Electronic Supplementary Information (ESI) for

Low-work-function LaB$_6$ for realizing photodynamic-enhanced photothermal therapy

Shuanglong Tang, ‡[a] Weicheng Huang, ‡[b] Yan Gao, [a] Na An,[a] Yadong Wu,[a] Bin Yang, [b] Mei Yan *[a] Jingyan Cao*[c] and Chongshen Guo *[a]

[a] *School of Chemistry and Chemical Engineering, Harbin Institute of Technology, Harbin, 150001, China. E-mail: chongshenguo@hit.edu.cn; meiyan@hit.edu.cn.*

[b] *School of Instrumentation Science and Engineering, Harbin Institute of Technology, Harbin 150001, China*

[c] *Department of Medical Oncology, Harbin Medical University Cancer Hospital, Harbin 150001, China. E-mail: caojingyan@126.com*
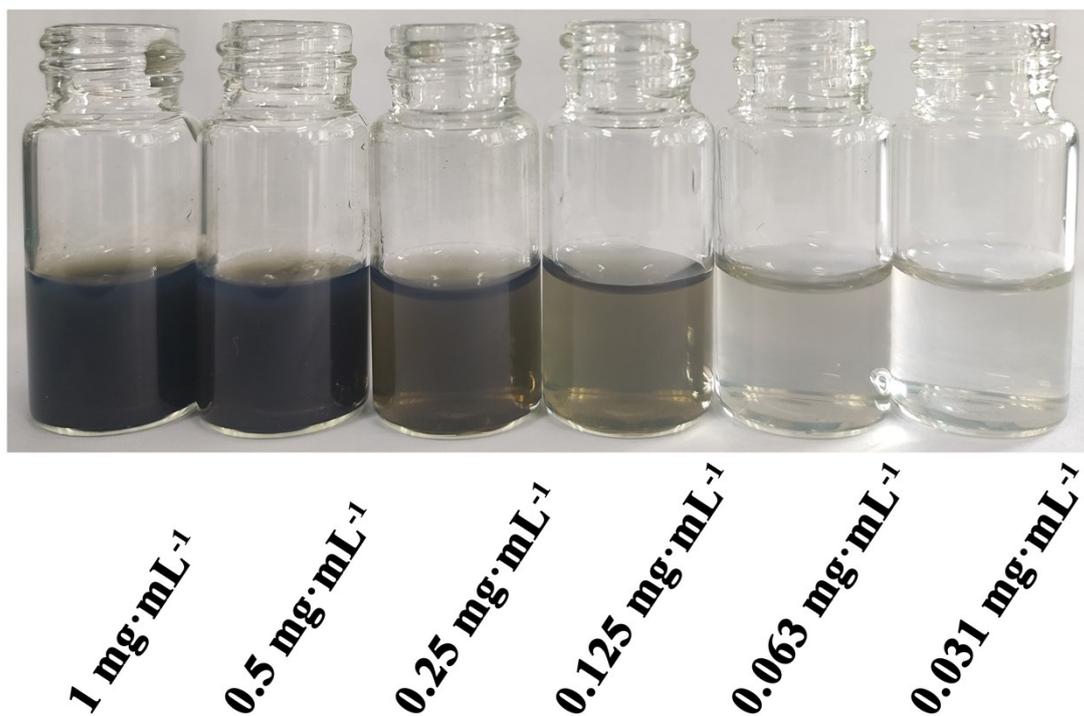
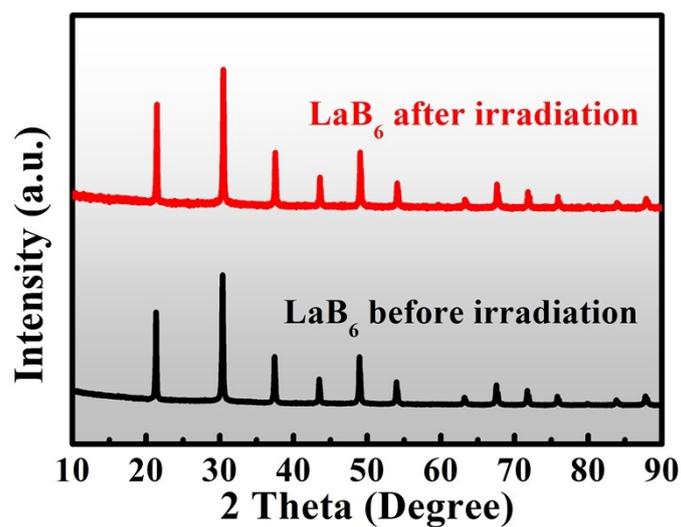**Fig. S1** Digital photo of different-concentration LaB6 aqueous dispersions.

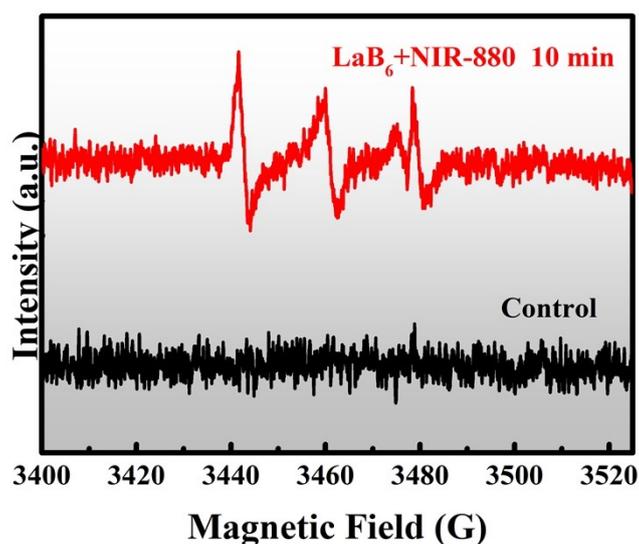**Fig. S2** XRD pattern of LaB$_6$ samples before and after NIR irradiation (3.64 W·cm^{-2}).

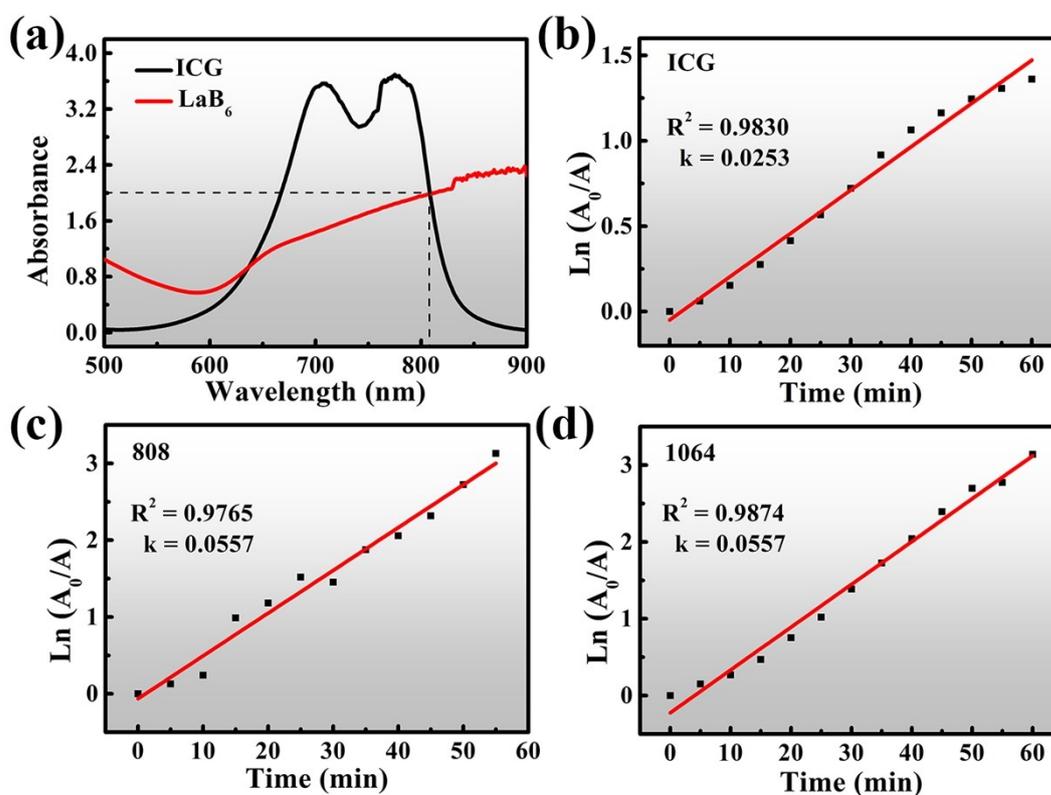**Fig. S3** ESR spectra of TEMP in the present of LaB$_6$ for $^1O_2$ detection.

Fig. S4 (a) Light absorption of ICG solution and LaB$_6$ dispersion, (b)-(d) the rate constants for DPBF decomposition by ICG at 808 nm and by LaB$_6$ at 808 nm and 1064 nm.
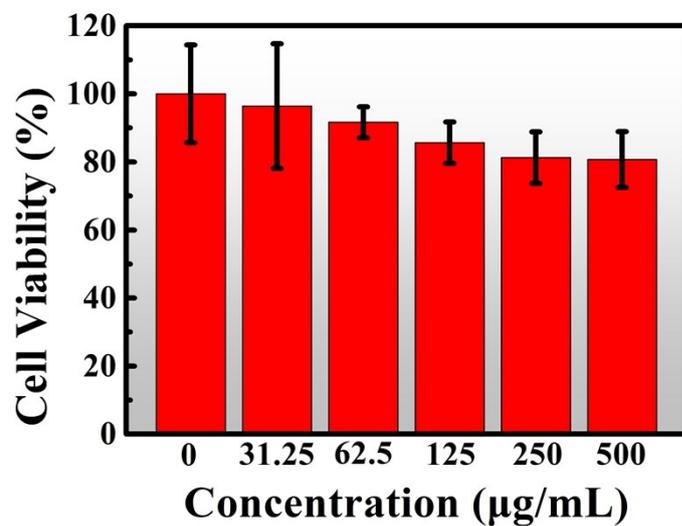
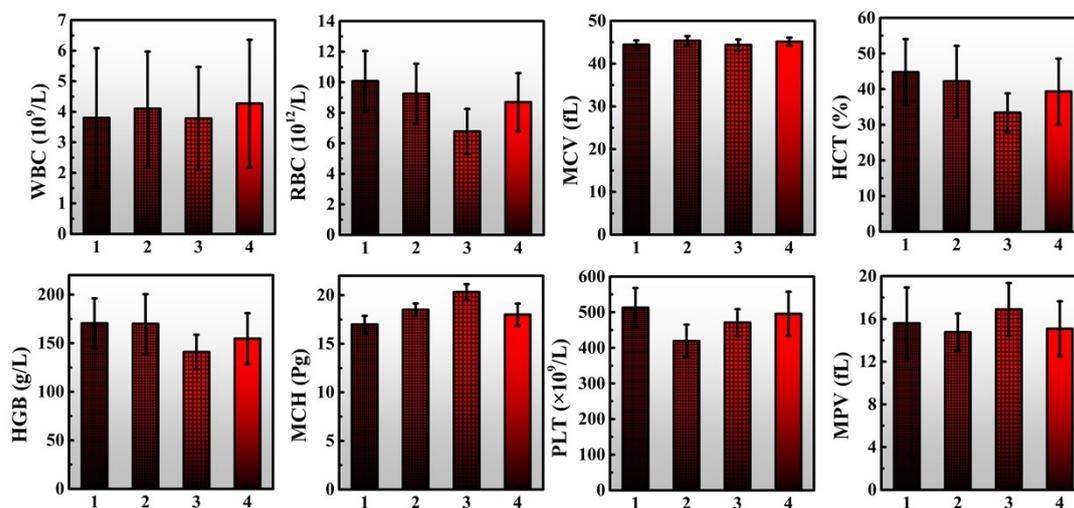**Fig. S5** Cell viability after incubation with LaB$_6$ at different concentrations for 24 h.

Fig. S6 Hematological data of the mice in different groups at 14th day. (1) Control, (2) NIR, (3) LaB$_6$, (4) NIR+LaB$_6$.
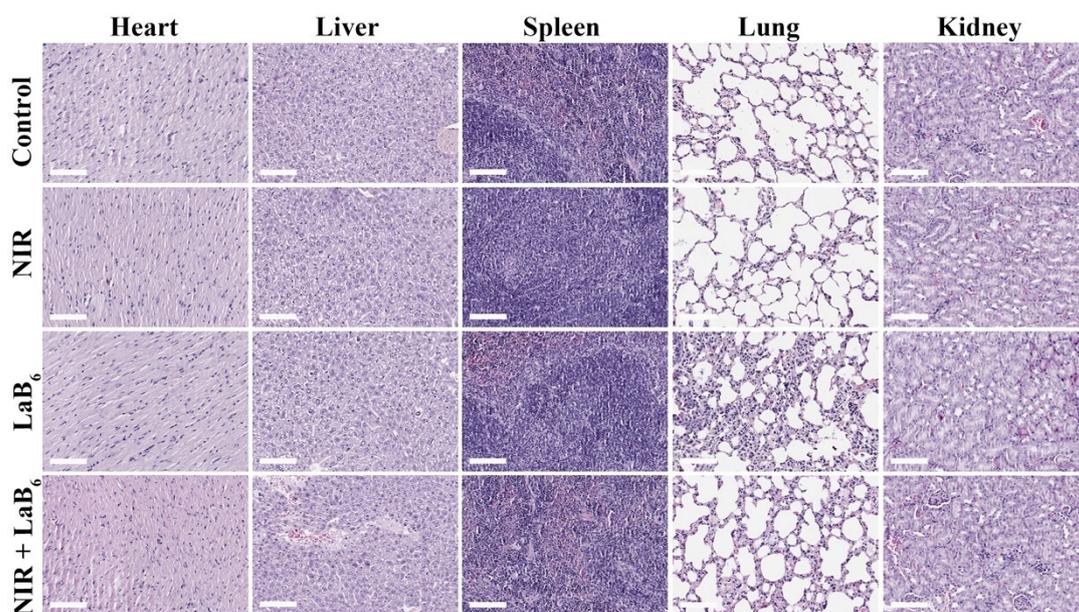
Fig. S7 H&E staining results of major organs from the mice in different groups.
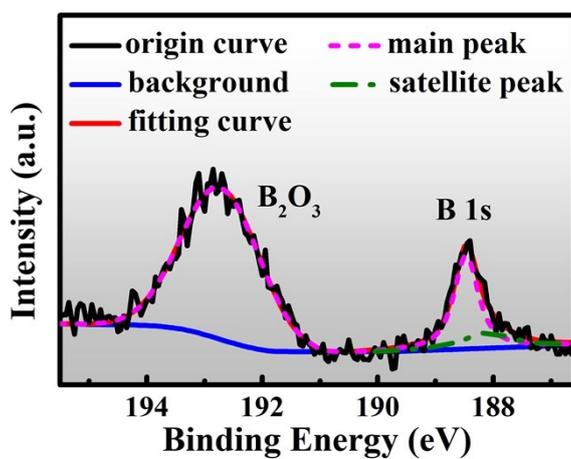

Fig. S8 High resolution deconvoluted B 1s XPS.

Calculation of photothermal conversion efficiency[1, 2]

The total energy balance for the system could be expressed as Equation S1 according to a well-established method.

$$\sum m_d c_d \frac{dT}{dt} = Q_{LaB_6} + Q_{dis} - Q_{surr} \tag{S1}$$

Herein, m_d and C_d are the mass and heat capacity of water, T is the temperature of LaB_6 aqueous dispersion, Q_{LaB6} is the energy inputted by LaB_6, Q_{dis} is energy inputted by the quartz cell (it was measured independently using a sample cell with water only). Q_{surr} is heat conduction away from the system.

Obviously, the NIR laser induced Q_{LaB6} could be calculated as follow:

$$Q_{LaB_6} = I \cdot (1 - 10^{-A_{880}}) \cdot \eta$$

(S2)

Here, I is the laser power (W), A_{880} is the optical absorbance of LaB_6 dispersion at 880 nm, and η is the photothermal conversion efficiency we want to obtain.

On the other hand, Q_{surr} is the thermal energy loss (Equation S3), which linearly increases with temperature difference between system and surrounding.

$$Q_{surr} = hA(T - T_{surr})$$

(S3)

In this equation, h is heat transfer coefficient, A is the surface area of the container, and T_{surr} is the surroundings temperature.

When kept the laser power to be constant, the value $(Q_{LaB6}+Q_{dis})$ is fixed. As the value of Q_{surr} increases with the increment of $(T-T_{surr})$, the system temperature would arrive at a maximum equilibrium temperature eventually when the input and output energies are equal. If we define the $Q_{LaB6} + Q_{dis}$ as $Q_{surr-max}$, we can obtain Equation S4.

$$Q_{LaB_6} + Q_{dis} = Q_{surr-max} = hA(T_{max} - T_{surr})$$

(S4)

In Equation S4, $Q_{surr-max}$ is heat conduction from the surface to air when the sample cell arrive at the maximum equilibrium temperature of T_{max}.

Then, we can obtain Equation S5 by substituting Equation S2 into Equation S4:

$$\eta = \frac{hA(T_{max} - T_{surr}) - Q_{dis}}{I \cdot (1 - 10^{-A_{880}})}$$

(S5)

To obtain the hA, a dimensionless driving force temperature of θ is defined with the maximum temperature of T_{max}

$$\theta = \frac{T - T_{surr}}{T_{max} - T_{surr}}$$

(S6)

Meanwhile, a time constant τ_s was defined as well as

$$\tau_s = \frac{\sum m_d c_d}{hA}$$

(S7)

Then, Equation S1 was expressed by S6 and S7 and rearranged into Equation S8.

$$\frac{d\theta}{dt} = \frac{1}{\tau_s}\left[\frac{Q_{LaB_6} + Q_{dis}}{hA(T_{max} - T_{surr})} - \theta\right]$$

(S8)

At the natural cooling stage, no energy was inputted, $Q_{LaB6}+Q_{dis} = 0$, getting the Equation S9

$$dt = -\tau_s\frac{d\theta}{\theta}$$

(S9)

Equation S10 was derived from S9 by integration:

$$t = -\tau_s\ln\theta$$

(S10)

By plotting the t versus $\ln\theta$, the τ_s is determined as 106.53 s (**Fig. 3e**). Then, hA was calculated as 0.020 $W\cdot°C^{-1}$ by Equation S7.

Q_{dis} could be worked out in the same way via cell with water only.

$$Q_{dis} = Q_{surr-max-water} = (hA)_{water}(T_{max-water} - T_{surr}) = \frac{m_d c_d (T_{max-water} - T_{surr})}{\tau_{s-water}}$$

(S11)

$\tau_{s-water}$ was determined to be 95.35 s (**Fig. S9**), ($T_{max-water}$ - T_{surr}) was 3.8 °C, then Q_{dis} was calculated to be 0.084 W.

Finally, the all the obtained data of hA = 0.020 $W\cdot°C^{-1}$, (T_{max}-T_{surr}) = 24.8°C, I = 1.029 W, ($1-10^{-A880}$) = 0.953 were substituted in the Equation S5 and the η was calculated as 41.35%.
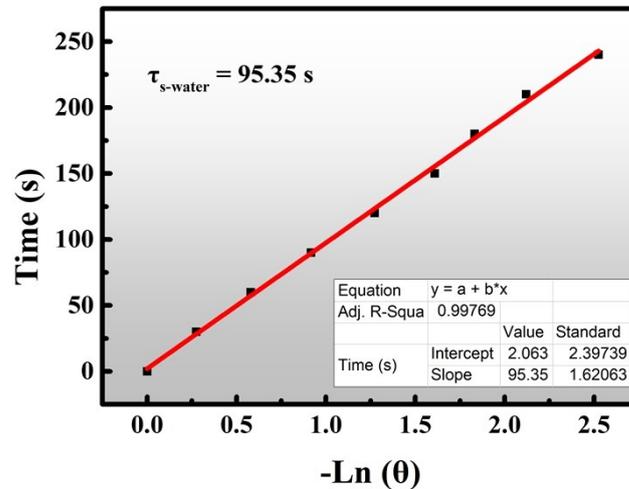

Fig. S9 The curve of time versus -ln(θ) for water.

Reference

[1]   D. K. Roper, W. Ahn and M. Hoepfner, *The Journal of Physical Chemistry C*, 2007, **111**, 3636-3641.

[2]   H. Lin, X. Wang, L. Yu, Y. Chen and J. Shi, *Nano Letters*, 2017, **17**, 384-391.