Mechanism Study on the Photothermal Function of Lignin: Effect of Electron-Withdrawing Group

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Calculation of photothermal efficiency of modified lignin

The detailed calculation method for the photothermal conversion efficiency of lignin was provided in the SI document.[1, 2]

Based on the law of conservation of energy, the input energy of laser irradiation is transformed into heat energy radiated to the environment and energy absorbed by lignin:

$$\sum_i m_i C_{p,\,i}\frac{dT}{dt} = Q_s - Q_{loss} \tag{1}$$

where m_i and $C_{p,i}$ are the mass and specific heat capacity of lignin, respectively, Q_s is the input energy of laser irradiation, and Q_{loss} is the heat energy radiated to the environment.

Q_{loss} is calculated as follows:

$$Q_{loss} = hS(T - T_{surr}) = hS\Delta T \tag{2}$$

where h is the heat transfer coefficient of lignin, S is the surface area of the test sample irradiated by laser, and T_{surr} is the ambient temperature.

The system is in equilibrium when the test sample reaches its maximum temperature. At this point, the input energy of the laser irradiation is equal to the thermal energy radiated to the environment:

$$Q_s = Q_{loss} = hS(T_{max} - T_{surr}) = hS\Delta T_{max} \tag{3}$$

Where T_{max} is the maximum temperature of the system at equilibrium, ΔT_{max} is the maximum value of the temperature change when the system reaches equilibrium, and the cooling section curve of the maximum temperature is used to calculate the photothermal conversion efficiency:

Photothermal conversion efficiency η is calculated as follows:

$$\eta = \frac{hS\Delta T_{max}}{I} \tag{4}$$

where I is the power of laser, which is 0.144 W.

Since the exact value of hS is difficult to obtain. Therefore, in order to replace hS for subsequent calculations, a dimensionless driving force temperature θ is introduced:

$$\theta = \frac{T - T_{surr}}{T_{max} - T_{surr}} \tag{5}$$

Calculating the differential of the above equation gives:

$$d\theta = \frac{1}{T_{max} - T_{surr}} dT = \frac{1}{\Delta T_{max}} dT \tag{6}$$

Where T is the test sample temperature (observed using an infrared camera), T_{max} is the maximum temperature of the system at equilibrium, and T_{surr} is the ambient temperature. By substituting Eq. 6 into Eq. 1, we get:

$$\frac{d\theta}{dt} = \frac{hS}{\sum_i m_i C_{p,i}} \left(\frac{Q_s}{hS\Delta T_{max}} - \frac{\Delta T}{\Delta T_{max}} \right) = \frac{hS}{\sum_i m_i C_{p,i}} \left(\frac{Q_s}{hS\Delta T_{max}} - \theta \right) \tag{7}$$

Cooling time constant τ_s of the test sample is then introduced:

$$\tau_s = \frac{\sum_i m_i C_{p,i}}{hS} \tag{8}$$

Substituting into Eq. 7 and get:

$$\frac{d\theta}{dt} = \frac{1}{\tau_s} \frac{Q_s}{hS\Delta T_{max}} - \frac{\theta}{\tau_s} \tag{9}$$

Switching off the laser irradiation, the input energy of laser to the test material Q_s = 0, get:

$$\frac{d\theta}{dt} = -\frac{\theta}{\tau_s} \tag{10}$$

$$t = -\tau_s \ln \theta \tag{11}$$

The cooling segment curve of the test sample is selected and plotted with time t (s) as y-axis and $ln\theta$ as x-axis, and the slope of the curve is the cooling time constant τ_s.

By combing Eq. 5 and Eq. 9, the calculation formula for the photothermal conversion efficiency is:

$$\eta = \frac{hS\Delta T_{max}}{I} = \frac{\sum_i m_i C_{p,i}}{\tau_s} \times \frac{\Delta T_{max}}{I} \tag{12}$$

The photothermal conversion efficiency of lignin can be calculated by combing the average specific heat capacity of lignin measured by DSC and the mass of the test sample (9 mg).

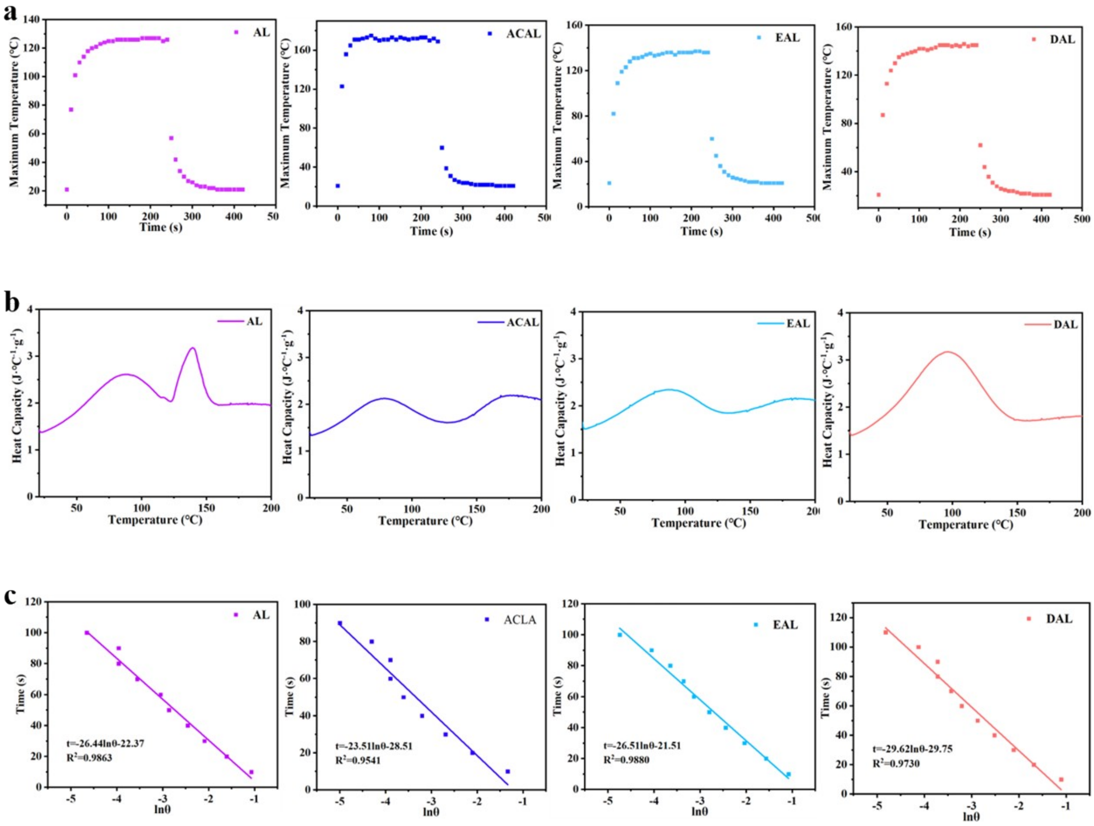

Fig. S1 (a) The heating and cooling cycle of lignin under 808 nm laser irradiation at 0.51 W·cm^{-2} (b) The change of specific heat capacity of lignin from 20 °C to 200 °C with DSC instrument (c) The corresponding time-lnθ linear curve of the heating and cooling cycle of lignin.

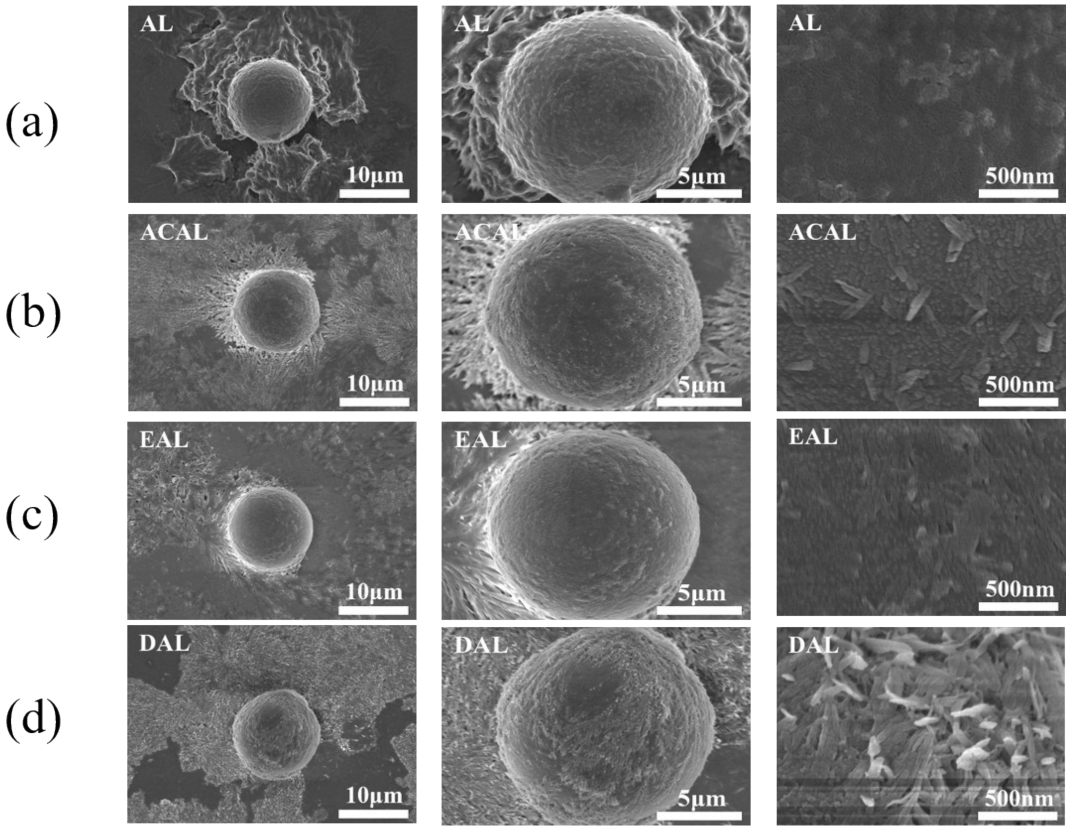

Fig. S2 SEM image of lignin-coated AFM probe.

Table S1 The characteristic parameters of lignin

	AL	**ACAL**	**EAL**	**DAL**
Specific heat capacity C_p ($J \cdot g^{-1} \cdot °C^{-1}$)	2.16	1.86	2.01	2.15
Cooling time τ_s(s)	26.44	23.51	26.51	29.62
Photothermal conversion efficiency η(%)	53.6%	73.2%	54.5%	56.3%

Table S2 Summary of photothermal conversion efficiency of organic photothermal materials presented in this work comparing with reported literatures.

Materials	Photothermal Conversion Efficiency (%)	Excited Laser (nm)	Power Density ($W\cdot cm^{-2}$)
This work	73.2	808	0.51
Polydopamine[3]	25.6	808	2.00
Organic molecules with donor-acceptor structures (2TPE-2NDTA)[4]	54.9	808	0.80
Copolymers with benzothiadiazole-fused acenaphthenequinone imide[5]	58.2	1064	1.00
Thiadiazoloquinoxaline-based semi-conducting polymers[6]	61.6	1060	1.00
Quaterrylenediimide nanoparticles[7]	64.7	808	1.00
Coronene-F4TCNQ cocrystal[8]	69.3	808	0.28
BODIPY tetramers[9]	72.4	808	0.50
D-π-A-π-D typed small molecule (2DMTT-BBTD)[10]	74.8	808	0.80
Croconium derivative[11]	79.5	808	0.80
Borondifluoride bridged azafulvene complex[12]	80.0	1064	0.75

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