

Supporting Information

Synthesis and properties of hollow Fe₃O₄@Au hybrid nano-structures for T₁-T₂ MR imaging and combination of magnetic and photo-induced heating

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Table S1. Influence of synthesis conditions on the Fe₃O₄ particle size.

Fe(acac) ₃ (mM)	OA (mM)	OLA (mM)	OCD-ol (mM)	T (°C)	T (min)	Size (nm)
190	744	744	300	295	10	3.4 ± 0.5
					30	6.7 ± 0.7
					60	8.1 ± 0.7
					120	13.9 ± 1.1
190	558	558	300	295	60	6.3 ± 0.9
	744	744			60	8.1 ± 0.7
	930	930			14.7 ± 1.3	
190	744	744	300	295	30	6.7 ± 0.7
673					7.2 ± 0.9	
920					14.3 ± 1.5	

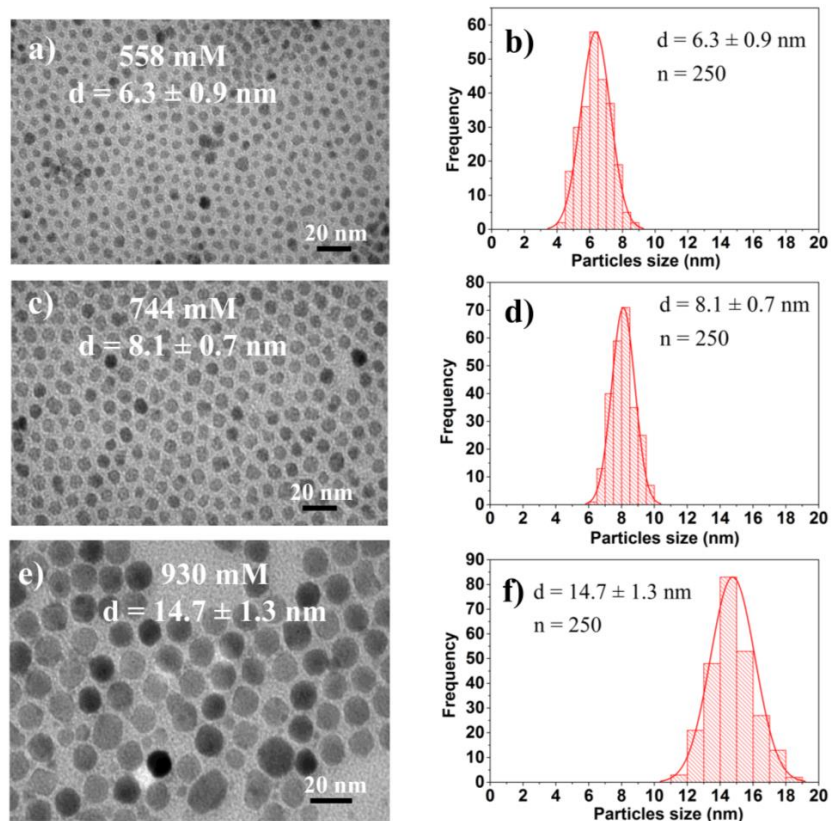


Fig. S1 TEM images and their corresponding size distribution histograms of Fe_3O_4 nanoparticles synthesised with different surfactant concentrations: 558 mM (a, b), 744 mM (c, d), 930 mM (e, f).

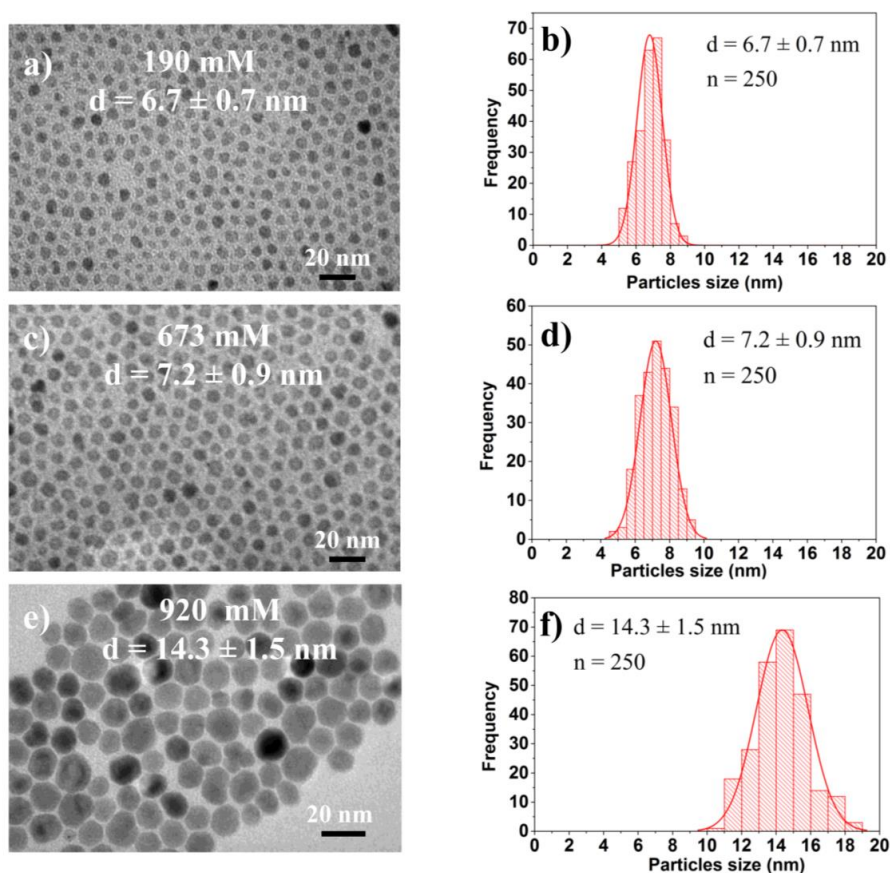


Fig. S2 TEM images and their corresponding size distribution histograms of Fe_3O_4 nanoparticles synthesised with different precursor concentrations: 190 mM (a, b), 673 mM (c, d), 920 mM (e, f).

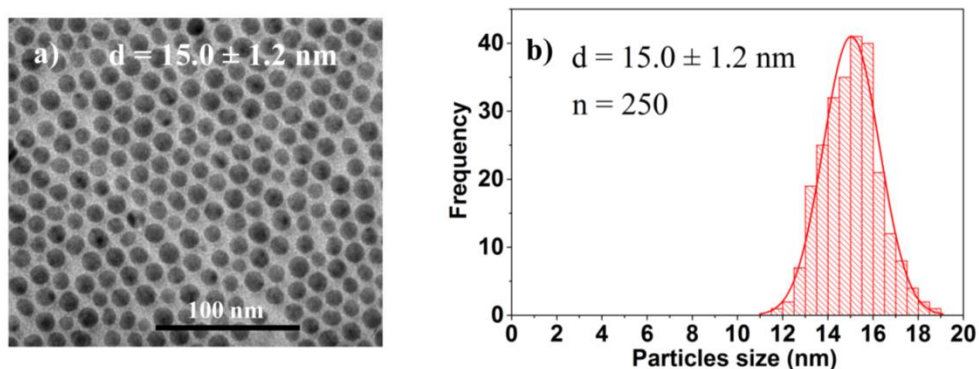


Fig. S3 TEM image and size distribution histogram of Ag nanoparticles synthesised under similar conditions but without Fe_3O_4 NPs at reaction time of 60 min.

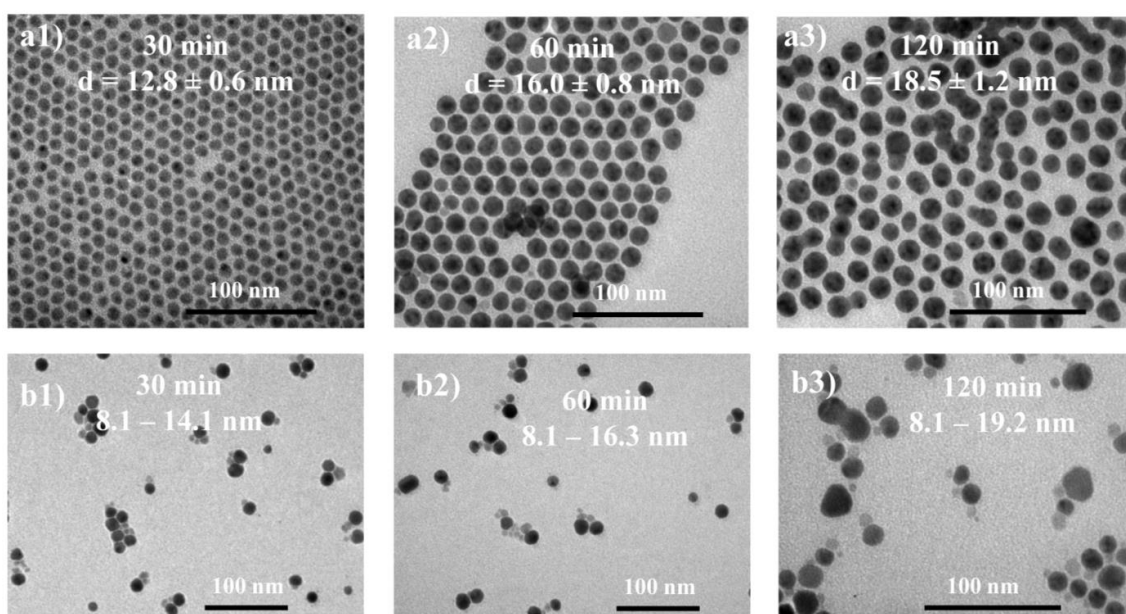


Fig. S4 TEM images of HNP synthesised with Fe_3O_4 seeds of 8.1 nm at different reaction times: (a1-a3) core-shell Fe_3O_4 @Ag HNPs and (b1-b3) dumbbell-like Fe_3O_4 -Ag HNPs.

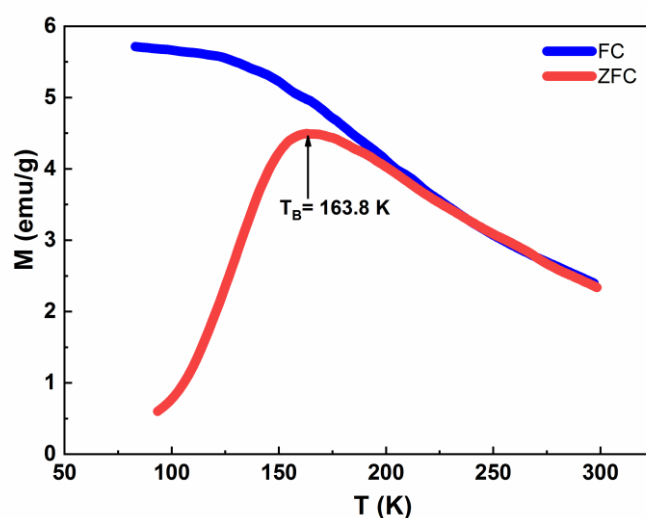


Fig. S5 Temperature dependence of magnetization (in ZFC and FC regimes at a magnetic field of 8 kA/m) for Fe_3O_4 NPs (8.1 ± 0.7 nm).

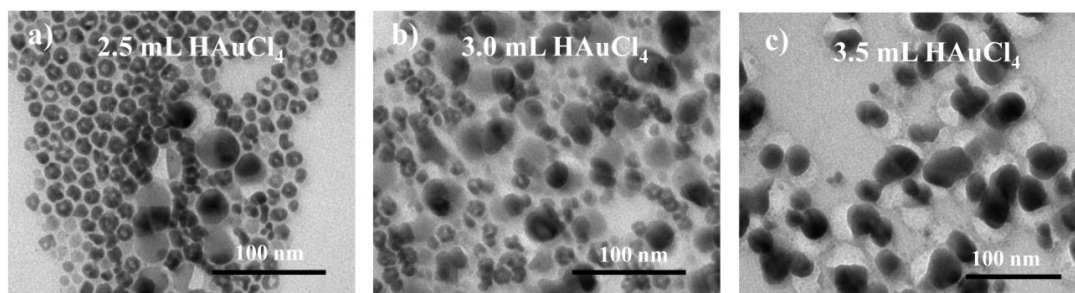


Fig. S6 TEM images of $\text{Fe}_3\text{O}_4@Au$ h-NPs prepared at different HAuCl_4 solution volumes: 2.5 (a), 3.0 (b) and 3.5 mL (c) showing the formation of solid NPs.

Table S2. Effect of the amount of HAuCl_4 solution on the size and morphology of h-NPs.

The volumes of HAuCl_4 solution (mL)	The particle size (nm)	Morphology
0	16.0 ± 0.8	Solid sphere ($\text{Fe}_3\text{O}_4@Ag$ templates)
0.5	16.1 ± 0.8	Solid sphere
1.0	16.4 ± 0.9	Hollow sphere
1.5	16.6 ± 1.0	Hollow sphere
2.0	17.0 ± 1.1	Hollow sphere
2.5	18.8 ± 2.1	Hollow sphere and solid sphere
3.0	26.3 ± 3.4	Hollow sphere and solid sphere
3.5	33.2 ± 5.7	Solid sphere

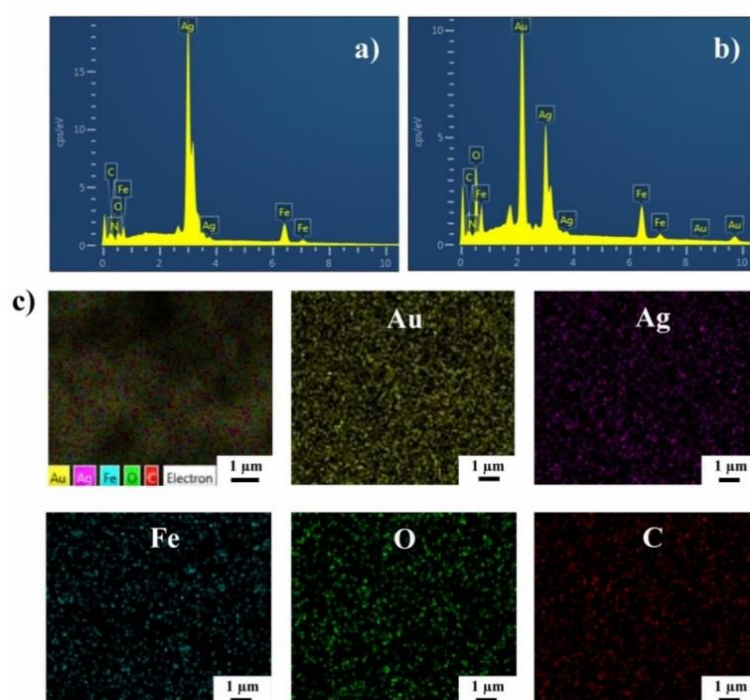


Fig. S7. EDS spectra of $\text{Fe}_3\text{O}_4@Ag$ nanotemplates (a) and hollow $\text{Fe}_3\text{O}_4@Au$ h-NPs (b); and EDS elemental mapping of hollow $\text{Fe}_3\text{O}_4@Au$ h-NPs (c) prepared at 2.0 mL HAuCl_4 solution.

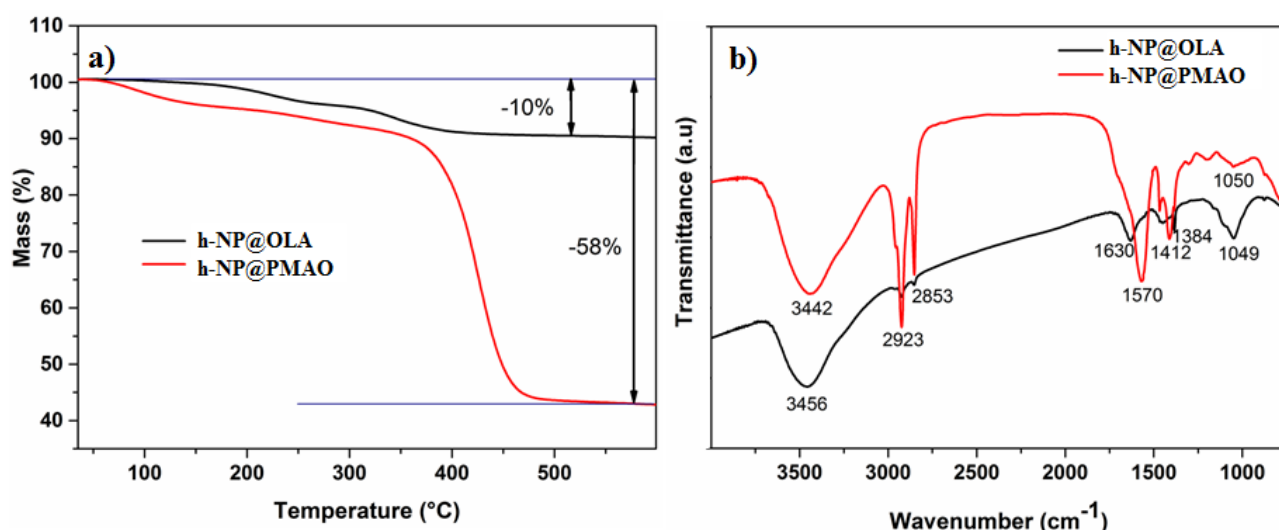


Fig. S8. a) TGA scans and b) FT-IR spectra of OLA and PMAO encapsulated hollow $\text{Fe}_3\text{O}_4@Au$ h-NPs.

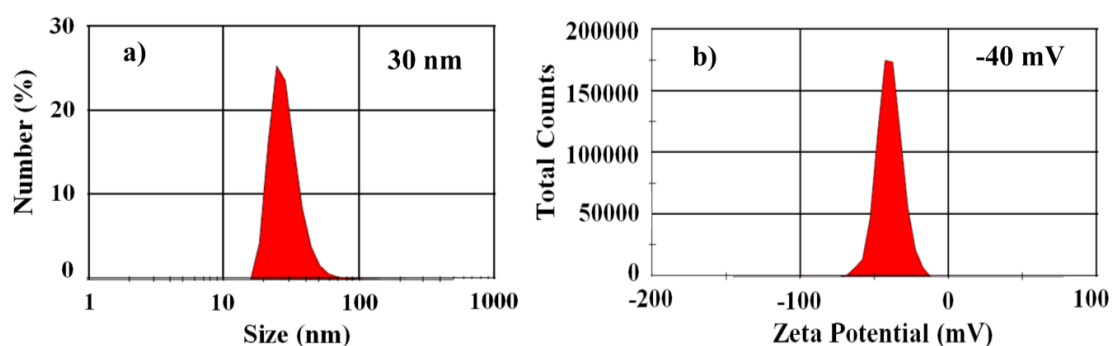


Fig. S9 Hydrodynamic size distribution (a) and zeta potential (b) of PMAO encapsulated hollow $\text{Fe}_3\text{O}_4@Au$ HNPs.

Table S3. MRI relaxivities of the commercial gadolinium-(GBCAs), iron oxide nanoparticle-based contrast agents and the hollow $\text{Fe}_3\text{O}_4@Au$ h-NPs.

Brand Name	Ligand shell/Generic Name (INN)	Core size (nm)	Overall size (nm)	r_1 ($\text{mM}^{-1} \text{s}^{-1}$)	r_2 ($\text{mM}^{-1} \text{s}^{-1}$)	r_2/r_1	Company/refs
Hollow $\text{Fe}_3\text{O}_4@Au$ h-NPs	PMAO	17.0	28.84	8.47	74.45	8.79	Current study
Dotarem®	Gadoterate meglumine (Gd-DOTA)	-	-	3.6 (3.4-3.8)	4.3 (3.4-5.2)	1.19	Belgium for Guerbet ¹
Magnevist®	Gadopentetate dimeglumine (Gd-DTPA)	-	-	4.1 (3.9-4.3)	4.6 (3.8-5.4)	1.12	Bayer Schering (Germany) ¹
MultiHance®	Gadobenate dimeglumine (Gd-BOPTA)	-	-	6.3 (6.0-6.6)	8.7 (7.8-9.6)	1.38	Bracco ¹
Omniscan®	Gadodiamide (Gd-DTPA BMA)	-	-	4.3 (4.0-4.6)	5.2 (4.2-6.2)	1.21	GE Healthcare ¹
ProHance®	Gadoteridol (Gd-HPDO3A)	-	-	4.1 (3.9-4.3)	5.0 (4.2-5.8)	1.22	Bracco ¹

Gadovist®	Gadobutrol (Gd-DO3A-butrol)	-	-	5.2 (4.9–5.5)	6.1 (5.2–7.0)	1.17	Bayer Schering (Germany) ¹
Teslascan®	Mangafodipir trisodium (Mn- DPDP)	-	-	1.6 (1.5–1.7)	2.1 (1.4–2.8)	1.31	Amersham ¹
Ferumoxtran (Sinerem)	Dextran + citrate	4.5	34	5.0	66.0	13.2	²
VSOP-C184	Citrate	8.6	19	8.0	34	4.25	³
Ferumoxytol®	Dextran (C7228)	6.7	35	7.5	92	12.26	AMAG Pharma- ceutical Inc ⁴
Resovist®	Ferucarbotran (SHU 555 A) Carboxydextran		60	7.4	151	20.40	Schering ¹
Feridex/Endore m®	Ferumoxide (AMI-25) Dextran	4.5	160	10.1	120	11.88	Berlex/Guer bet ⁵
Ferucarbotran®/ Supravist	Ferucarbotran (SHU555C) Dextran	3-5	21	7.3	57	7.81	Schering ⁶
PEG (5) – BP - USPIO	PEG- bisphosphonate ^b	5.5	23	9.5 (3.0 T)	28.2 (3.0 T)	2.97	³
ESION	PEG-phosphine oxide (γ -Fe ₂ O ₃)	2.2	15	4.8 (3.0 T)	29.2 (3.0 T)	6.08	⁷
USPIO	PEG-phosphine oxide (Fe ₃ O ₄)	12	-	2.37 (3.0 T)	58.8 (3.0 T)	24.81	⁷
GdIO	Dopaminesulfona te Fe ₃ O ₄ +Gd ₂ O ₃	4.8	6.50	7.85 (0.5 T)	41.14 (0.5 T)	5.24	⁸
MnMEIO	2,3- dimercaptosuc- cnic acid (DMSA) MnFe ₂ O ₄	12	-	-	358	-	⁹
NiMEIO	2,3- dimercaptosuc- cnic acid (DMSA) NiFe ₂ O ₄	-	-	-	152	-	⁹
Au-Fe ₃ O ₄ heterodimer	-	-	30.4	-	245 (3.0T), 723 HU at 100 mM Au	-	¹⁰
F-AuNC@ Fe ₃ O ₄	Au nanocages Folic acid functionalized	2.2	110	6.26	28.11	4.49	¹¹

^b1,2-distearoyl-sn-glycero-3-phosphoethanolamine-N-[methoxy(polyethylene glycol)-2000].

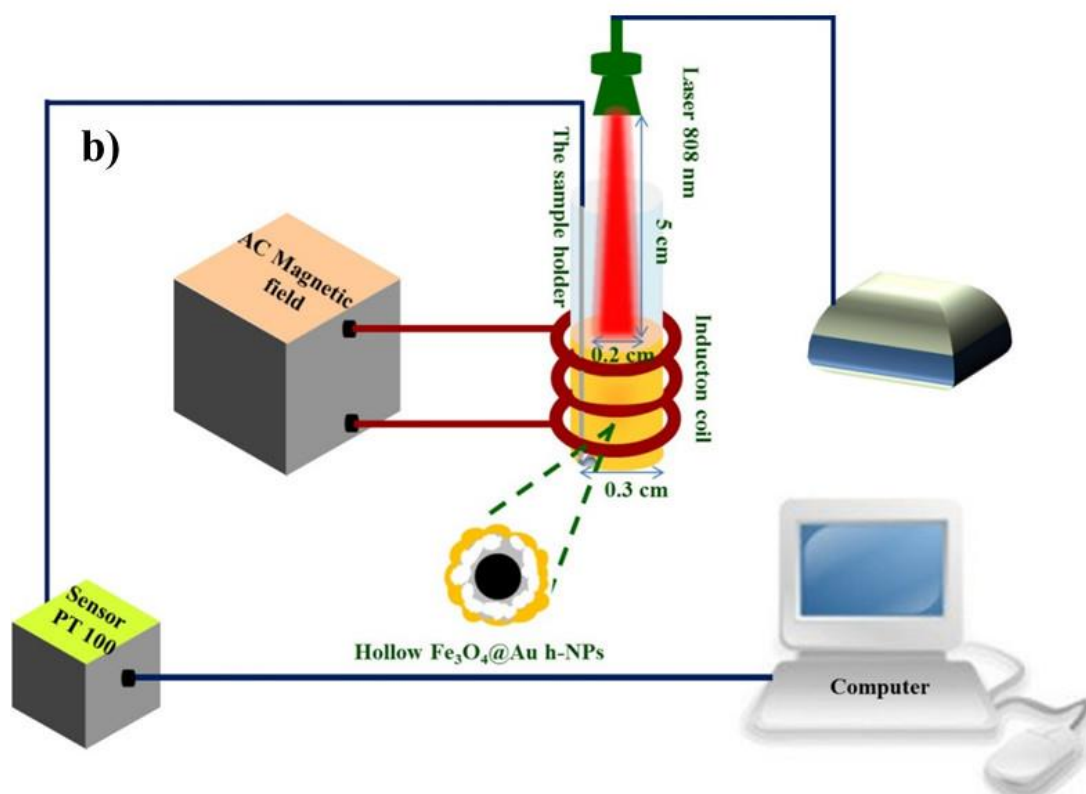


Fig. S10 The magnetic and photoinduced heating experiment (a) and schematic diagram (b)

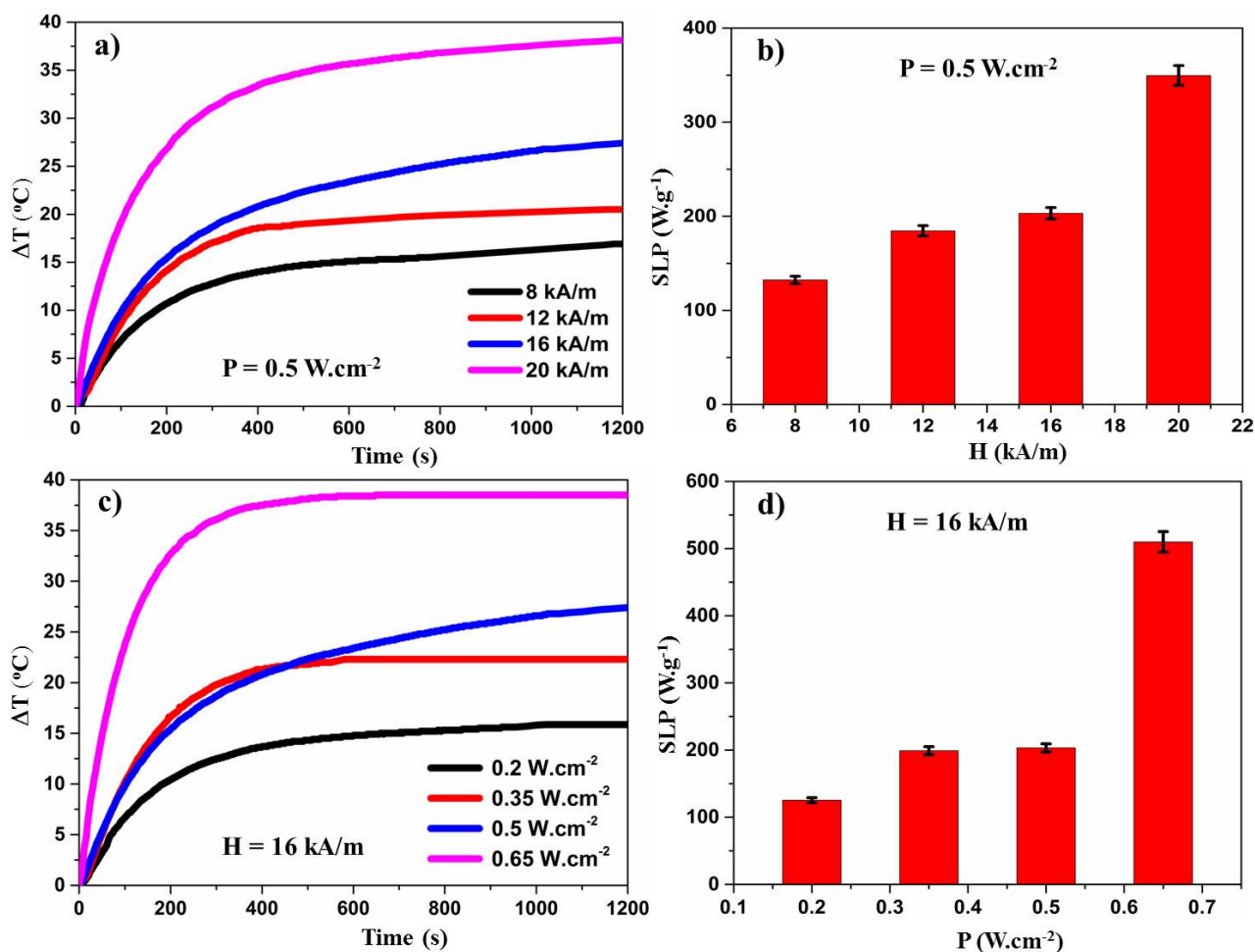


Fig. S11 The heating curves (a), and the corresponding SLP values (b) for the hollow $\text{Fe}_3\text{O}_4@Au$ h-NPs solutions under different applied fields (from 8 to 20 kA/m) at a constant frequency of 450 kHz and a laser power density 0.5 W.cm^{-2} . The heating curves (c), and the corresponding SLP values (d) for the h-NPs solution under a constant applied field of 16 kA/m at a frequency 450 kHz and different power densities (from 0.2 to 0.65 W.cm^{-2}).

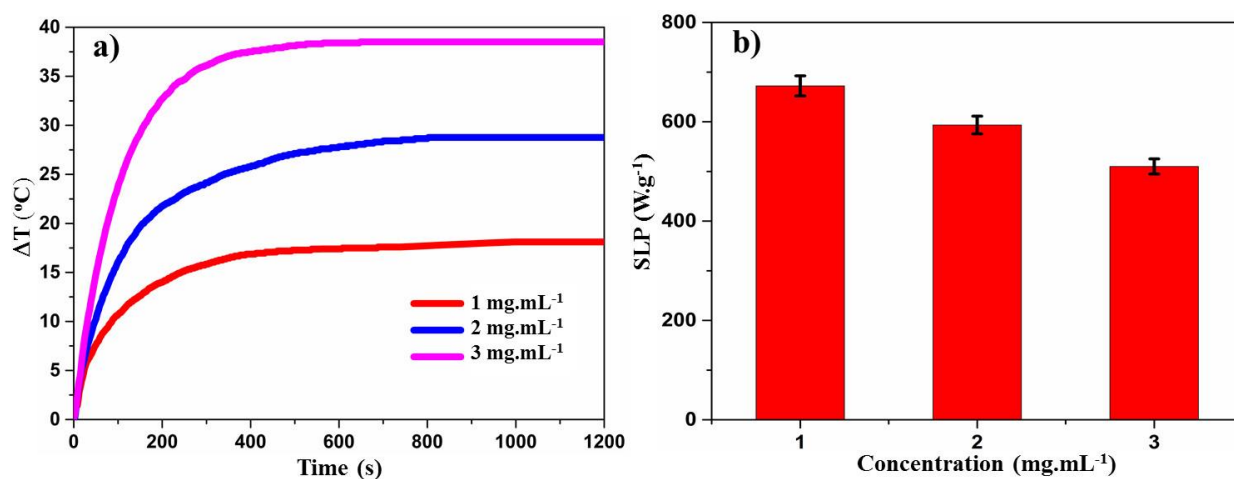


Fig. S12 The heating curves (a), and the corresponding SLP values (b) for the hollow $\text{Fe}_3\text{O}_4@Au$ h-NPs solutions at different concentrations under an applied field of 16 kA/m at a frequency 450 kHz and a laser power density 0.65 W.cm^{-2} .

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