Electronic Supplementary Information

Aqueous phase preparation of ultrasmall $MoSe_2$ nanodots for efficient photothermal therapy of cancer cells

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S1. Characterization of $MoSe_2$ NDs

TEM measurements were performed on a HT7700 electron microscopy (Hitachi, Japan) at an acceleration voltage of 100 kV. Field emission transmission electron microscopy JEM-2100F (JEOL, 200 kV) was used to obtain high-resolution TEM images. Energy-dispersive X-ray spectroscopy (EDS) data of $MoSe_2$ NDs was obtained from filed-emission high-resolution scanning electron microscopy (S-4800, Hitachi) equipped with an energy-dispersive X-ray analyzer (EDAX). The UV-Vis-NIR absorption spectra of $MoSe_2$ NDs were recorded on an UV-3600 spectrophotometer (Shimadzu, Japan). Atomic force microscopy (AFM) images were acquired on Nanoscope IIIa (Bruker, USA). X-ray photoelectron spectroscopy (XPS) was performed using a PHI 5000 VersaProbe (Ulvac-Phi, Japan) with Al Kα (hv=1486.6 eV) as the excitation source. X-ray diffraction patterns were obtained by using a D8 ADVANCE X-ray diffractometer (Bruker, Germany) with Cu Kα radiation. Raman spectra were recorded on a micro-Raman spectroscopy system (Renishaw, UK) equipped with a 532 nm laser. The concentration of $MoSe_2$ NDs was determined by Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES, Optima 5300DV, Perkin Elmer). Photothermal study was performed by using a 785 nm continuous-wave semiconductor laser as light source (BWT Beijing, China). The temperature of the samples was detected by a non-contact visual IR thermometer (Fluke VT02). The power density of laser irradiation was measured by a digital power meter (PM100D, Thorlabs, USA). DLS and Zeta potential were performed on a ZetaPALS Potential Analyzer (Brookhaven Instruments Corporation, USA).

S2. The size distribution and Zeta potential of $MoSe_2$ NDs

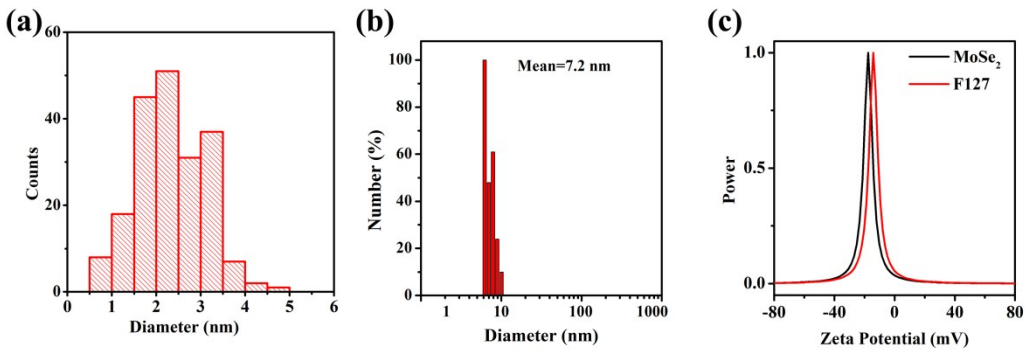

Fig. S1 (a) Size statistics of $MoSe_2$ NDs based on more than 150 nanoparticles by TEM; (b) Hydrodynamic size and (c) Zeta potential of $MoSe_2$ NDs determined by DLS.

S3. EDS of $MoSe_2$ NDs

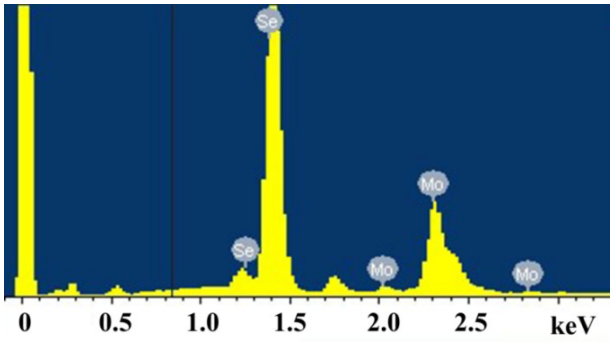

Fig. S2 Energy-dispersive X-ray spectroscopy (EDS) of $MoSe_2$ NDs.

S4. Calculation of Extinction coefficient

According to the Beer-Lambert Law (Eq. 1), the mass extinction coefficient ε of the $MoSe_2$ NDs can be calculated using Eq. 2:

$$A = \varepsilon LC \tag{1}$$

$$\varepsilon = \frac{A}{LC} \tag{2}$$

The term A refers to the absorbance of $MoSe_2$ NDs at 785 nm, ε is the mass extinction coefficient of $MoSe_2$ NDs ($Lg^{-1}cm^{-1}$), L is the optical length of the quartz cuvette (cm), and C is the mass concentration (gL^{-1}).

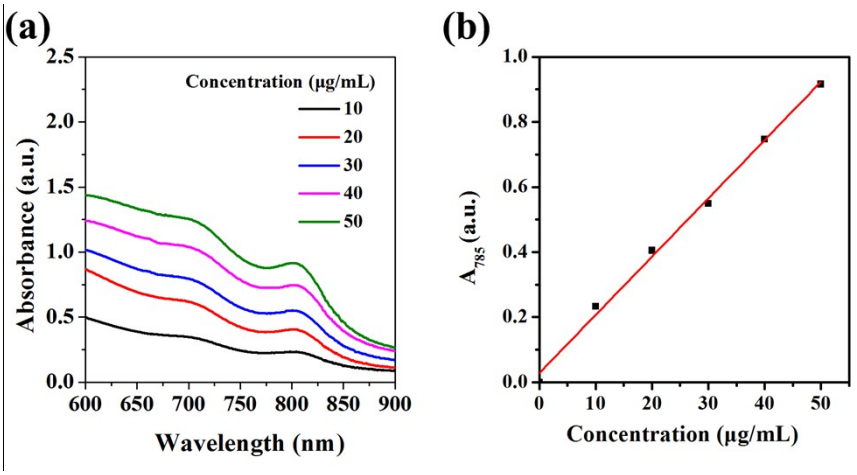

Fig. S3 (a) UV-vis-NIR absorption spectra of $MoSe_2$ NDs aqueous dispersion with different concentrations (10, 20, 30, 40, and 50 μg/ml); (b) The linearly fitted plots of absorbance versus concentration of $MoSe_2$ NDs aqueous suspension at 785 nm.

S5. Calculation of Photothermal Conversion Efficiency

Under laser irradiation at 785 nm, the temperature of $MoSe_2$ NDs aqueous suspensions increases dT in a short time dt, the total energy change can be expressed using Eq.3, as follows:

$$\sum_i m_i C_{p,i} \frac{dT}{dt} = Q_{ND} + Q_0 - Q_e \tag{3}$$

Where m_i and $C_{p,i}$ are the mass and specific heat capacity of component i, Q_{ND} is the heat input of the absorbed laser energy by $MoSe_2$ NDs, Q_0 is the energy absorbed by the sample vial and solvent, and Q_e is the sum of heat dissipated to the surrounding environment by conduction, radiation, and so on.

$$Q_{ND} = I_0(1-10^{-A})\eta \tag{4}$$

The energy input from $MoSe_2$ NDs can be calculated from Eq. 4, where I_0 refers to the incident power of laser irradiation, A is the absorbance of the $MoSe_2$ NDs suspension, and η is the photothermal conversion efficiency of $MoSe_2$ NDs at 785 nm.

$$Q_e = hS(T - T_s) \tag{5}$$

The total external heat flux of the system presents in Eq. 5, where h is the heat transfer coefficient, S is the surface area of the sample vial, and T_s is the temperature of surrounding environment.

$$\theta \equiv \frac{T - T_s}{T_{\max} - T_s} \tag{6}$$

In order to describe a dimensional driving force temperature, θ is defined in Eq. 6, where T_{max} is the steady-state temperature of the system, T is the transient temperature of the system. A thermal equilibrium system time constant τ_s is defined as Eq. 7.

$$\tau_s \equiv \sum_i m_i C_{p,i} / hS \tag{7}$$

From all the equations mentioned above, dθ/dt can be expressed in the form of Eq. 8.

$$\frac{d\theta}{dt} = \frac{1}{\tau_s}\left[\frac{Q_{ND} + Q_0}{hS(\mathrm{T}_{\max} - \mathrm{T}_s)} - \theta\right] \tag{8}$$

When the sample system under laser irradiation reaches the equilibrium temperature, the laser is turned off, and the system input energy $Q_{ND}+Q_0=0$. Thus, Eq. 8 can be changed to the following expression:

$$\frac{d\theta}{dt} = -\frac{\theta}{\tau_s} \tag{9}$$

At the initial moment of laser-off, the transient temperature of the system $T=T_{max}$, and $\theta=1$ at $t=0$, which gives θ as:

$$\theta = \exp(-\frac{t}{\tau_s}) \tag{10}$$

Eq. 10 can be further rearranged to Eq. 11 by substituted Eq. 6 into the expression. By using Eq. 11, τ_s can be calculated to be 139.1 s by plotting t versus lnθ.

$$\ln\left(\frac{T-T_s}{T_{\max}-T_s}\right) = -\frac{1}{\tau_s}t \tag{11}$$

The heat transfer constant of the system hS can be determined to be 6.0 mW/℃ by using Eq. 12, where m=0.2 g, C=4.2 J/g·℃, and τ_s = 139.1 s.

$$hS = \frac{\sum_i m_i C_{p,i}}{\tau_s} \tag{12}$$

During the irradiating of laser, the total energy input is $Q_{ND}+Q_0$, and the system temperature increases until reaching the equilibrium temperature T_{max}, at when the energy input equals heat transfer to surrounding environment, which can be described in Eq. 13.

$$Q_{ND} + Q_0 = hS(\mathrm{T_{max}} - \mathrm{T_s}) \tag{13}$$

By substituting Eq. 4 and Eq. 5 into Eq. 13, the photothermal conversion coefficient η can be expressed in Eq. 14. Since hA has been calculated from Eq. 12, Q_0 is measured to be 54 mW, and other parameters in this system are as follows: T_{max}=50.4℃, T_s=29.5℃, A=0.0444, I_0=1600 mW. The photothermal conversion coefficient (η) of $MoSe_2$ NDs is calculated to be 46.5%.

$$\eta = \frac{hS(\mathrm{T_{max}} - \mathrm{T_s}) - \mathrm{Q_0}}{I_0(1-10^{-A})} \tag{14}$$