Supplementary Information

Stable lignin-based afterglow materials with ultralong phosphorescence lifetime in solid state and aqueous solution

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Optimization of NL-CDs@SiO_2

The reaction temperature, reaction time and the quality of EDA were optimized for preparing NL-CDs with the aim of high value application in information encrypting. The phosphorescence QY of subsequently prepared NL-CDs@SiO_2 was selected as criteria. Meanwhile, the fluorescence QY of NL-CDs was tested to indicate the optical change of NL-CDs for assistance in revealing the mechanism for the phosphorescence change of NL-CDs@SiO_2.

As shown in Fig. S1A, the phosphorescence QY value of NL-CDs@SiO_2 increased from 0.56% to 4.82% as the reaction temperature was increased from 160°C to 200°C. Nevertheless, further increasing the reaction temperature to 220°C led to a decline in the fluorescence and phosphorescence QY value of NL-CDs@SiO_2. In addition, as shown in Fig. S1B, the QY value of NL-CDs displayed similar change tends with the fluorescence QY of NL-CDs@SiO_2.

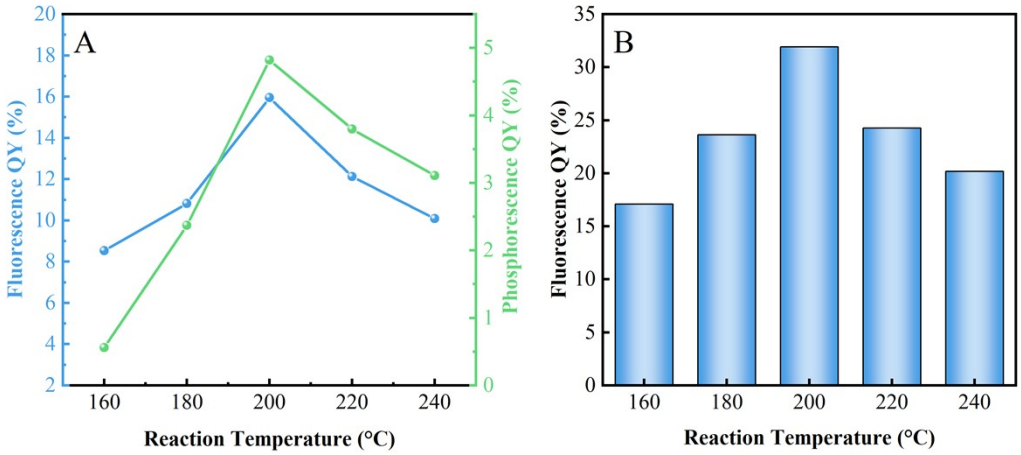

Fig. S1 (A) The effect of the reaction temperature on the fluorescence and phosphorescence QY value of NL-CDs@SiO_2, (B) the effect of the reaction temperature on the QY value of NL-CDs.

Fig. S2 A shows that the fluorescence and phosphorescence QY value of NL-CDs@SiO_2 reached a maximum value under the optimized reaction time of 8 h. As the reaction time increased to 12 h, the phosphorescence QY value of NL-CDs@SiO_2 decreased to 4.10%. With the change in reaction time and temperature, the altering trends of the fluorescence and phosphorescence QY

value were consistent. The phenomenon could be ascribed to the decrease of surface fluorescent functional groups of NL-CDs, which was caused by the increase in reaction temperature and time. Meanwhile, the excessive reaction temperature and time further led to the deepening of the carbonation of NL-CDs with the reduction of luminescent sites, which was not conducive to the formation of ISC and thus reduced the phosphorescence QY value of NL-CDs@SiO_2. Hence, the reaction temperature of 200°C and the reaction time of 8 h were selected in subsequent experiments.

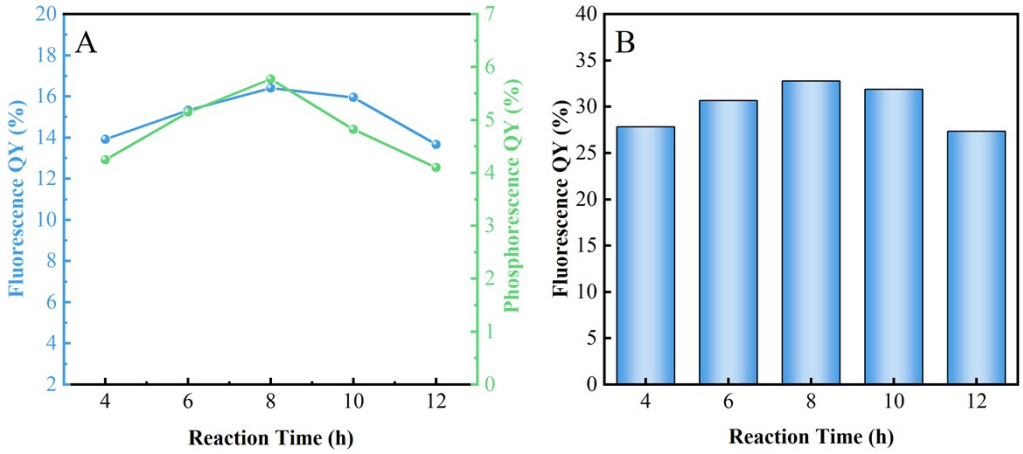

Fig. S2 (A) The effect of the reaction time on the fluorescence and phosphorescence QY value of NL-CDs@SiO_2, (B) the effect of the reaction time on the QY value of NL-CDs.

Fig. S3 reveals the effect of the EDA quality on the fluorescence and phosphorescence QY value of NL-CDs@SiO_2. With increasing the quality of EDA from 50 to 200 μL, the phosphorescence QY value of NL-CDs@SiO_2 increased from 1.08% to 5.97% and the fluorescence QY value increased from 8.74% to 15.02%, which was caused by the pyridine N was well distributed at the edge and center of carbon core, and the graphite N was regularly doped in the skeleton of carbon core. Interestingly, the phosphorescence QY value of NL-CDs@SiO_2 did not change significantly with further increasing the amount of EDA to 600 μL, but the fluorescence QY value of NL-CDs@SiO_2 was increased to 19.11%. The increase of the QY value of NL-CDs@SiO_2 could be caused by

the introduction of surface luminescence sites (–NH_2) was increased along with the increase of EDA, while the main functional group beneficial to the phosphorescence QY was mainly –COOH. Considering the low performance requirements for the QY value of NL-CDs@SiO_2 in subsequent applications and the balance of cost-effectiveness, the optimized EDA quality of 200 μL was selected in subsequent experiments.

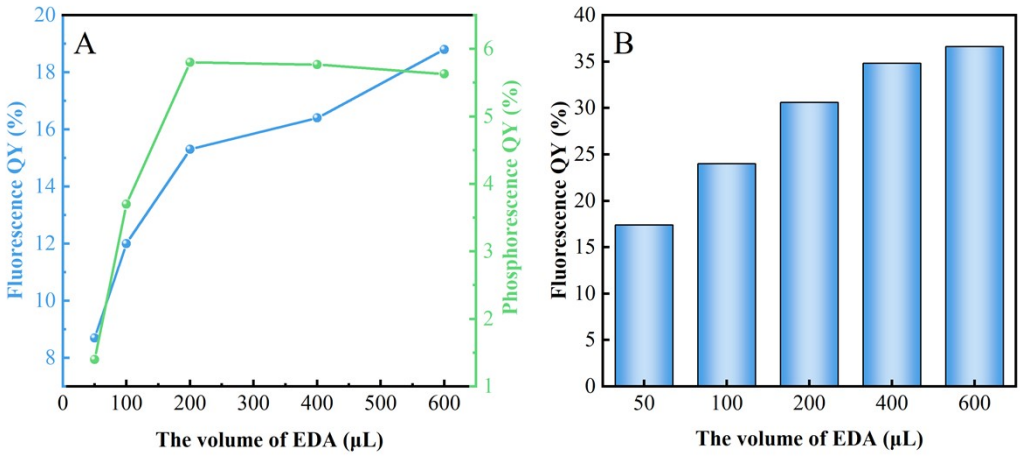

Fig. S3 (A) The effect of the volume of EDA on the fluorescence and phosphorescence QY value of (A) NL-CDs@SiO2, (B) the effect of the volume of EDA on the QY value of NL-CDs.

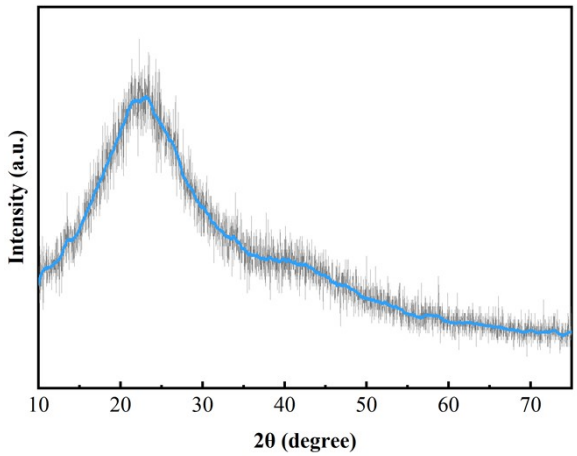

Fig. S4 The XRD pattern of NL-CDs.

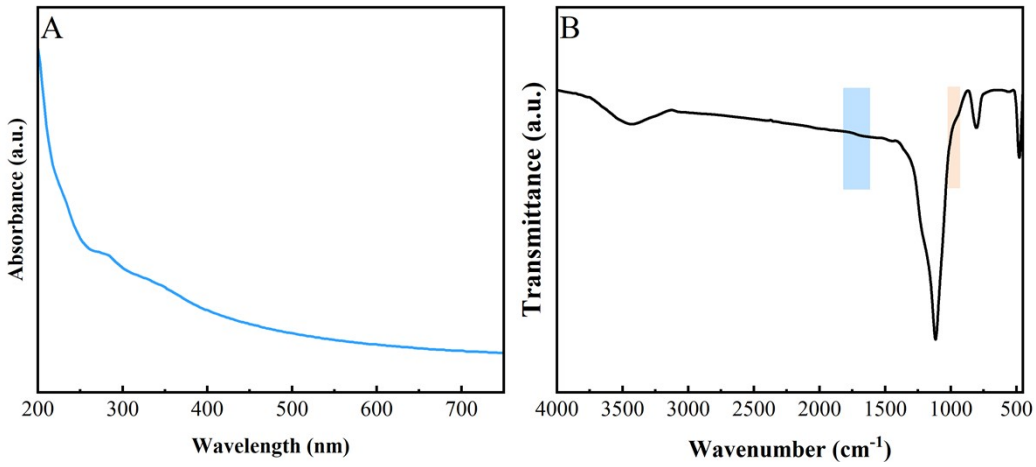

Fig. S5 (A) The UV-Vis and (B) FT-IR spectra of NL-CDs-2.

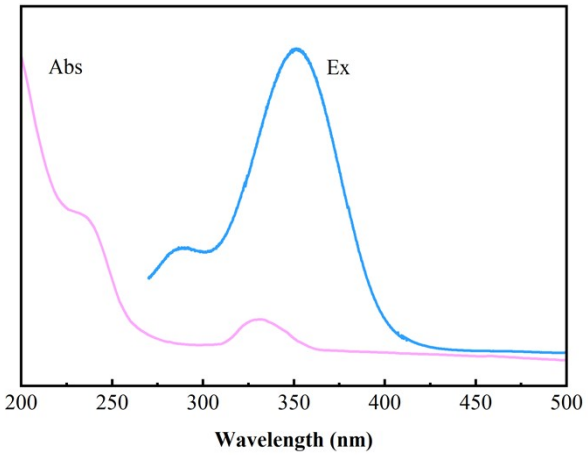

Fig. S6 UV-vis and phosphorescence excitation spectra of NL-CDs@SiO_2 aqueous solution.

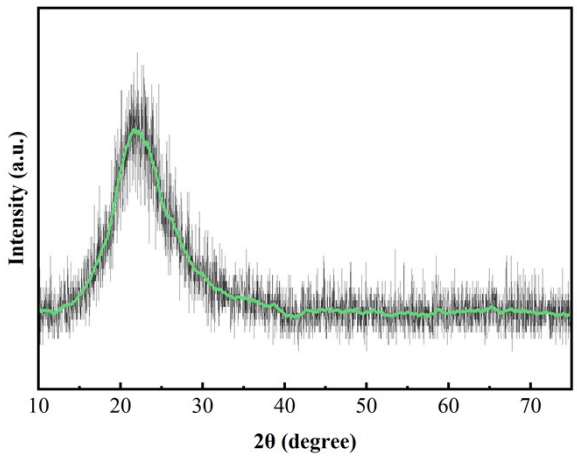

Fig. S7 The XRD pattern of NL-CDs@SiO_2.

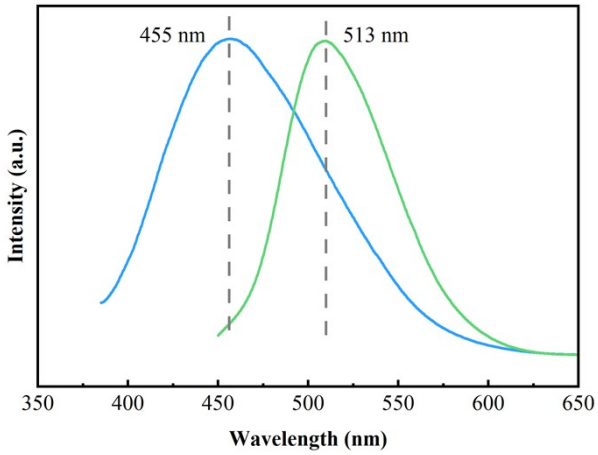

Fig. S8 Fluorescence and phosphorescence spectra of NL-CDs@SiO_2 at low temperature (77 K).

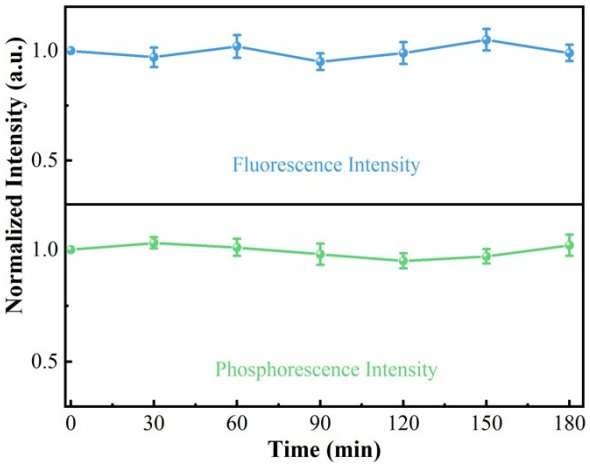

Fig. S9 Fluorescence and phosphorescence intensity of NL-CDs@SiO_2 powder under continuous UV light irradiation.

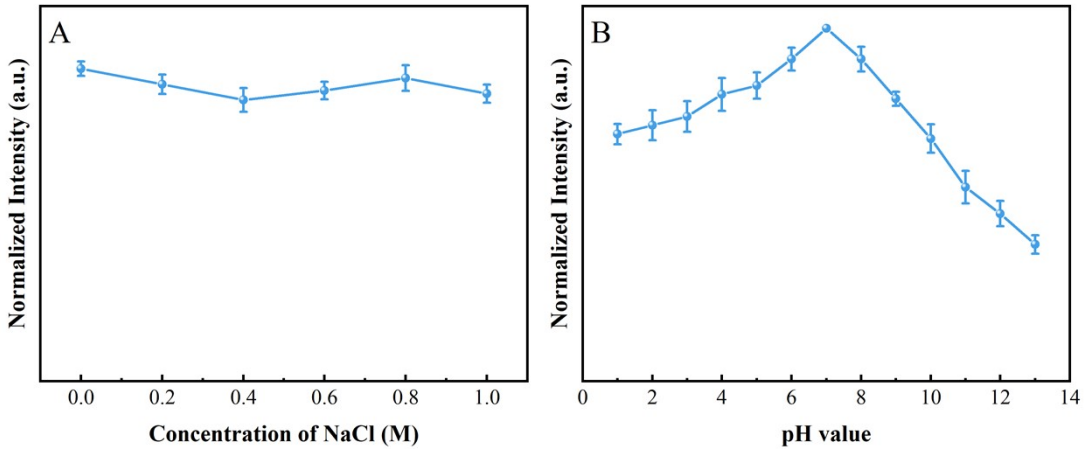

Fig. S10 Fluorescence intensity of NL-CDs solution with different (A) concentrations of NaCl and (B) pH values.

Table S1 Comparison of the presented NL-CDs@SiO_2 with other reported afterglow materials.

Raw materials	Lifetime (ms)	Phosphorescence QY (%)	Maintaining phosphorescence in water	Ref.
CDs, rhodamine B, and SiO_2	910	3.56	Yes	1
CDs and SiO_2	260	4.36	Yes	2
MOFs and SiO_2	215	-	No	3
CDs and polyacrylamide	503	4.4	No	4
CDs and polyvinyl alcohol	292	-	No	5
Cellulose-based CDs and cellulose	167	-	No	6
$ZnCl_4^-$	215	6	No	7
Lignin-based CDs and SiO_2	834	5.97	Yes	This work

References

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