Supporting Information

Na^+: the key to ultra-long afterglow lifetime of carbon dots in dense SiO_2 matrices

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Experimental Section

Materials: Tetraethyl orthosilicate (TEOS), ammonia solution (25-28%), sodium hydroxide, ethylene glycol, NaF, NaCl, NaBr, NaI, LiCl, KCl, $MgCl_2$, $GaCl_2$, citric acid, m-phenylenediamine, p-phenylenediamine, aniline, poly (acrylic acid) (M.W.~3000) 50% solution (PAA) and quercetin were purchased from Aladdin. Ethylenediamine (EDA) and hydrochloric acid (36-38%) were purchased from Guangzhou Chemical Reagent Factory. The ultrapure water used in the experiment was purified by the Master-E water purification system (Milli-Q). All the chemicals were used without further purification.

Characterization: The field emission scanning electron microscopy (FE-SEM) images were taken on Verios 460. The HR-TEM images were captured using a Talos L120C transmission electron microscope. X-ray diffraction (XRD) patterns were measured by Ulitma IV. FT-IR spectra were performed on a Nicolet IS10 instrument from Thermo Fisher. The X-ray photoelectric spectroscopy (XPS) measurement was conducted on a Thermo Scientific K-alpha using Al Kα X-ray as excitation source. PL excitation spectra, emission spectra, and PL lifetime curves were recorded on a FL-7000 Hitachi spectrometer. The confocal images were captured by Leica TCS SP8 STED 3X.

Synthesis of Na/CDs@SiO_2 and CDs@SiO_2: NaOH (1 M, 100 μL), 0.25 mL of ammonia (25-28%), 10 mL of TEOS and 2 mL of ethylene glycol were added to 20 mL of deionised water and the mixture was then stirred for 5 hours at a maintained temperature of 35 °C to form a homogeneous liquid. The mixture was then transferred to a 50 mL reactor and kept at 200 ℃ for 2 h. After cooling, the silica gel was mashed and dried at 60 ℃ for 4 h. Subsequently, the dried sample was ground and heated in a muffle furnace at 600 ℃ for 1.5 h with a temperature increase rate of 5 ℃/min to obtain Na/CDs@SiO_2. Keeping all other conditions unchanged, CDs@SiO_2 was obtained without the addition of NaOH.

Synthesis of A-CDs, R-CDs, V-CDs, GT-CDs, TP-CDs: 2.0 g avocado powder, 1.0 g rosemary powder, 1.0 g vegetable powder, 0.4 g green tea powder and 0.4 g tangerine peel powder were weighed and added with 20 mL of ethanol, and then loaded into a 50 mL polytetrafluoroethylene lined stainless steel reactor and kept at 180 ℃ for 6 h. The reaction was carried out at 180 ℃. After the reaction was finished and cooled down, the upper liquid was filtered through 0.22 μm aqueous microporous filter membrane to obtain A-CDs, R-CDs, V-CDs, GT-CDs, TP-CDs, respectively.

Synthesis of CEM-CDs, CEP-CDs, CEA-CDs, CEQ-CDs: 0.4 g of m-phenylenediamine, p-phenylenediamine, aniline and quercetin were weighed and added to 30 mL of deionized water respectively. 0.6 g citric acid, 3 mL ethylenediamine were taken and added to the above solutions and stirred well. Then loaded into a 100 mL stainless steel reactor with PTFE lining and kept at 180 ℃ for 6 h. After the reaction was finished and cooled down, the upper layer of liquid was filtered through 0.22 μm aqueous microporous filtration membrane to obtain CEM-CDs, CEP-CDs, CEA-CDs, and CEQ-CDs, respectively.

Synthesis of CPDs: 0.36 g of PAA (50% aqueous solution) and 350 μL of EDA were added to 25 mL of deionized water. Subsequently, it was transferred to 50 mL of hydrothermal reactor liner made of PPL material, and the reaction was carried out at 200 ℃ for 8 h. After the reaction was finished and cooled down, the liquid was filtered through 0.22 μm aqueous microporous filtration membrane to obtain CPDs.

Synthesis of Na/X-CDs@SiO_2 and X-CDs@SiO_2: Maintaining the same synthesis conditions as for Na/CDs@SiO_2 and CDs@SiO_2, only 100 μL of X-CDs liquid prepared above was added.

Synthesis of other metal ion@SiO_2 materials: NaF, NaBr, NaCl, NaI, LiCl, KCl, $MgCl_2$ and $GaCl_2$ are all configured as 1 M solutions. Keep the same synthesis conditions as for Na/CDs@SiO_2, only replace NaOH with other metal ion solutions.

Cell viability: The HeLa cell line is a human cervix epithelioid carcinoma cell line (Laboratory animal center of Sun Yat-sen University). HeLa cells were cultured in DMEM medium supplemented with 10% FBS and 1% PS at 37 ℃ in a humidified atmosphere having 5% of CO_2. To investigate the cytotoxicity of the Na/CDs@SiO_2 towards HeLa cells, HeLa cells were incubated with various concentrations of these nanoparticles for 48 h. The MTT assay was then used to measure the cellular viability.

Cellular imaging: HeLa cells at a density of 2×10^5 /cell were seeded on a confocal dish (Φ: 35 mm, Biosharp brand). After 12 h of incubation, Na/CDs@SiO_2 solution (0.1 mg/mL) was added into the cell culture system, which was incubated for another 12 h. After washing twice with PBS buffer, the cells were measured by using laser-scanning confocal fluorescence microscope (λ_{ex} = 405 nm; collection range: 415-470 and 470-550 nm). The PL images were separately collected without time gating and time gating of 8.5-12 ns. The 405 nm CW laser was used as excitation source.

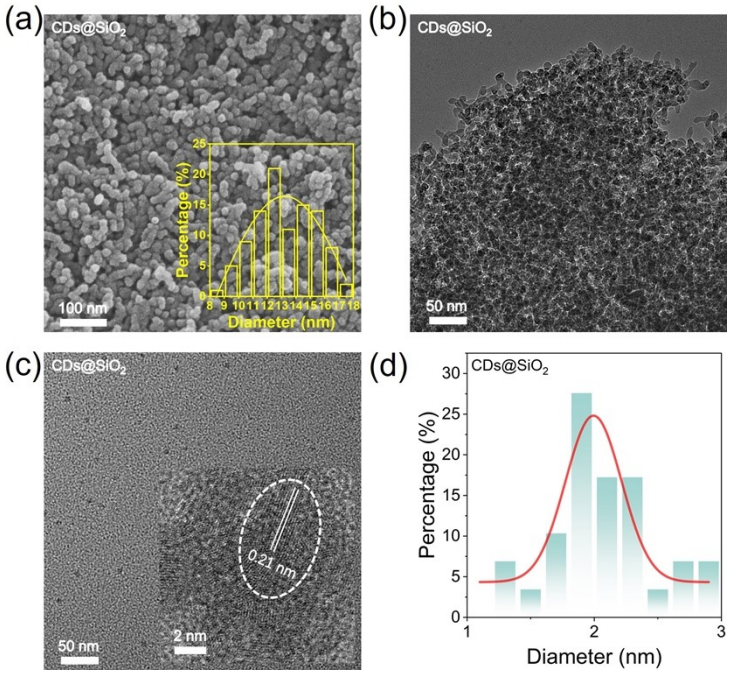

Fig. S1. The SEM images (a) and TEM images (b) of CDs@SiO_2. The HRTEM images (c) and particle size distribution (d) of CDs in CDs@SiO_2.

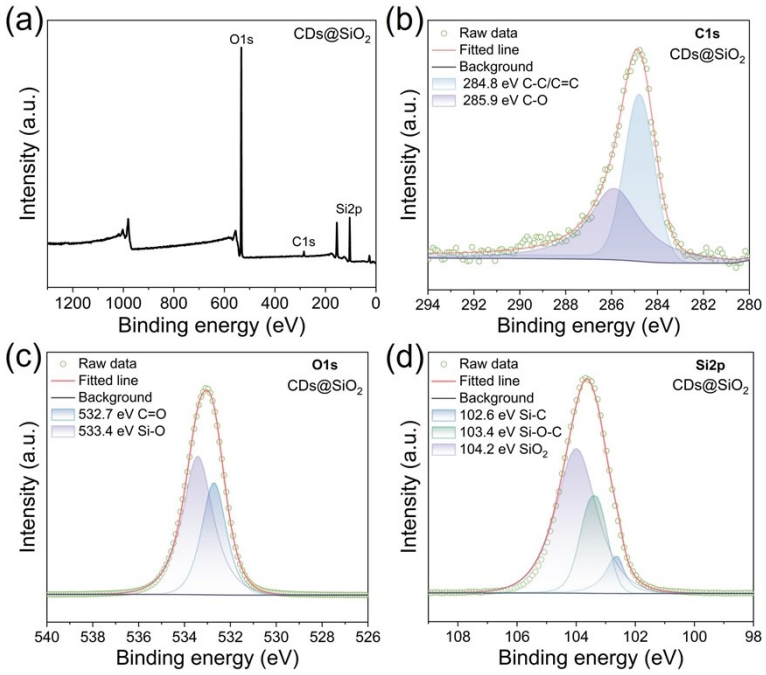

Fig. S2. The XPS survey curve of CDs@SiO_2 (a). High-resolution C1s (b), O1s (c) and Si2p (d) XPS results for Na/CDs@SiO_2.

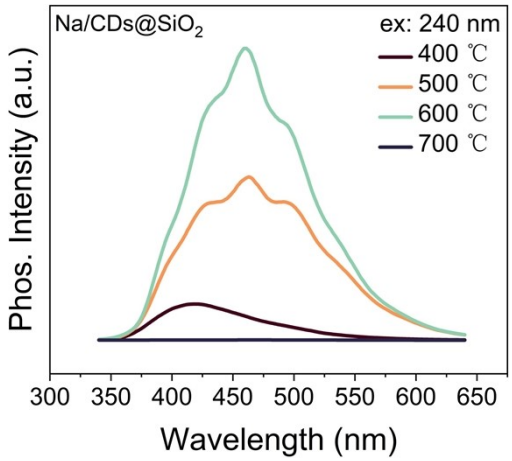

Fig. S3. Phosphorescence emission spectra of Na/CDs@SiO_2 prepared at different temperatures

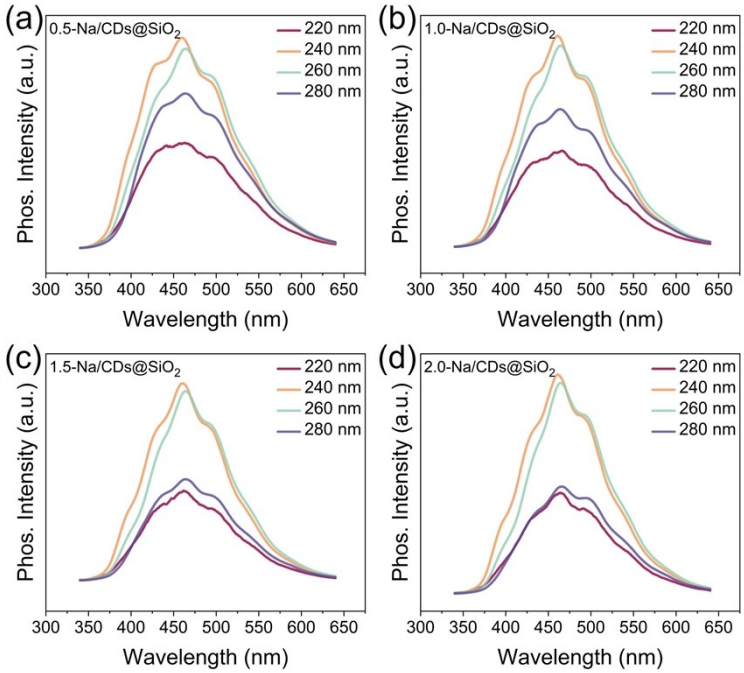

Fig. S4. The phosphorescence emission spectra of 0.5-Na/CDs@SiO_2 (a), 1.0-Na/CDs@SiO_2 (b), 1.5-Na/CDs@SiO_2 (c), 2.0-Na/CDs@SiO_2 (d).

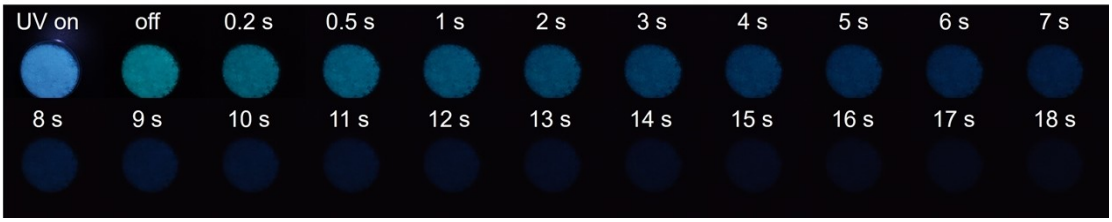

Fig. S5. The Optical photographs of CDs@SiO_2 under illumination of 254 nm UV lamp "on" and "off" states.

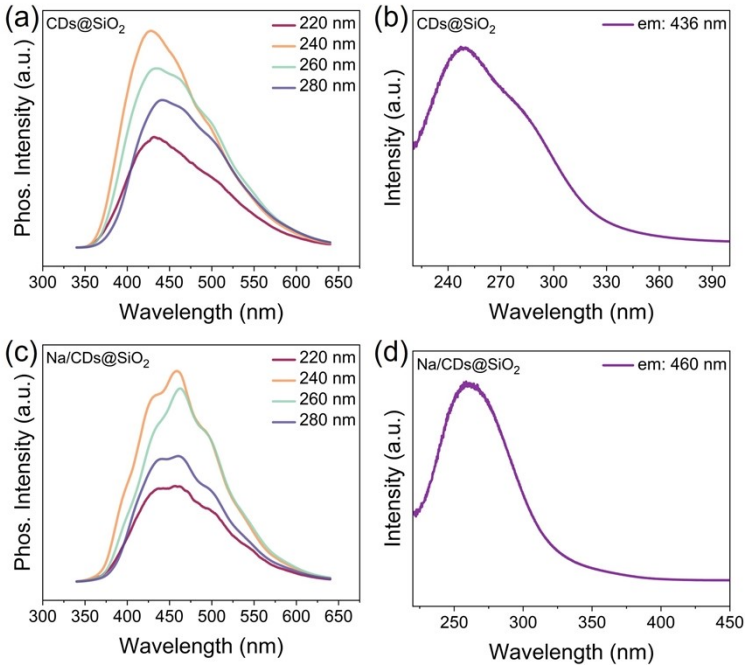

Fig. S6. The phosphorescence emission spectra of CDs@SiO_2 (a) and Na/CDs@SiO_2 (c). The phosphorescence excitation spectra of CDs@SiO_2 (b) and Na/CDs@SiO_2 (d).

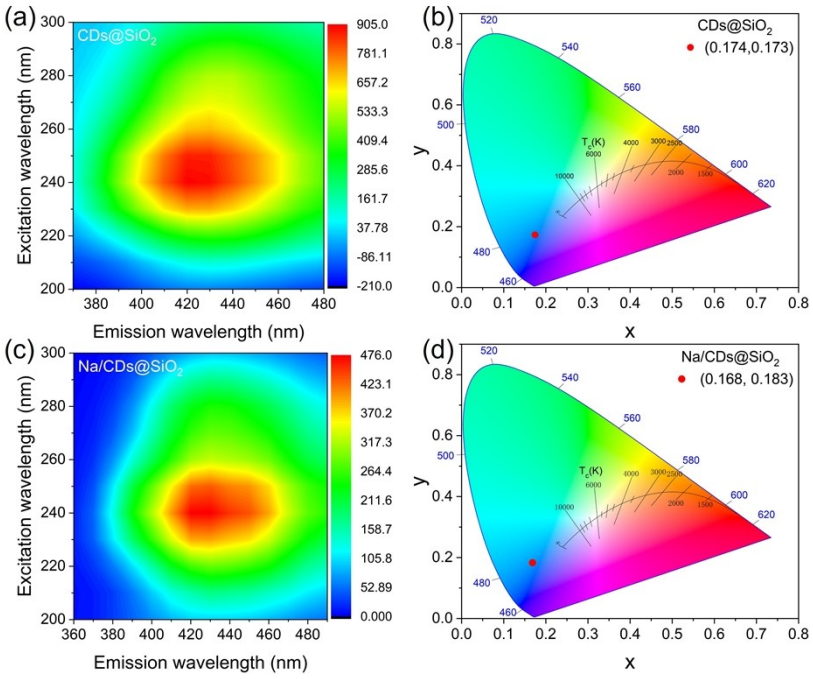

Fig. S7. The excitation-emission plot of $CDs@SiO_2$ (a) and $Na/CDs@SiO_2$ (c) monitored at phosphorescence mode. The CIE coordinate of the phosphorescence of $CDs@SiO_2$ (b) and $Na/CDs@SiO_2$ (d) (EX: 240 nm).

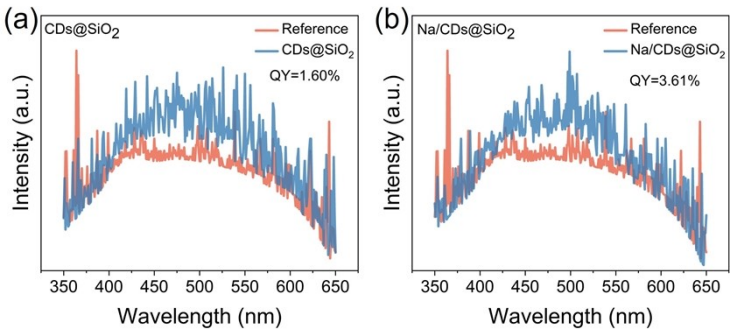

Fig. S8. Phosphorescence QY measurements of $CDs@SiO_2$ (a) and $Na/CDs@SiO_2$ (b).

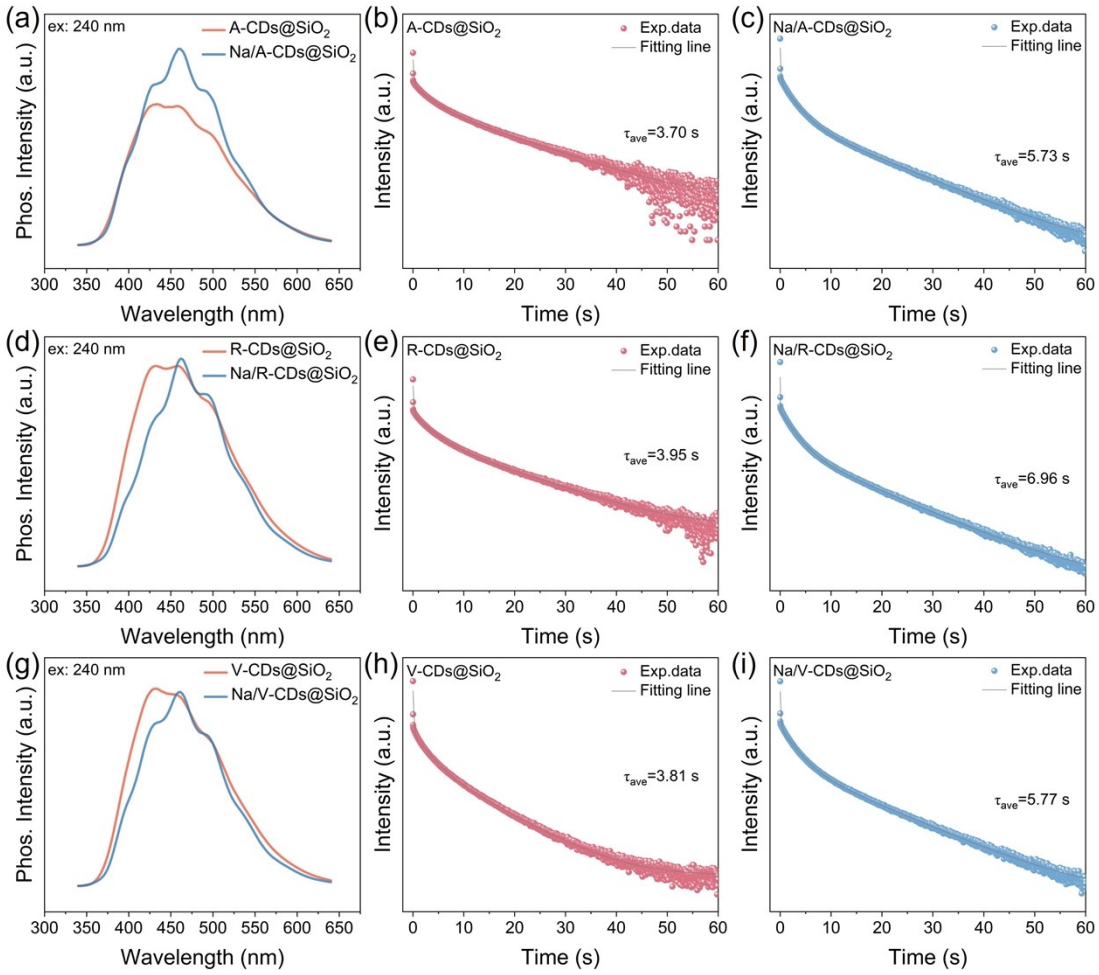

Fig. S9. The phosphorescence emission spectra of X-CDs@SiO_2 and Na/X-CDs@SiO_2 under 240 nm excitation (a), (d), (g). Time-resolved decay curves and fitted curves (grey lines) of X-CDs@SiO_2 (b), (e), (h) and Na/X-CDs@SiO_2 (c), (f), (i), monitored at EM: 460 nm and EX: 250 nm wavelengths. Note: X here stands for A, R and V, respectively.

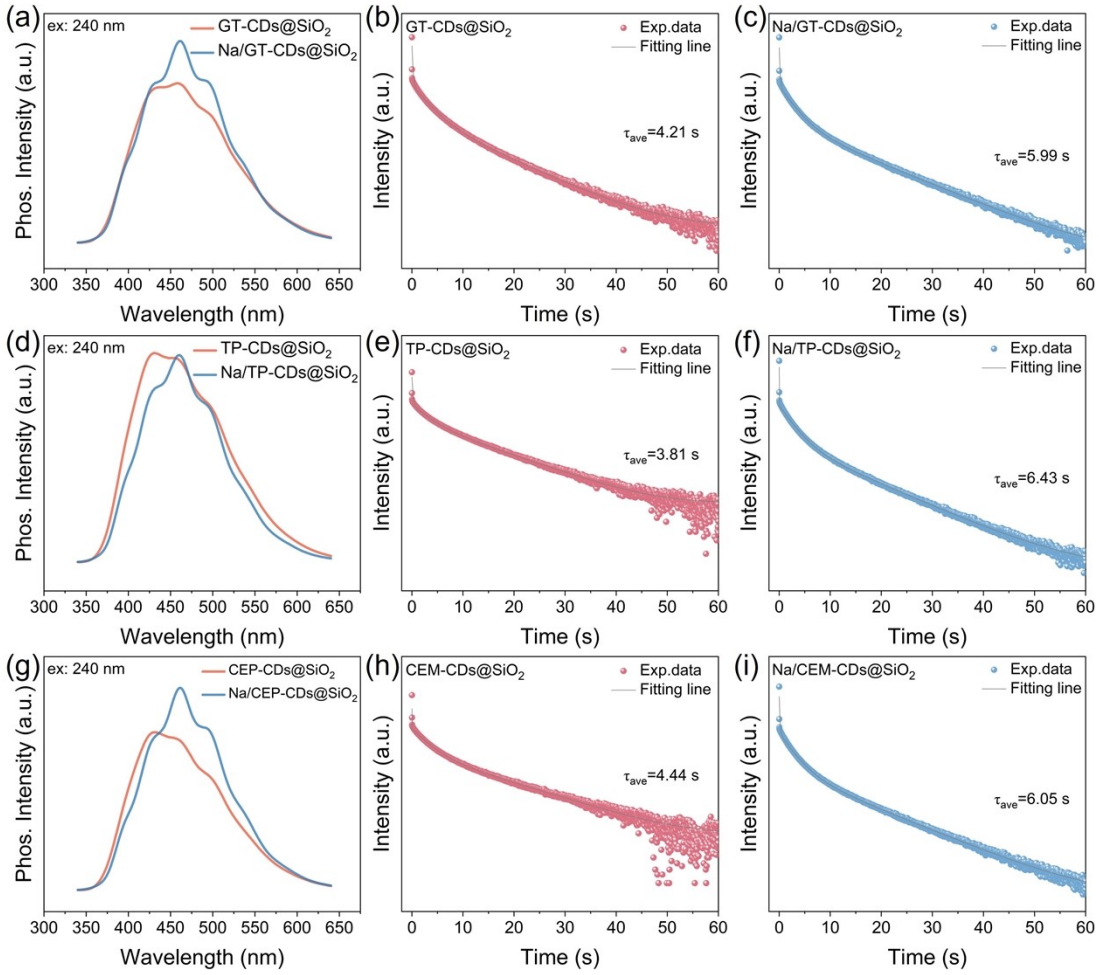

Fig. S10. The phosphorescence emission spectra of X-CDs@SiO_2 and Na/X-CDs@SiO_2 under 240 nm excitation (a), (d), (g). Time-resolved decay curves and fitted curves (grey lines) of X-CDs@SiO_2 (b), (e), (h) and Na/X-CDs@SiO_2 (c), (f), (i), monitored at EM: 460 nm and EX: 250 nm wavelengths. Note: X here stands for GT, TP and CEP, respectively.

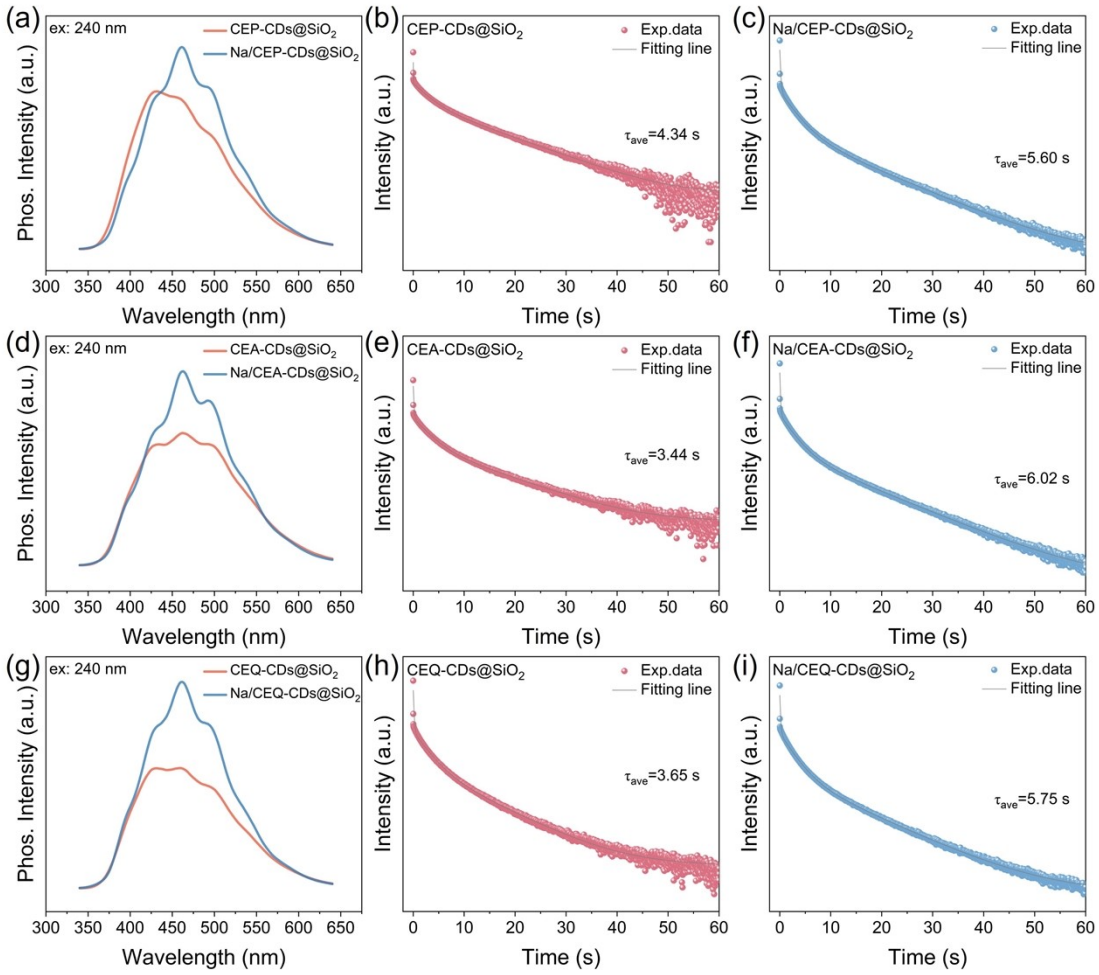

Fig. S11. The phosphorescence emission spectra of X-CDs@SiO_2 and Na/X-CDs@SiO_2 under 240 nm excitation (a), (d), (g). Time-resolved decay curves and fitted curves (grey lines) of X-CDs@SiO_2 (b), (e), (h) and Na/X-CDs@SiO_2 (c), (f), (i), monitored at EM: 460 nm and EX: 250 nm wavelengths. Note: X here stands for CEP, CEA and CEQ, respectively.

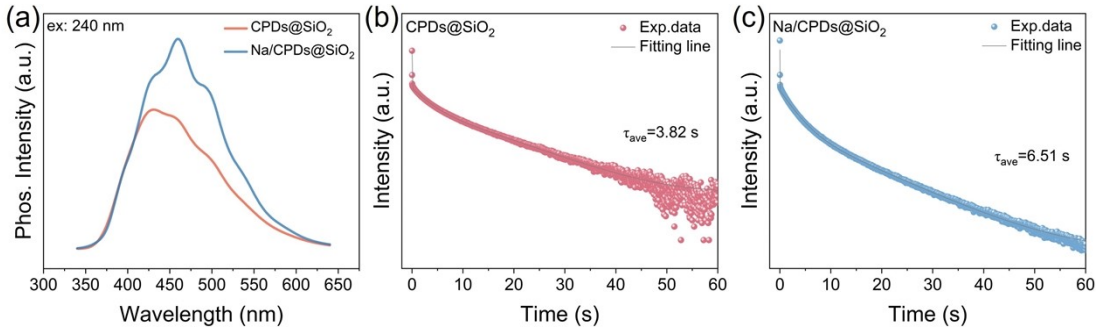

Fig. S12. The phosphorescence emission spectra of CPDs@SiO_2 and Na/CPDs@SiO_2 under 240 nm excitation (a). Time-resolved decay curves and fitted curves (grey lines) of CPDs@SiO_2 (b) and Na/CPDs@SiO_2 (c), monitored at EM: 460 nm and EX: 250 nm wavelengths.

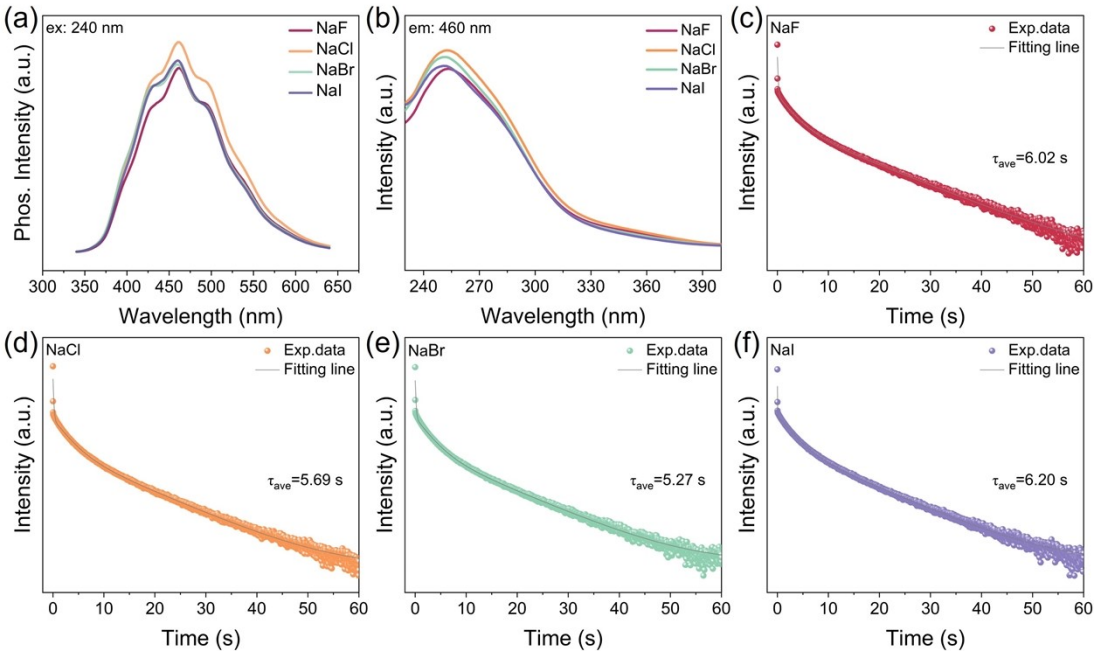

Fig. S13. The phosphorescence emission (a) and excitation (b) spectra of X/CDs@SiO_2. Note: X here stands for NaF, NaCl, NaBr and NaI, respectively. Time-resolved decay curves and fitted curves (grey lines) of NaF/CDs@SiO_2 (c), NaCl/CDs@SiO_2 (d), NaBr/CDs@SiO_2 (e) and NaI/CDs@SiO_2 (f), monitored at EM: 460 nm and EX: 250 nm wavelengths.

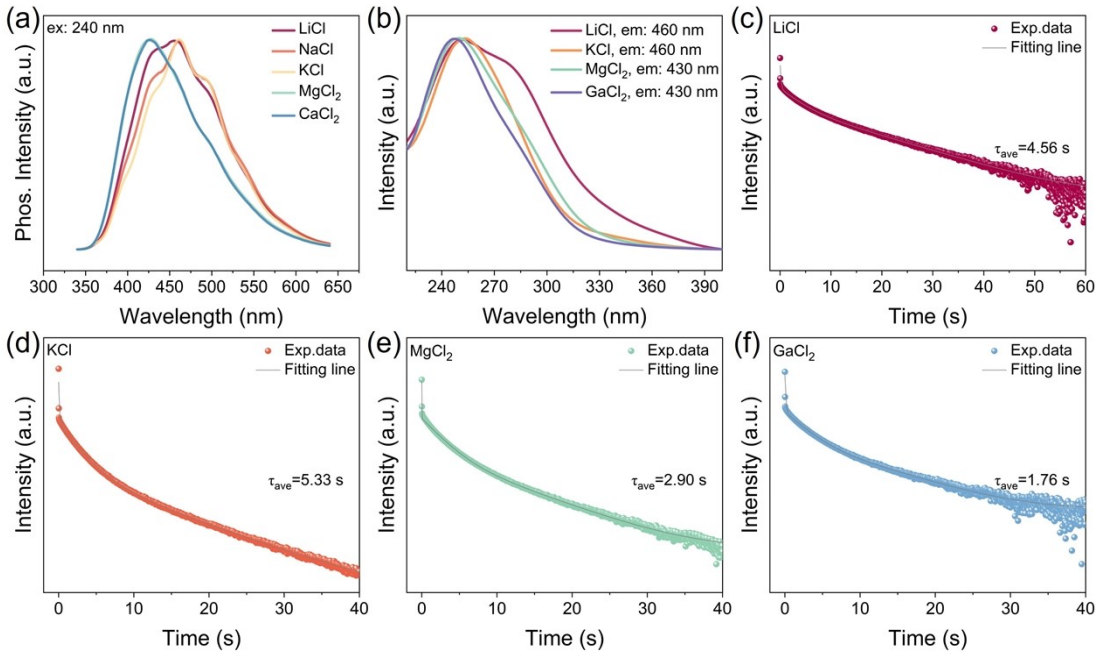

Fig. S14. The phosphorescence emission (a) and excitation (b) spectra of X/CDs@SiO_2. Note: X here stands for LiCl, NaCl, KCl, $MgCl_2$ and $GaCl_2$, respectively. Time-resolved decay curves and fitted curves (grey lines) of LiCl/CDs@SiO_2 (c), KCl/CDs@SiO_2 (d), $MgCl_2$/CDs@SiO_2 (e) and $GaCl_2$/CDs@SiO_2 (f), monitored at EM: 460 nm and EX: 250 nm wavelengths.

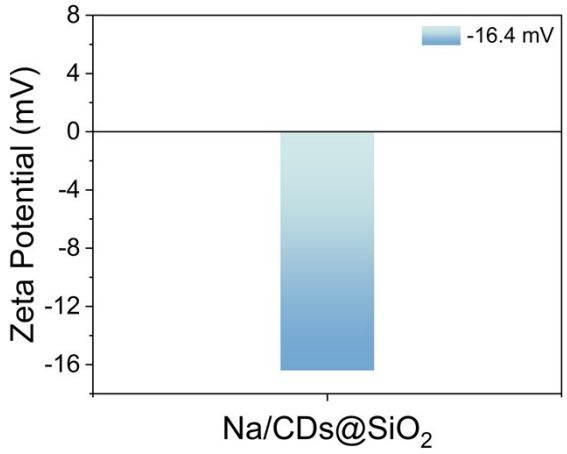

Fig. S15. The Zeta potential of Na/CDs@SiO_2.

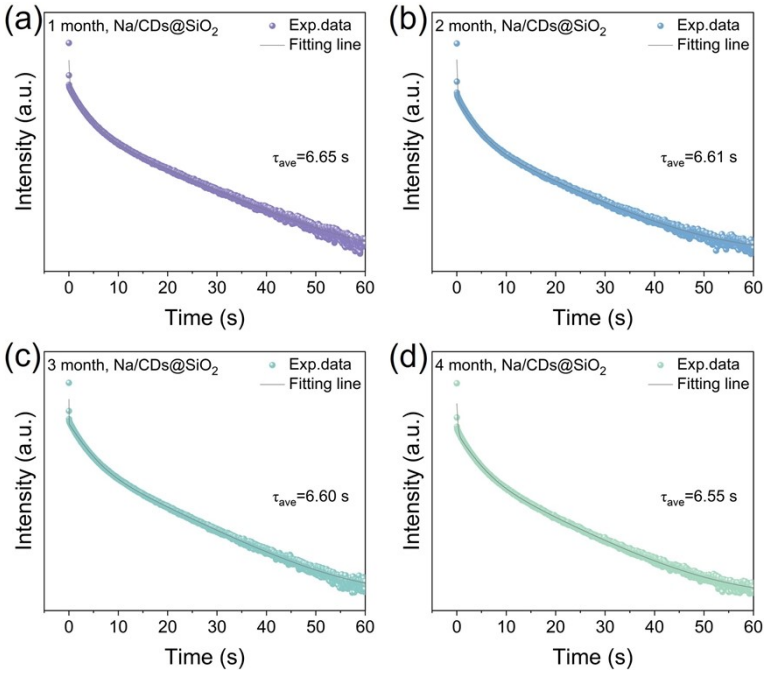

Fig. S16. The Time-resolved decay curves and fitted curves (grey lines) of Na/CDs@SiO_2 placed for 1 (a), 2 (b), 3 (c) and 4 (d) months, monitored at EM: 460 nm and EX: 250 nm wavelengths.