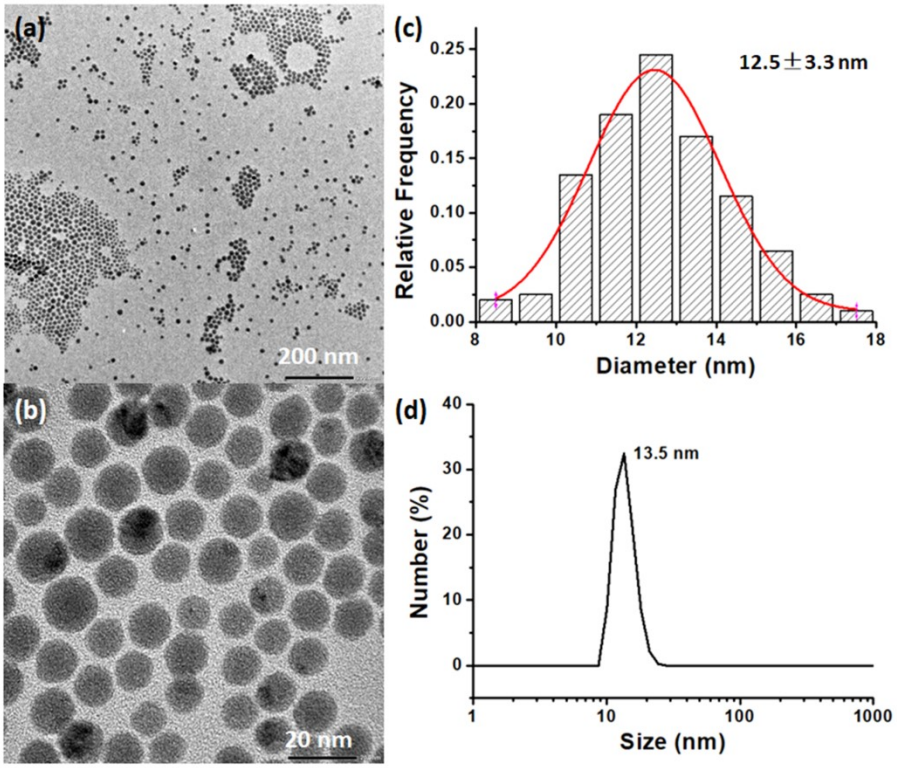

Fig. S1 TEM images of Ag_2S nanoparticles at different magnification (a)-(b). Size distribution of Ag_2S nanoparticles by TEM image statistics (d) and DLS measurement (e).

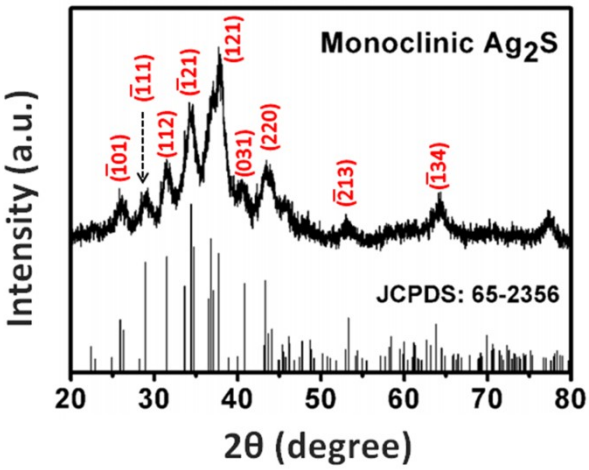

Fig. S2 XRD pattern of the Ag_2S nanoparticles

Table S1 Mean size and polydispersity index (PDI) of Ag_2S@PDA nanohybrids prepared at different mass ratio of F127 and SDS.

Sample	Mean size (nm)	Std. Dev.	PDI	Std. Dev.
F:S=12:0	221.3	4.460	0.036	0.018
F:S=9:3	192.9	2.421	0.131	0.041
F:S=6:6	154.1	0.9074	0.265	0.017
F:S=5:7	204.7	17.94	0.466	0.086
F:S=4:8	239.7	25.34	0.565	0.062
F:S=3:9	288.6	25.11	0.638	0.106
F:S=0:12	336.1	125.1	0.763	0.146

Note: Red shows that particles with polydispersity cannot pass the DLS test effectively.

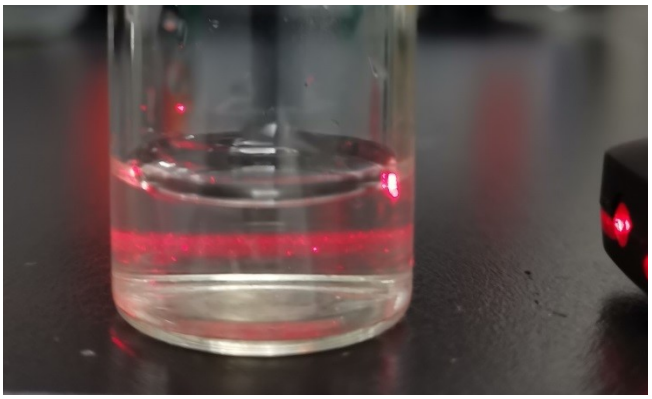

Fig. S3 Red light pathway in the F127 aqueous solution due to the Dundar effect.

Table S2 Mean size and PDI of Ag_2S@PDA nanohybrids synthesized in ethanol and water with different volume ratio.

Sample	Mean size (nm)	Std. Dev.	PDI	Std. Dev.
Ethanol:Water = 0:10	234.9	69.45	0.521	0.088
Ethanol:Water = 2:8	173.0	1.493	0.235	0.025
Ethanol:Water = 4:6	228.7	4.078	0.125	0.045
Ethanol:Water = 6:4	245.9	3.121	0.203	0.013

Table S3 Solubility parameters, permittivity and boiling point of different solvents.

	TMB	Toluene	$CHCl_3$	Ethanol	Water
$\delta/(J/cm^3)^{1/2}$	18.01	18.81	19.85	26.39	46.88
ε	2.40	2.37	4.81	24.3	80.4
Tb/°C	167	111	61	78	100

Table S4 Mean size and PDI of Ag_2S@PDA nanohybrids synthesized by using different oil solvent.

Oil solvent	Mean size (nm)	Std. Dev.	PDI	Std. Dev.
TMB	181.8	3.323	0.093	0.040
Toluene	188.1	7.583	0.098	0.085
$CHCl_3$	273.7	1.901	0.206	0.015
$CHCl_3$, no volatilization	313.4	3.044	0.476	0.046

Table S5 Mean size and PDI of Ag_2S@PDA nanohybrids synthesized by adding different DA amount.

DA Addition	Mean size (nm)	Std. Dev.	PDI	Std. Dev.
0.5 mg	653.8	45.06	0.890	0.096
1 mg	400.8	45.75	0.692	0.090
2 mg	205.3	4.359	0.240	0.030
5 mg	221.2	10.14	0.261	0.056
10 mg	270.6	2.082	0.159	0.026
15 mg	276.0	0.6557	0.124	0.075

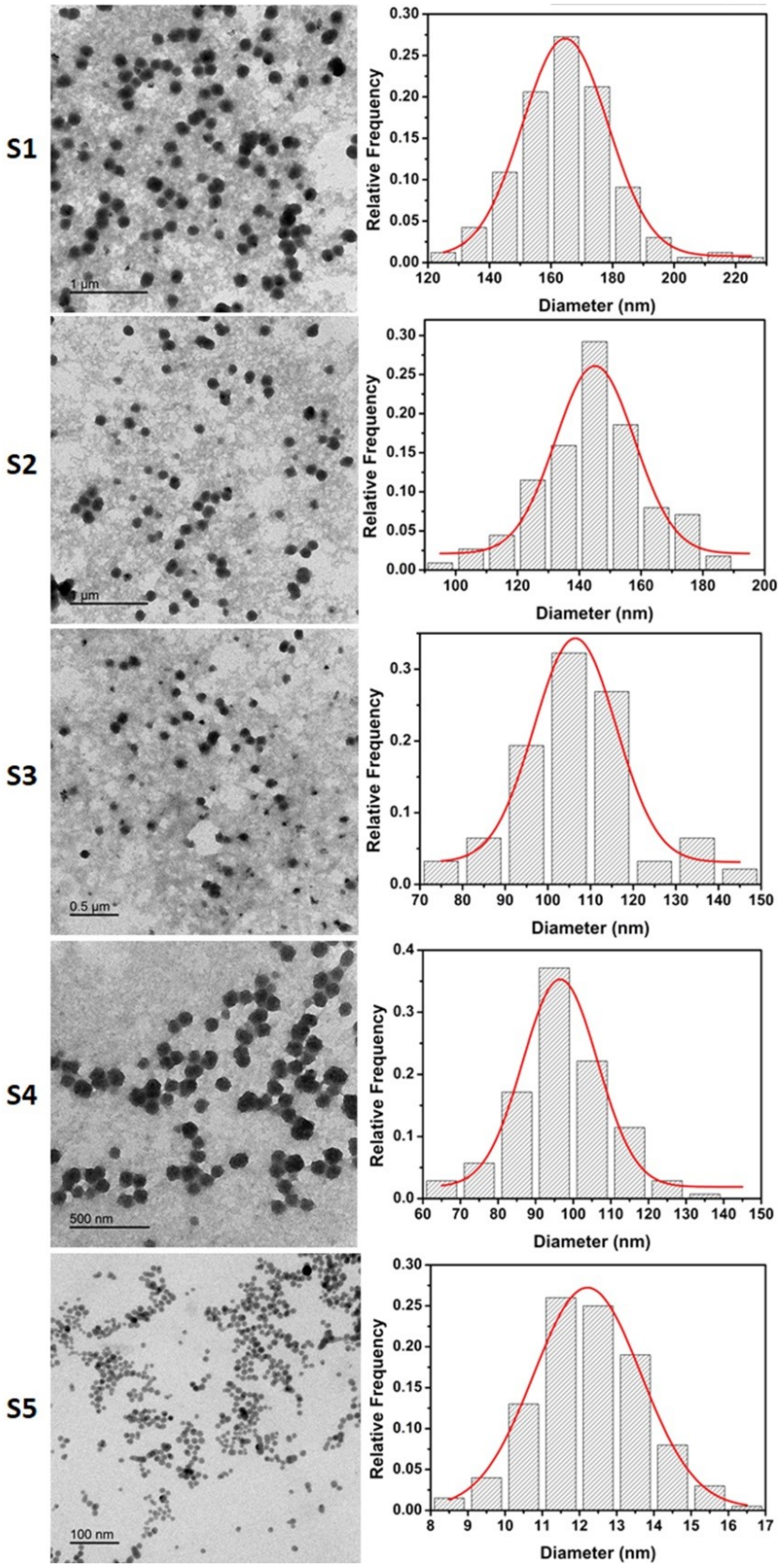

Fig. S4 TEM images and size distribution of five samples corresponding to **Table 2** (diameter statistics were obtained by counting at least 100 particles).

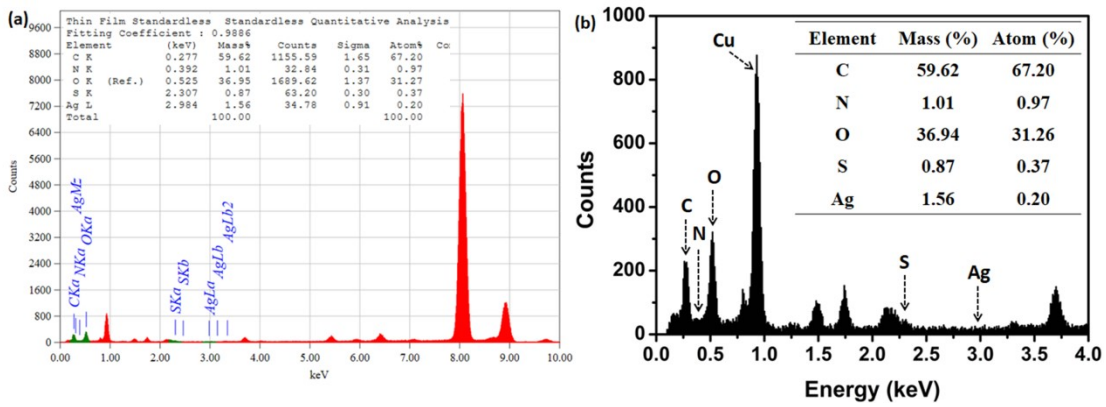

Fig. S5 Elemental distribution and content of Ag_2S@PDA nanohybrids: (a) the original picture; (b) the treated picture by Origin software.

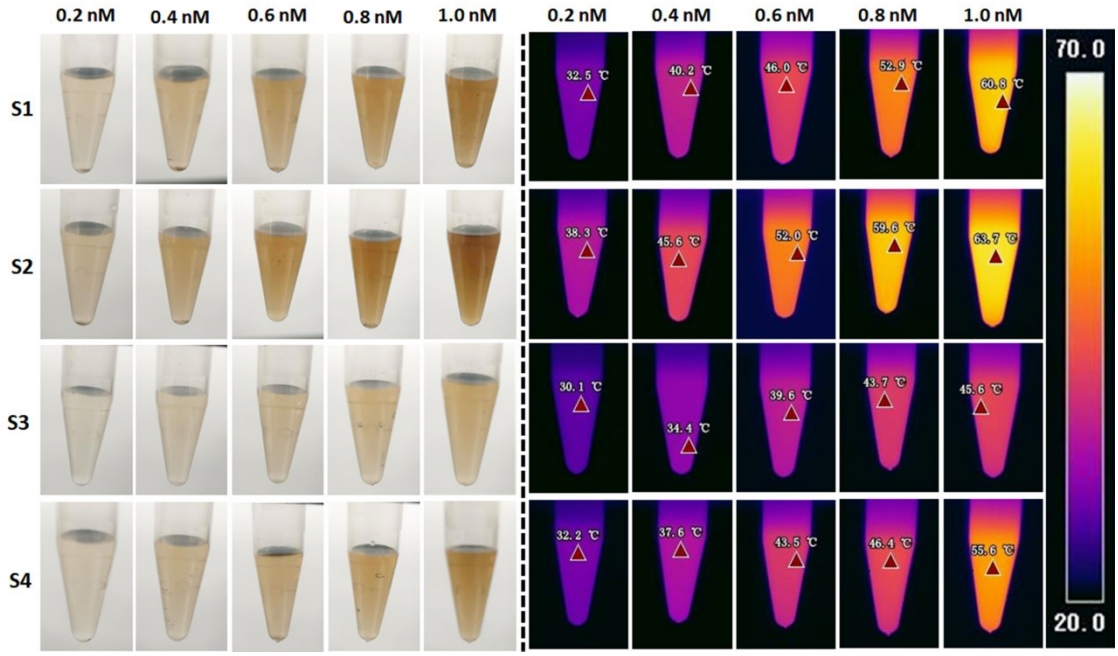

Fig. S6 Photographs of S1-S4 samples under visible light (left) and their photothermal images under 808 nm (1 W/cm^2) laser irradiation for 10 min (right) at different molar concentrations.

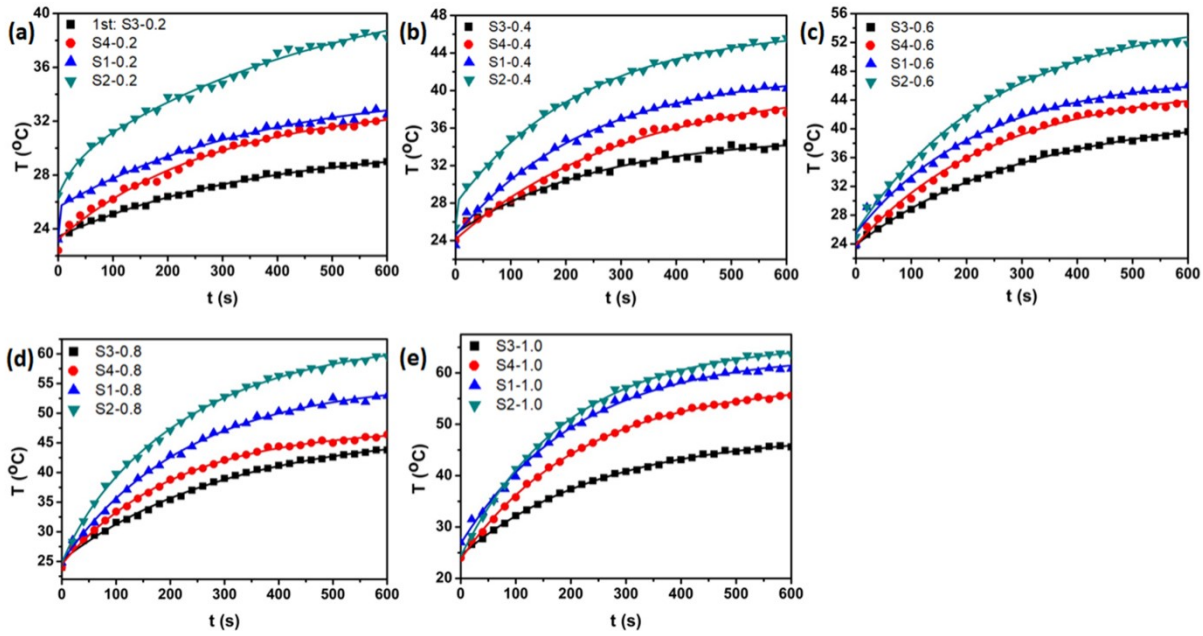

Fig. S7 Comparison of photothermal effects of S1-S4 samples at different concentrations: (a) 0.2 nM, (b) 0.4 nM, (c) 0.6 nM, (d) 0.8 nM, (e) 1.0 nM.

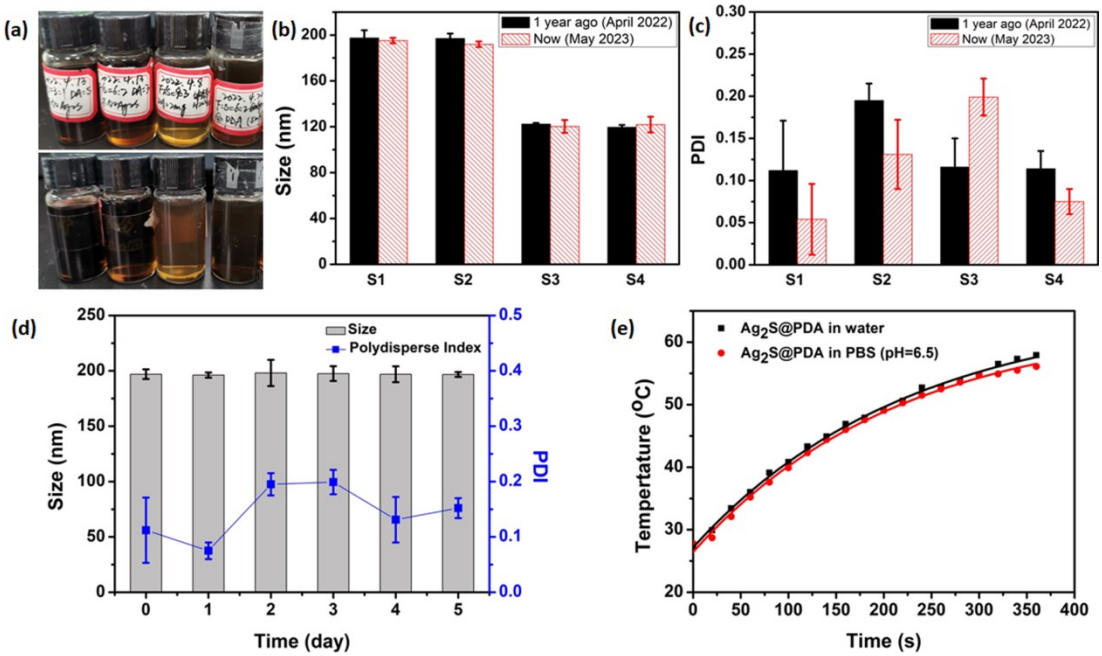

Fig. S8 (a) Digital pictures of S1-S4 samples in water (the top photo is taken from the front and the bottom is from back): S1 - big PDA particles; S2 - big Ag_2S@PDA nanohybrids; S3 - small PDA particles; S4 - small Ag_2S@PDA nanohybrids. Size comparison (b) and PDI (c) of S1-S4 samples measured in April 2022 and May 2023, respectively. (d) Size and PDI of big-sized Ag_2S@PDA nanohybrids in PBS (pH=6.5). (e) Temperature elevations of big-sized Ag_2S@PDA

in original aqueous solution and in PBS (pH=6.5) after 5 days, respectively. The irradiation by 808 nm laser at 1 W/cm^2 was used. All data were obtained after receiving the reviewers' comments (one year has passed since the preparation of the sample).

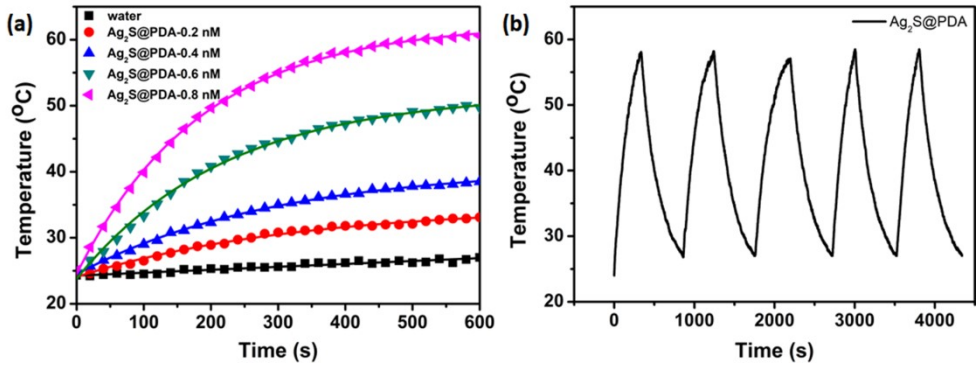

Fig. S9 (a) Temperature elevations of big-sized Ag_2S@PDA nanohybrids with different molar concentration under 808 nm (1 W/cm^2) laser irradiation. (b) Photothermal stability of big-sized Ag_2S@PDA nanohybrids (0.8 nM) over five cycles of heating-cooling processes upon 808 nm (1 W/cm^2) laser irradiation. These data were tested after receiving the reviewers' comments (one year has passed since the preparation of the sample).

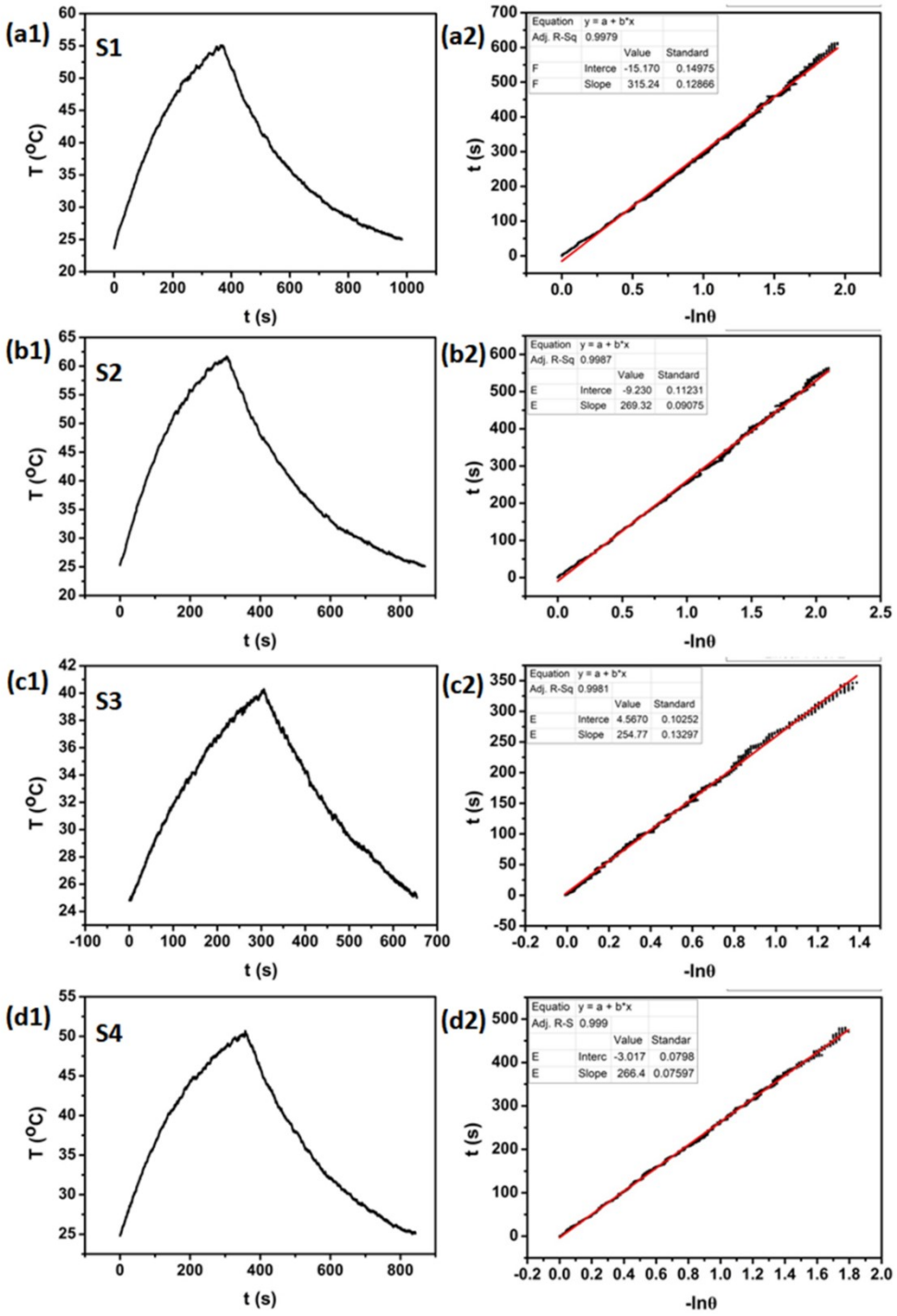

Fig. S10 The heating-cooling curves of S1-S4 samples (a1-d1) underwent once switch on-off under 808 nm (1 W/cm^2) laser irradiation. Time versus -lnθ plots (with θ being the driving force temperature) obtained using the data recorded during the cooling periods (a2-d2).

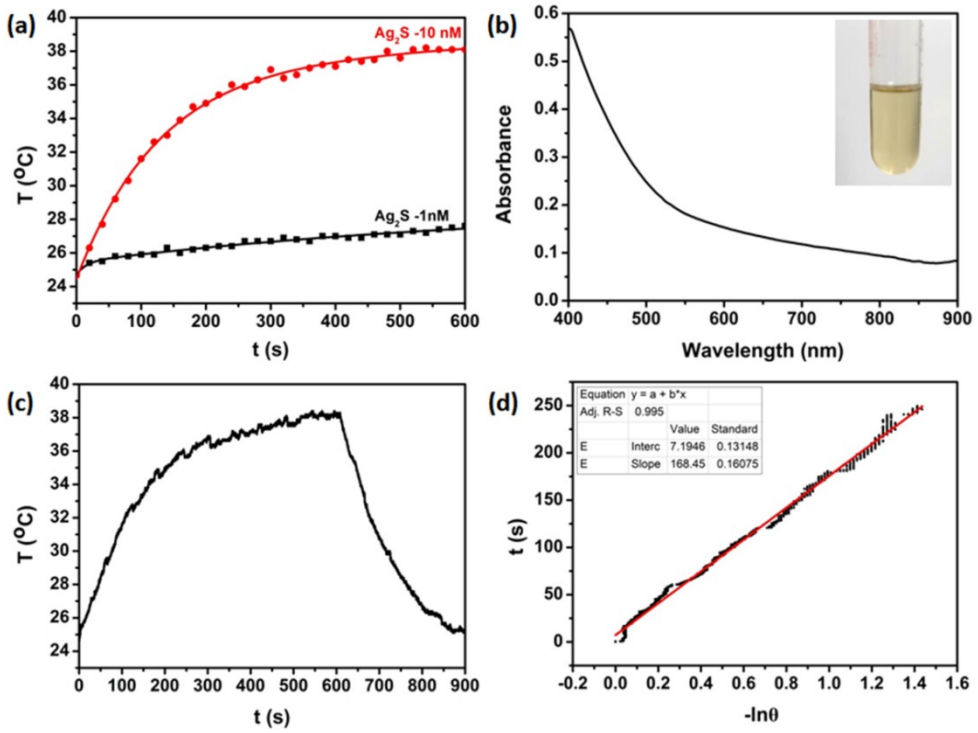

Fig. S11 (a) Photothermal heating curves of SDS-Ag_2S nanoparticles with concentrations of 1.0 and 10 nmol L^{-1} under 808 nm (1 W/cm^2) laser irradiation for 10 min. (b) The visible-NIR absorption spectrum of SDS-Ag_2S nanoparticles at 10 nM (upper right corner is the digital photograph of the sample). (c) The heating-cooling curve of SDS-Ag_2S nanoparticles (10 nM) underwent once switch on-off under 808 nm (1 W/cm^2) laser irradiation. (d) Time versus -lnθ plot obtained using the data recorded during the cooling period in (c).

Table S6 Average *CI* interval and interaction evaluation of combined compound

Average CI interval	Level of interaction
$CI < 0.1$	＋＋＋＋＋
$0.1 < CI < 0.3$	＋＋＋＋
$0.3 < CI < 0.7$	＋＋＋
$0.7 < CI < 0.85$	＋＋
$0.85 < CI < 0.90$	＋
$0.90 < CI < 1.10$	±
$1.10 < CI < 1.20$	－
$1.20 < CI < 1.45$	－－
$1.45 < CI < 3.30$	－－－
$3.30 < CI < 10$	－－－－
$CI > 10$	－－－－－

Note: “＋” and “－” represent the synergistic effect and antagonistic effect, respectively.

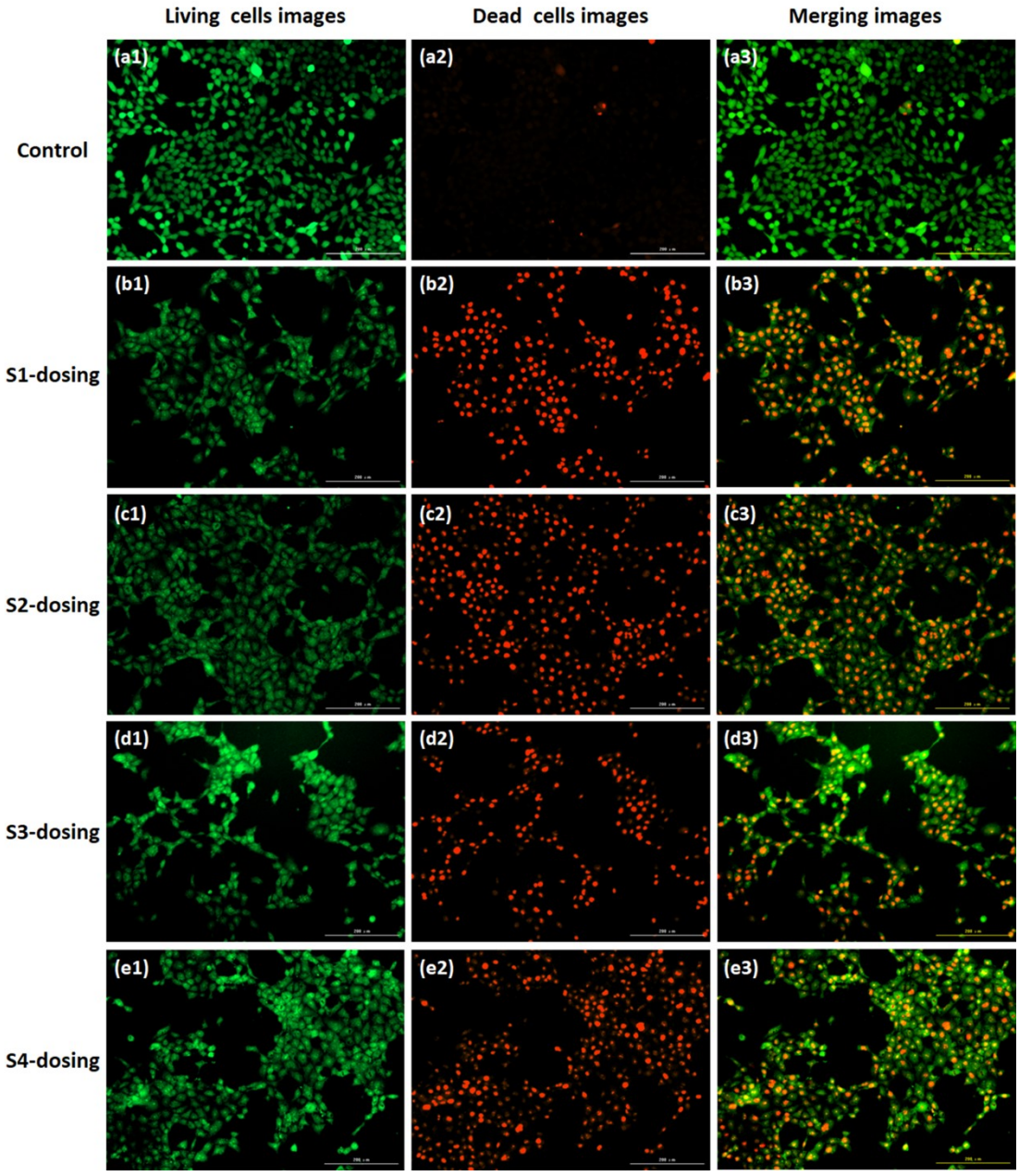

Fig. S12 Fluorescence images of 4T1 cells after calcein-AM/PI double staining: (a) control group; (b) dosing group by 1.0 nM S1 sample; (c) dosing group by 1.0 nM S2 sample; (d) dosing group by 1.0 nM S3 sample; (e) dosing group by 1.0 nM S4 sample. All samples were irradiated by 808 nm (1 W/cm^2) laser for 10 min before imaging. All scale bars are 200 μm.