Supporting Information

Eumelanin-Fe_3O_4 hybrid Nanoparticles for Enhanced MR/PA Imaging - assisted Local Photothermolysis

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†Electronic Supplementary Information (ESI) available.

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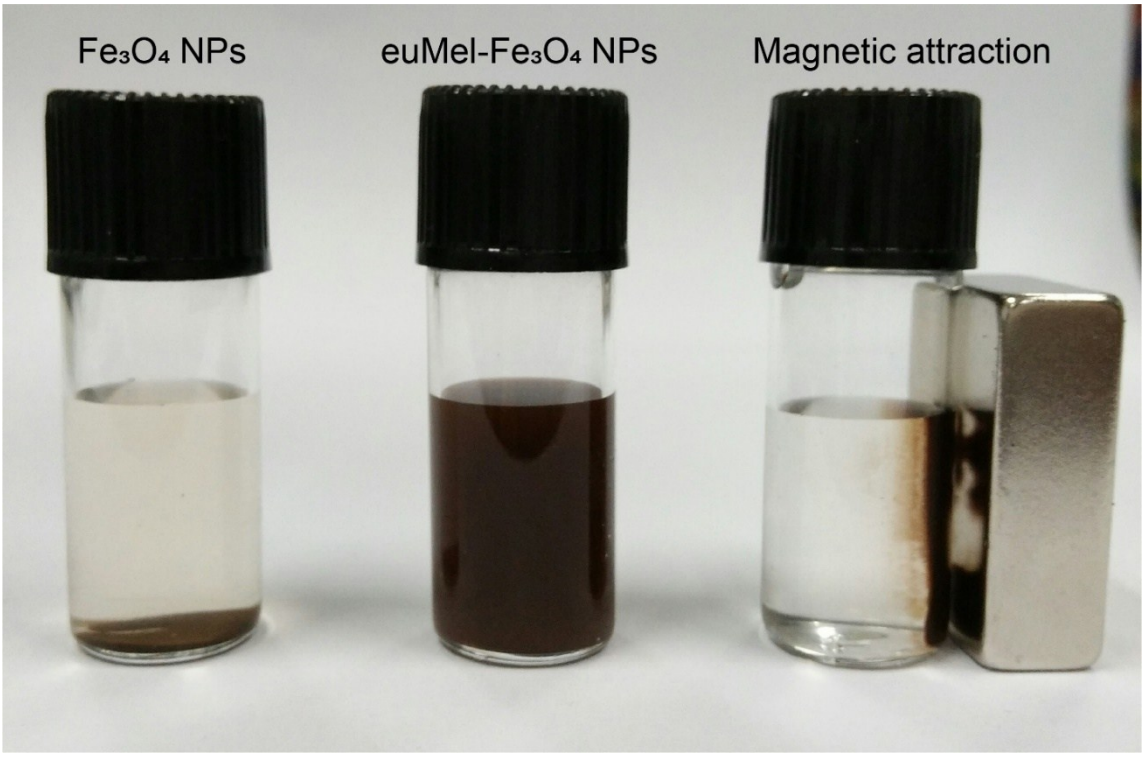

Figure S1. Photograph of precipitated pristine Fe_3O_4 NPs, as-prepared euMel-Fe_3O_4 NPs in aqueous solution after standing at room temperature for 24 h, and magnetic attraction for euMel-Fe_3O_4 NPs collection.

Table 1. Energy-dispersive X-ray (EDX) spectroscopy of euMel-Fe_3O_4 NPs.

Element	Weight %	Atomic %	Uncert. %	Correction	k-Factor
O (K)	59.23	83.53	0.82	0.51	1.889
Fe (K)	40.76	16.46	0.51	0.99	1.401

Table 2. Relative tumor volume changes after first day treatment by euMel-Fe_3O_4 NPs.

Day	Control		NPs only		Laser only		NPs+Laser
1	1	SD	1	SD	1	SD	1
3	1.29558	0.18036	1.44259	0.09925	1.31351	0.10561	0
5	1.73621	0.00264	2.166	0.18211	1.44076	0.15937	0
7	2.35275	0.00809	2.48301	0.0347	1.85108	0.33449	0
9	2.78191	0.20528	2.75106	0.35605	2.28814	0.30636	0
11	3.48114	0.29323	3.17993	0.25547	2.87842	0.39979	0
13	3.82852	0.45987	3.65228	0.35834	3.56133	0.54166	0
15	4.32365	0.54282	4.21164	0.1536	4.21825	0.39338	0

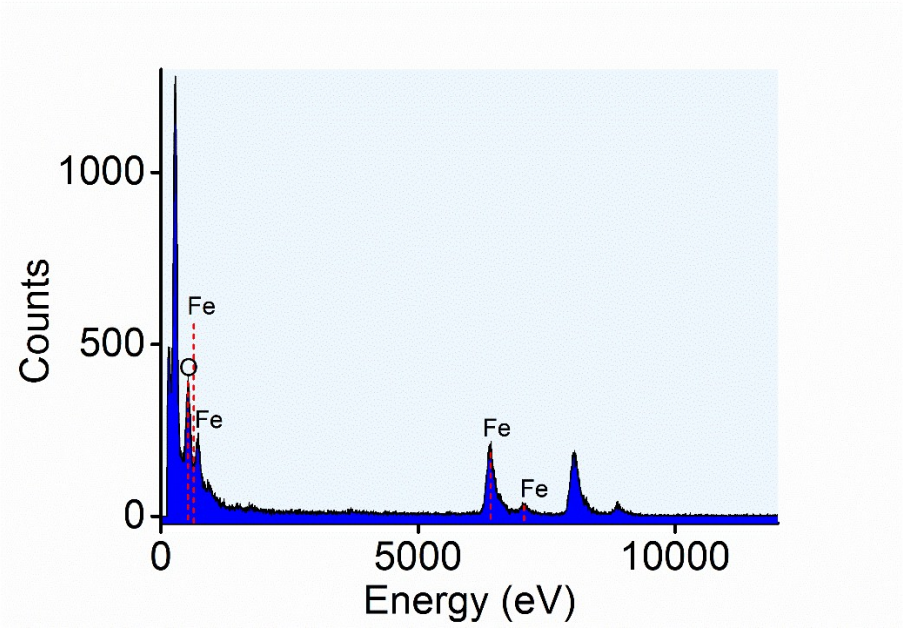

Figure S2. EDX spectrum of euMel-Fe_3O_4 NPs.

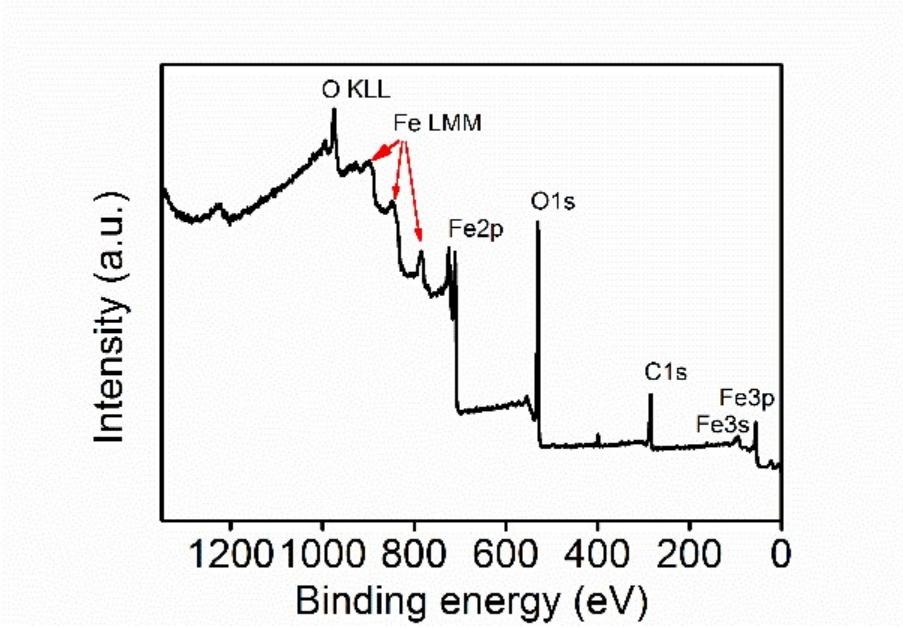

Figure S3. XPS wide scans of euMel-Fe_3O_4 NPs.

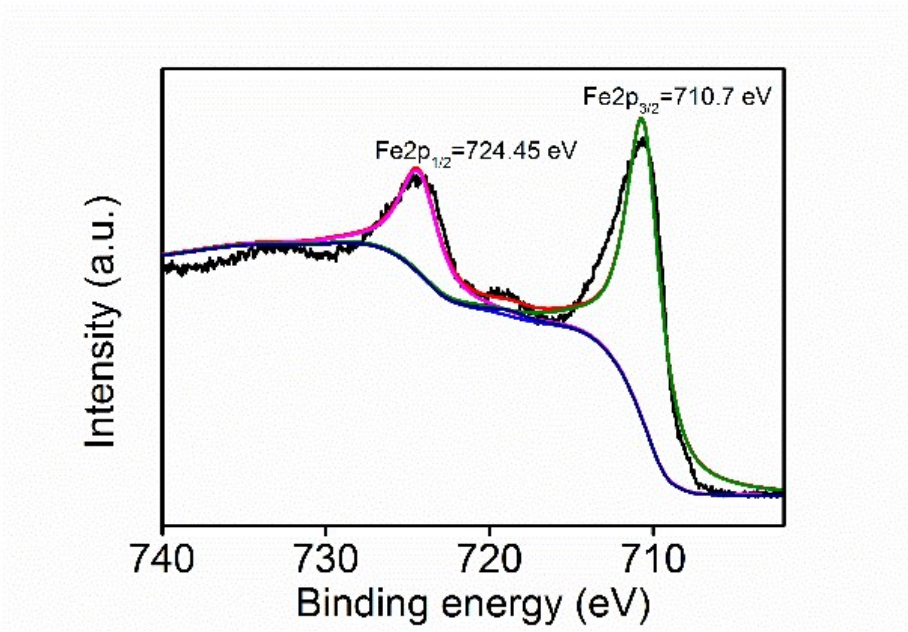

Figure S4. $Fe2p_{1/2}$ and $Fe2p_{3/2}$ spectra of euMel-Fe_3O_4 NPs.

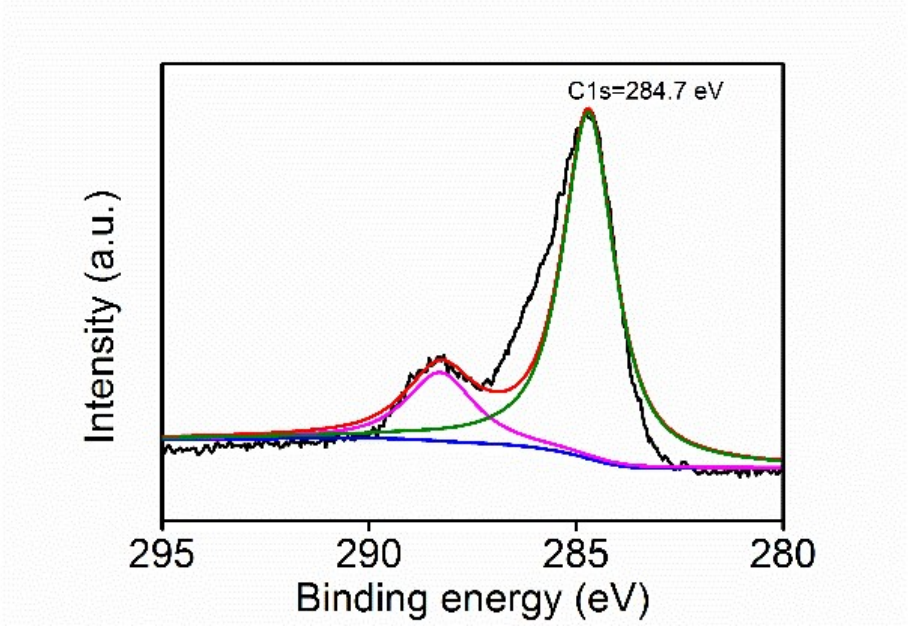

Figure S5. C1s spectrum of euMel-Fe_3O_4 NPs.

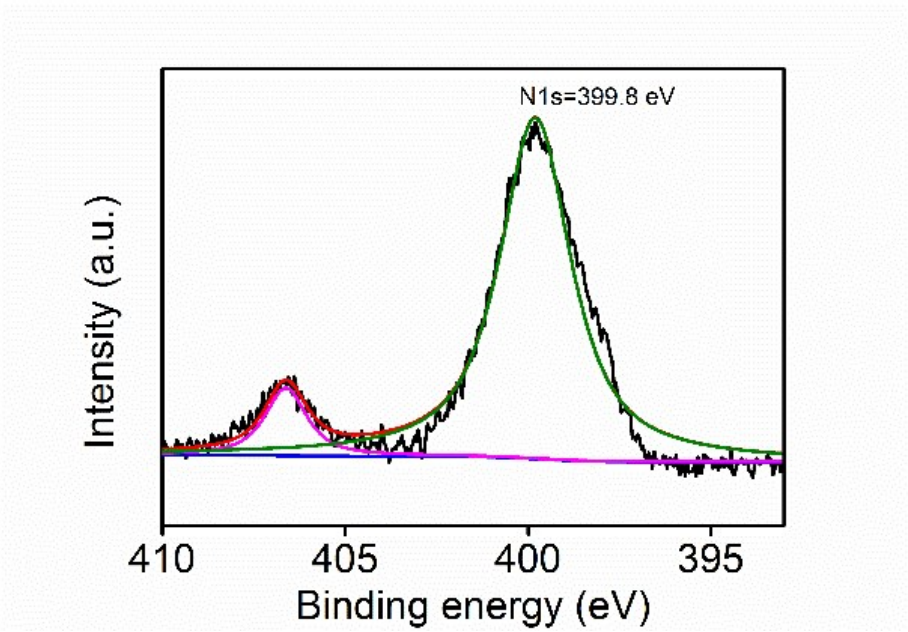

Figure S6. N1s spectrum of euMel-Fe_3O_4 NPs.

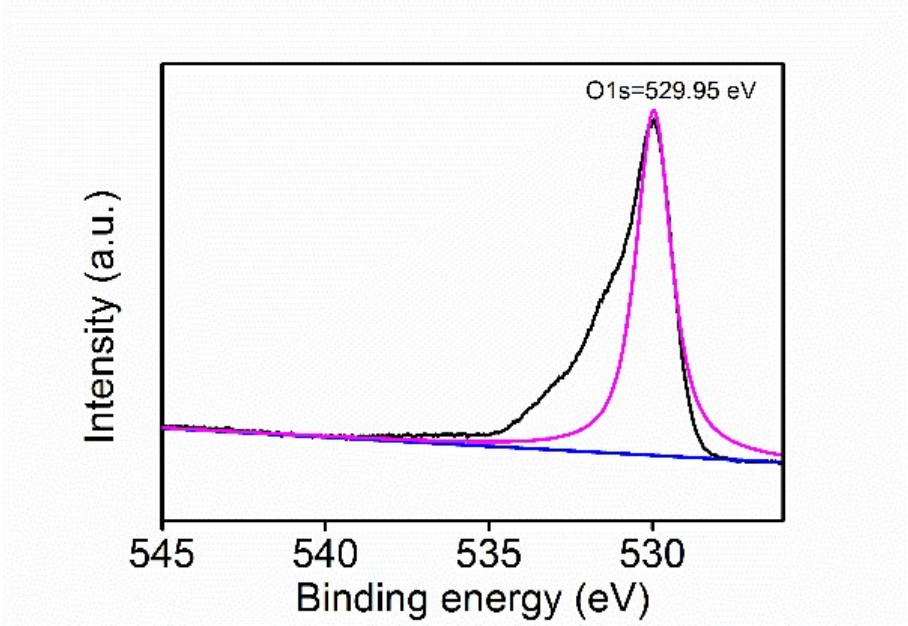

Figure S7. O1s spectrum of euMel-Fe_3O_4 NPs.

XPS analysis (**Figure S4**) showed two further peaks at 710.7 and 724.45 eV, attributed to $Fe2p_{3/2}$ and $Fe2p_{1/2}$, respectively, which is related to the magnetite in agreement with the XRD and literature results. Furthermore, the O1s spectrum (**Figure S7**) showed a peak with a binding

energy close to 529.95 eV, which is assigned to the Fe-O binding in Fe_3O_4. Besides, with respect to the carbon peak positions (C1s), a peak with a binding energy of 284.7 eV assigned to Fe-C was observed (**Figure S5**), which has the same value as a graphitic structure (aromatic ring).

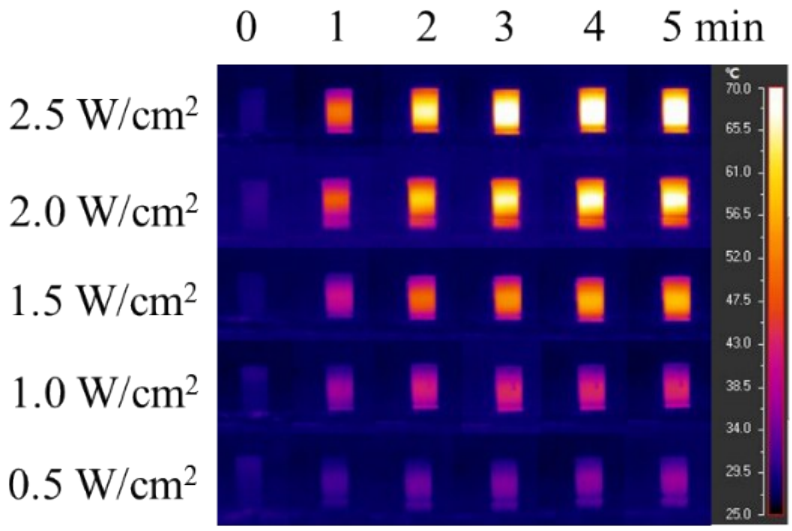

Figure S8. Infrared thermal images of euMel-Fe_3O_4 NP aqueous solution (10 mM Fe) exposed to 808 nm laser with different power densities.

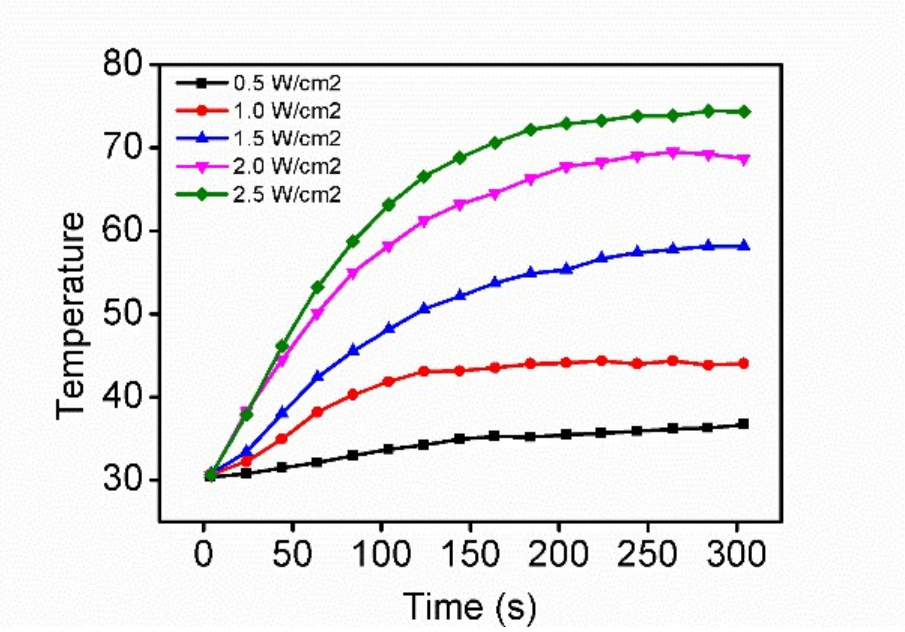

Figure S9. Temperature elevation of euMel-Fe_3O_4 NP aqueous solution (10 mM Fe) exposed to 808 nm laser with different power densities.

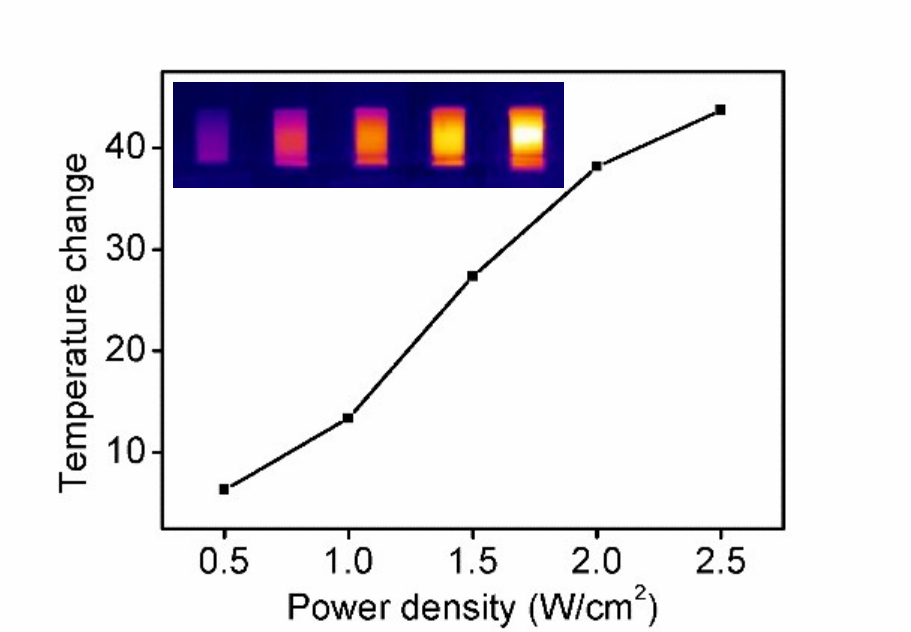

Figure S10. Plot of temperature change (ΔT) over a period of 5 min versus power densities.

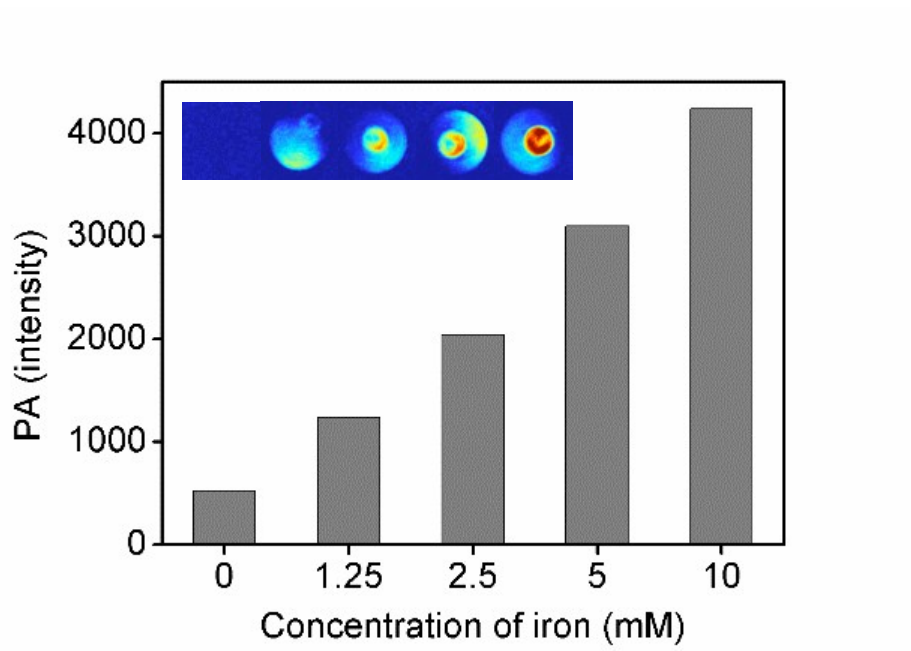

Figure S11. The linearity of PA signal intensities under 800 nm laser irradiation as a function of the concentration of euMel-Fe_3O_4 NPs.

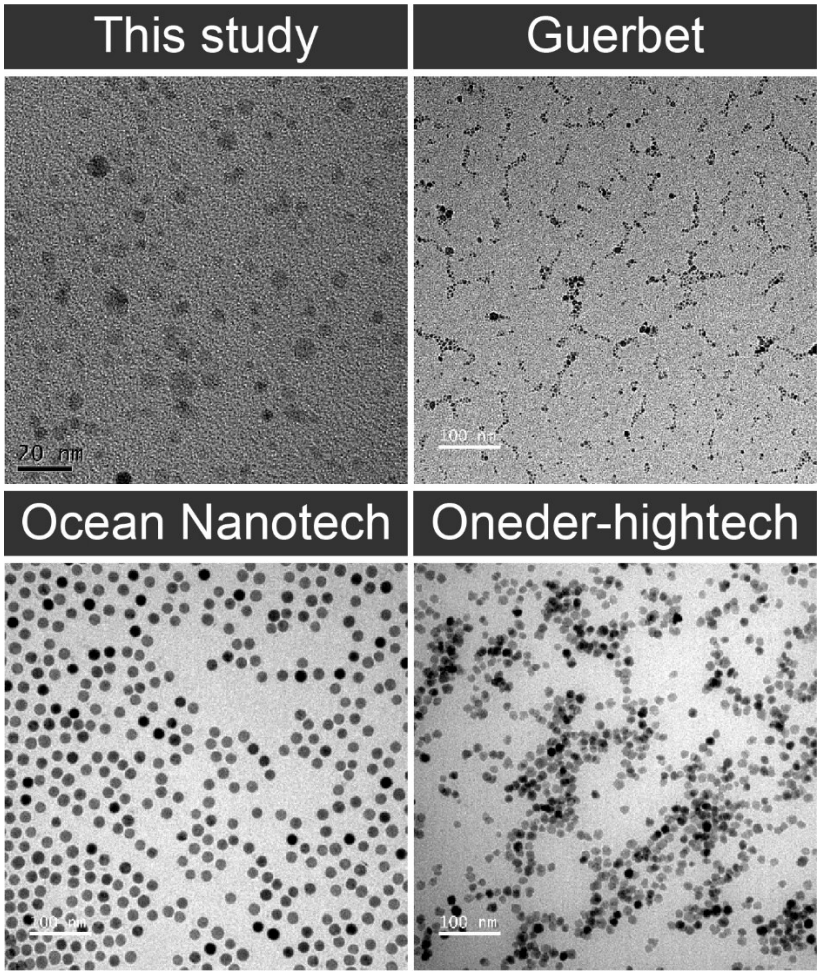

Figure S12. TEM image of euMel-Fe_3O_4 NPs and several commercially available magnetic nanoparticles at equivalent iron molar concentration (10 mM).

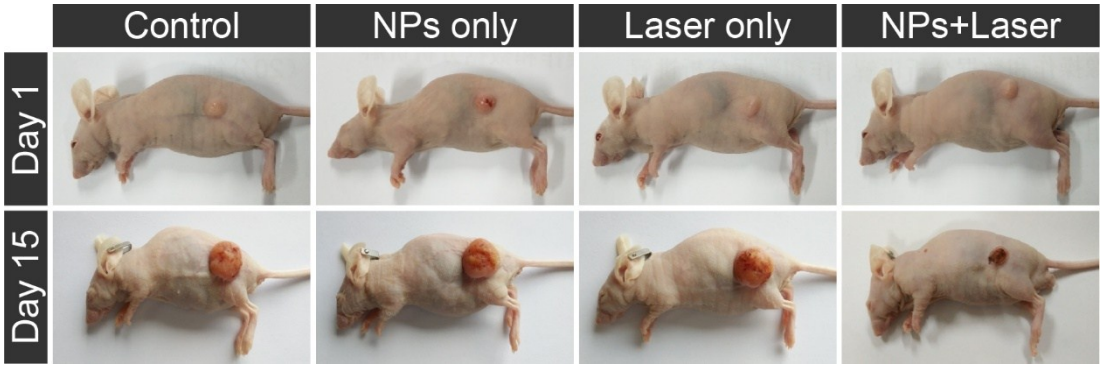

Figure S13. Representative photographs of U-87 MG tumor-bearing mice from different groups at day 1 before treatment and at day 15 after treatment.

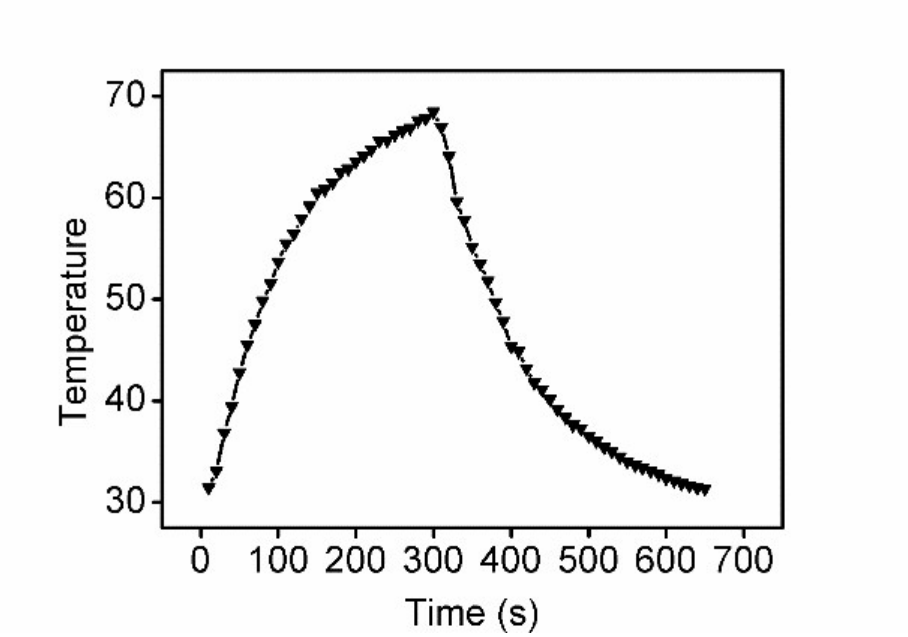

Figure S14. Photothermal heating curves of euMel-Fe_3O_4 NPs (10 mM Fe) irradiated by 808 nm NIR laser at 2 W/cm^2 over one laser on/off cycle.

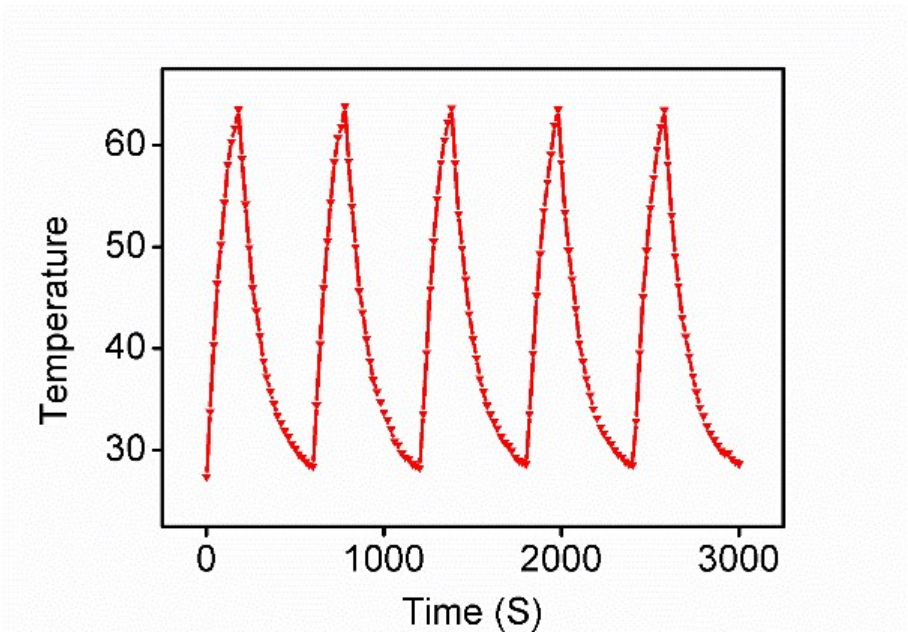

Figure S15. Photothermal heating curves of euMel-Fe_3O_4 NPs (10 mM Fe) irradiated by 808 nm laser at 2 W/cm^2 over five laser on/off cycles (on: 5 min, off: 6 min).

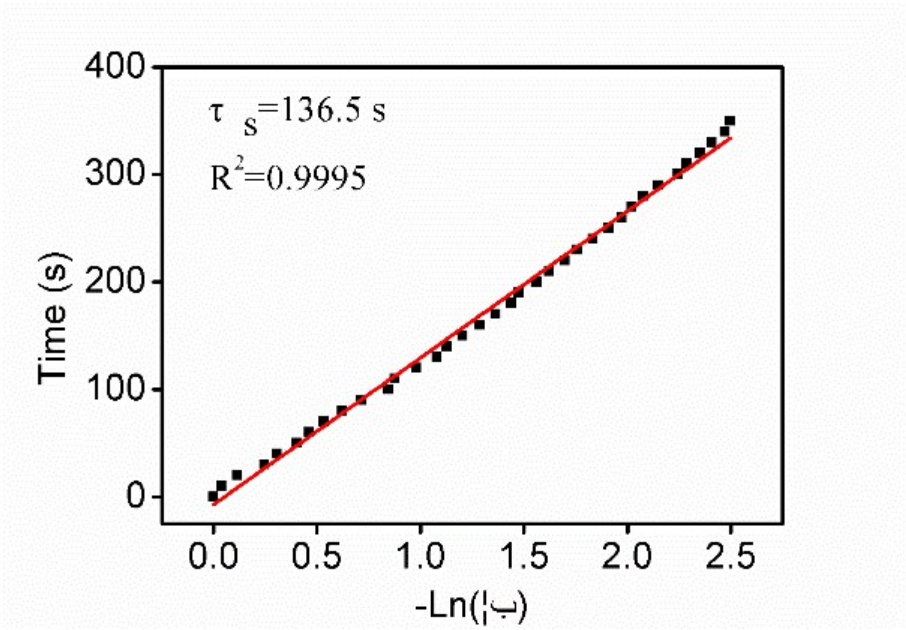

Figure S16. Linear time data versus −Lnθ obtained from the cooling period. Time constant (τs) for heat transfer was determined to be 136.5 s.

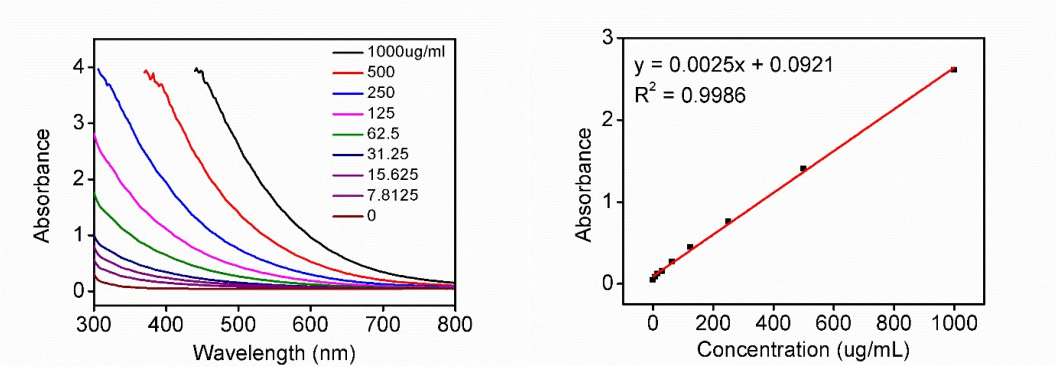

Figure S17. Standard absorbance curve of eumelanin solution at 500 nm.

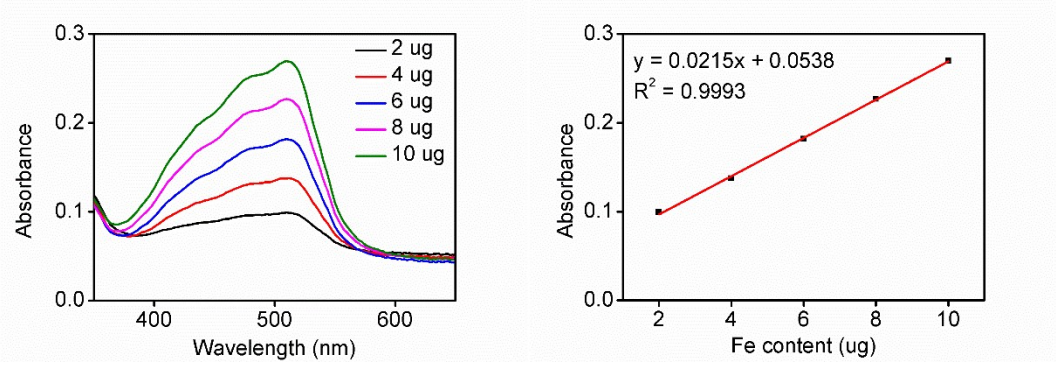

Figure S18. Standard absorbance curve of iron content at 510 nm. There were about 0.26 mg eumelanin for per mg Fe.