

Supplementary Information

Photothermal-Activatable PDA Immune Nanomedicine Combine with PD-L1 Checkpoint Blockade for Anti-metastatic Cancer Photoimmunotherapy

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To calculate the photothermal conversion efficiency (η) of the final formulation, the temperature change was recorded as a function of time under continuous 808 nm laser irradiation with a 1.5 W/cm² power density until the solution reached a steady state temperature. The η value was calculated by the following formula¹:

$$\eta = \frac{hS(T_{\max} - T_{\text{Surr}}) - Q_s}{I(1 - 10^{-A_{808}})} \quad (1)$$

where h is the heat transfer coefficient, S is the surface area of the container, T_{\max} is The equilibrium temperature (T_{\max}) is 52.4 °C, the ambient temperature (T_{Surr}) is 24.9 °C, Q_s is heat dissipated from the light absorbed by the container itself, which was determined independently to be 3.5 mW using a container, containing pure water. The incident laser power (I) is 1.5W/cm² and the absorbance of the PDA-PEG-R848-CDs NPs at 808 nm (A_{808}) is 0.348.

A dimensionless parameter θ is calculated as followed:

$$\theta = \frac{T - T_{\text{Surr}}}{T_{\max} - T_{\text{Surr}}} \quad (2)$$

A sample system time constant τ_s can be calculated as Eq.3.

$$t = -\tau_s \ln \theta \quad (3)$$

According to Fig. 3f, time constant for heat transfer from the system is determined to be $\tau_s = 306.45$ s by applying the linear time data from the cooling period vs $-\ln\theta$.

$$hS = \frac{m_D C_D}{\tau_s} \quad (4)$$

In addition, m_D is 0.5g and C_D is 4.2 J/g °C.

Thus, substituting corresponding values of each parameter to Eq. 1, the photothermal conversion efficiency (η) of the PDA-PEG-R848-CDs NPs could be calculated to be 22.41%.

Ref:

1. Roper, D. K.; Ahn, W.; Hoepfner, M., Microscale Heat Transfer Transduced by Surface Plasmon Resonant Gold Nanoparticles. *J Phys Chem C Nanomater Interfaces* **2007**, *111* (9), 3636-3641.

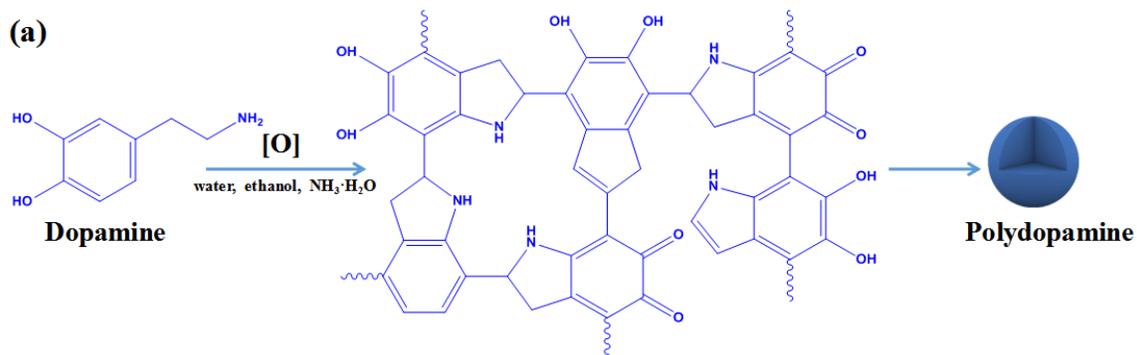


Fig.S1. (a) Schematic showing the preparation of PDA.

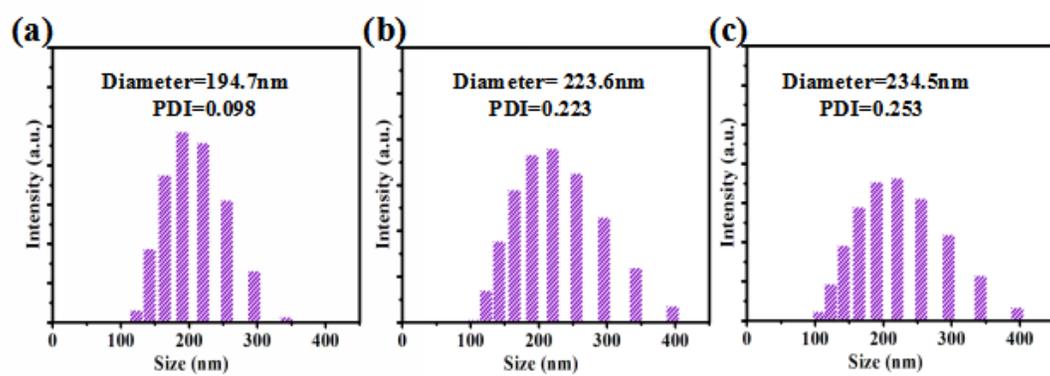


Fig.S2. Dynamic light scattering (DLS) size distribution of the PDA, PDA-PEG and PDA-PEG-R848-CDs nanoparticles.

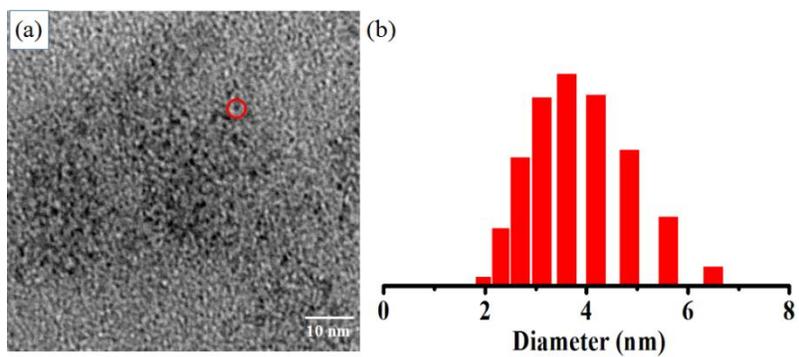


Fig.S3. (a) TEM images of CDs. (b) Dynamic light scattering (DLS) size distribution of the CDs.

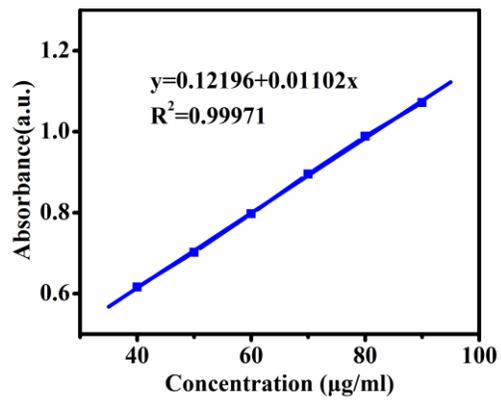


Fig.S4. (a) Calibration curve between the concentration of R848 and its absorbance at 320 nm. The loading efficiency.

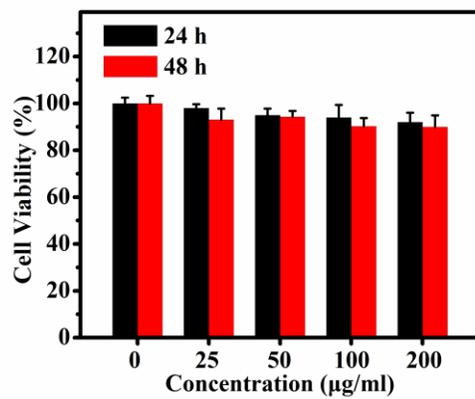


Fig.S5. Cytotoxicity of the PDA-PEG-R848-CDs NPs in 4T-1 cells after 24 and 48 h incubation.

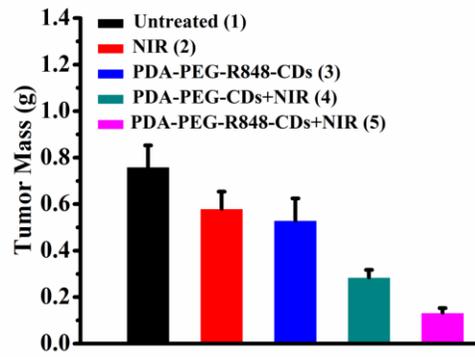


Fig.S6. The average tumor weights of different groups taken out from mice at the end of treatment.

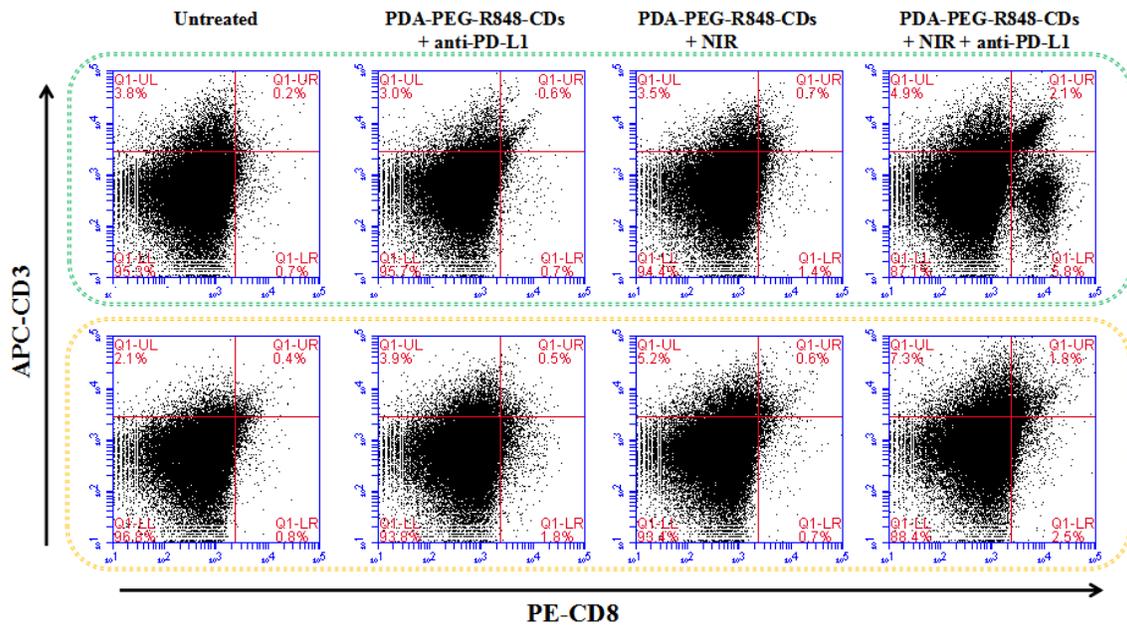


Fig.S7. Flow cytometry analysis of 4T1 cells for primary tumors (green box :left tumor) and distant tumor (yellow box :right tumor) after various treatments. Data are presented as means \pm SD (n = 3), ** $P < 0.01$.