

Supplementary Materials

Enhancement of emission and luminescent thermal stability $K_2SiF_6:Mn^{4+}$ by synergy of co-doping with Na^+ and coating with GQDs

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1. Cl-contained graphene quantum dots (Cl-GQDs)

Cl-GQDs were purchased from the Nanjing XFNANO Materials Tech Co. Ltd.,
China ([Http://www.xfnano.com](http://www.xfnano.com)).

Table 1s Essential information

Items	Content
Synthesis method	Hydrothermal method
Standard	Emitting blue light
Purity	~ 80% quantum dots
Concentration	Standard concentration: 1 mg/mL, Maximum concentration: 20 mg/mL
Packaging	Minimum package is 100 mL
Quantum yield	< 5%

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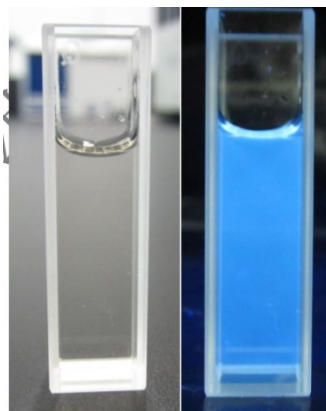


Figure S1. Photos, photo under the natural light (left), photo under 365 nm UV light (right) of Cl-

GQDs.

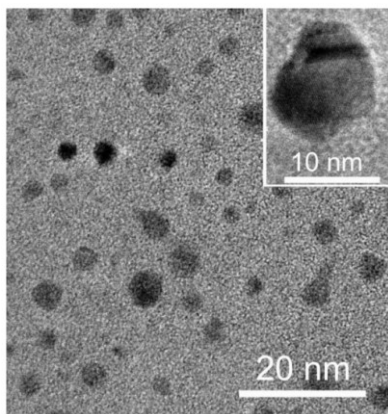


Figure S2. TEM image of Cl-GQDs.

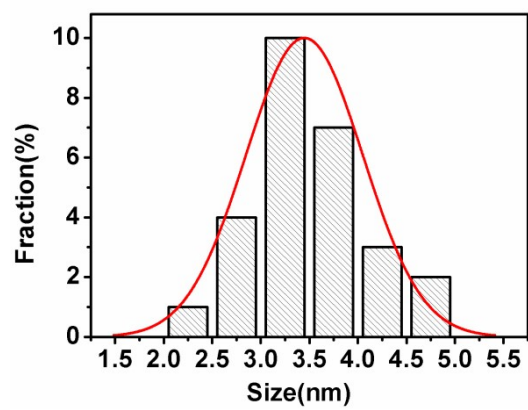


Figure S3. Size distribution of Cl-GQDs.

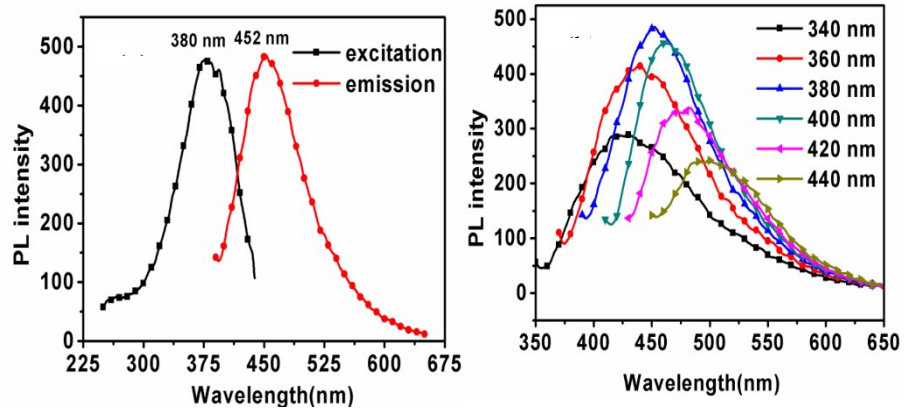


Figure S4. PLE&PL spectra of Cl-GQDs: a) PLE&PL spectra, b) PL spectra excited at different excitations.

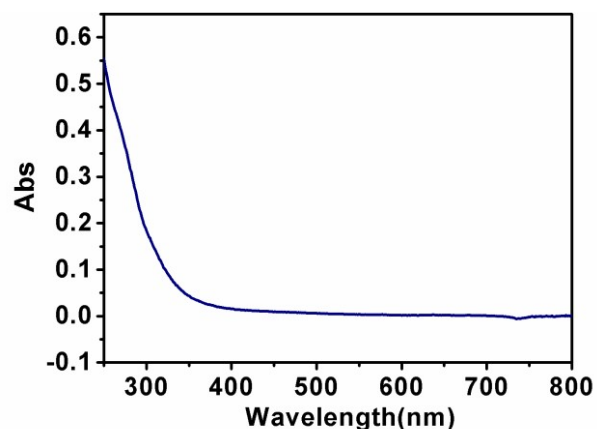


Figure S5. UV-Vis absorption spectrum of Cl-GQDs.

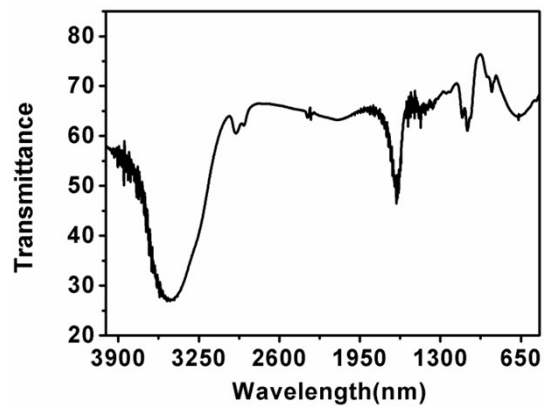


Figure S6. FT-infrared spectrum of Cl-GQDs.

2. Experimental and methodology

2.1. Reagent and apparatus

Cl-GQDs (Cl-contained graphene quantum dots) were purchased from the Nanjing XFNANO Materials Tech Co. Ltd., China (Supplementary materials). Besides, most of the chemical reagents were analytical reagents and purchased from the Sinopharm Chemical Reagent Co. Ltd., China. The elemental contents of samples were identified by the Perkin-Elmer Optima 3100 RL inductively coupled plasma atomic emission spectrometry (ICP-AES). Firstly, the samples were dissolved in 10 mL HCl solution ($V_{\text{HCl}}/V_{\text{H}_2\text{O}} = 1:1$). Then the solution was diluted to 100 mL with deionized water. Finally, the contents of metal element in the solution were determined with ICP-AES. X-ray diffraction (XRD) was examined by Rigaku D/max 2500 V diffractometer. The morphologies of the samples were analyzed by Hitachi S-3400 scanning electron microscopy (SEM) and an attached energy-dispersive x-ray spectrometer (EDS). Samples were installed on an aluminum sheet coated with Au. The photoluminescence and photoluminescence excitation spectra (PL&PLE) at room temperature were recorded by using a Horiba Fluoro Max-4-R F6000 spectrophotometer. The luminescent decay curves were measured by an Edinburgh FLS980 fluorescence spectrophotometer. The internal quantum yield of the samples were measured by an Edinburgh FLS980 fluorescence spectrophotometer by recording excitation and emission intensities with and without the samples. Fourier Transform Infrared Spectroscopy (FT-IR) was registered by a Bruker Tensor 27 Spectrometer (Germany) with a KBr disc in the

wavelength range of 4000–400 cm^{-1} . TG was measured by a NETZSCH STA 409 PC/PG thermogravimetric analyzer. The sample powder with a mass of 10 ± 0.1 mg was used in the experiment, and the sample was loaded without being pressed into a platinum crucible, and the heating rate was 10 $^{\circ}\text{C}/\text{min}$. The protective atmosphere was pure nitrogen gas (99.999%) with flow rate of 20 ml/min. The performances of WLEDs were determined by an auto-temperature LED optoelectronic analyser (LATA-1000, Everfine). X-ray Photoelectron Spectroscopy (XPS) were made with a Thermo Scientific K-Alpha X-ray Photoelectron Spectroscopy energy spectrometer.

2.2. Preparation of samples

2.2.1. $\text{KSF}:x\text{Na}^+$

Sample of $\text{KSF}:0.10\text{Na}^+$ was synthesized as follows: First, 95 mmol (13.13 g) K_2CO_3 , 5 mmol (0.53 g) Na_2CO_3 and 21 ml H_2O were mixed with stirring to obtain a solution. Then, 200 mmol (28.86 g) of H_2SiF_6 (50%) was slowly added to the solution with stirring. Grind the mixture with agate mortar for 1 h. Finally, $\text{KSF}:0.10\text{Na}^+$ was obtained by drying the mixture at 120 $^{\circ}\text{C}$ for 3 h. Samples of $\text{KSF}:x\text{Na}^+$ ($x = 0.02$ – 0.14) were synthesized in the same way as $\text{KSF}:0.10\text{Na}^+$.

2.2.2. $\text{KSF}:y\text{Mn}^{4+}$

Sample of $\text{KSF}:y\text{Mn}^{4+}$ was synthesized as follows: First, 1.8 mmol (0.2845 g) KMnO_4 , 0.5 g $\text{KF}\cdot 2\text{H}_2\text{O}$, 16 ml of HF (40%) were mixed with stirring until the KMnO_4 was completely dissolved. Then, 28.2 mmol (6.21 g) KSF powder ($y/I =$ atomic ratio of $\text{Mn}/(\text{Mn}+\text{Si}) = 0.06$) was added to the potassium permanganate solution and stirred for

48 h at room temperature. Finally, the crystals were collected, washed several times with absolute ethanol and the sample (i) (KSF:y/Mn^{4+} , $y = 0.06$) was obtained after drying at 70 °C for 3 h. Samples of KSF:y/Mn^{4+} ($y = 0.01-0.12$) were synthesized in the same way as KSF:y/Mn^{4+} .

2.2.3. $\text{KSF:y/Mn}^{4+},x\text{Na}^+$

Sample of $\text{KSF:y/Mn}^{4+},0.10\text{Na}^+$ was synthesized as follows: First, 1.8 mmol (0.2845 g) KMnO_4 , 0.5 g $\text{KF}\cdot 2\text{H}_2\text{O}$, 16 ml HF (40%) were mixed with stirring until the KMnO_4 was completely dissolved. Then, 28.2 mmol (6.17 g) $\text{KSF}:0.10\text{Na}^+$ powder was added to potassium permanganate solution and stirred for 48 h at room temperature. Finally, the crystals were collected, and washed several times with absolute ethanol and the sample (ii) ($\text{KSF:y/Mn}^{4+},0.10\text{Na}^+$) was obtained after drying at 70 °C for 3 h. Samples of $\text{KSF:y/Mn}^{4+},x\text{Na}^+$ ($y = 0.01-0.12$, $x = 0.02-0.14$) were synthesized in the same way as $\text{KSF:y/Mn}^{4+},0.10\text{Na}^+$.

2.2.4. $\text{KSF:y/Mn}^{4+},0.10\text{Na}^+@\text{GQDs}$ $z \text{ mg/mol}$

Sample of $\text{KSF:y/Mn}^{4+},0.10\text{Na}^+@\text{GQDs}$ 10 mg/mol was synthesized as follows: (1) First, 10 ml HF (40%), 0.5 g $\text{KF}\cdot 2\text{H}_2\text{O}$ were dissolved to give a solution, then 20 mmol (4.41 g) $\text{KSF:y/Mn}^{4+},0.10\text{Na}^+$ powder was added into the solution and fully mixed to get mixture (I). (2) Then, 200 μl (10 mg/ml) GQDs were mixed with 5 ml HF (40%) in a hydrothermal tank. (3) Third, under stirring, the mixture (I) was added to the hydrothermal tank. The hydrothermal tank was placed in an oven and kept at 120 °C for 3 h. (4) Finally, the crystals were collected, washed several times with absolute ethanol

and the sample (iii) (KSF:y/Mn⁴⁺,0.10Na⁺@GQDs_{10 mg/mol}) was obtained after drying at 70 °C for 3h. Samples of KSF:y/Mn⁴⁺,0.10Na⁺@GQDs_{z mg/mol} (z = 0-16 mg/mol) were synthesized in the same way as KSF:y/Mn⁴⁺,0.10Na⁺@GQDs_{10 mg/mol}.

3. Mathematical calculation methods

3.1 Color purity

The formula (Eq. S1) is used to calculating color purity:^[37–39]

$$C_p = \frac{\sqrt{(x - x_i)^2 + (y - y_i)^2}}{\sqrt{(x_d - x_i)^2 + (y_d - y_i)^2}} \times 100\% \quad (\text{S1})$$

Here (x, y) stands for the chromaticity coordinates of the sample; (x_i, y_i) stands for the CIE of an equal-energy illuminant with a value of (0.33, 0.33); and (x_d, y_d) stands for the color coordinates corresponding to the dominant wavelength of the excitation.

3.2 Fluorescence lifetime

The luminescence decay curve of the sample can be well fitted by linear equation (Eq. (S3)), which is transformed from Eq. (S2):^[40]

$$y_t = A1 * \exp(-x/\tau) + y_0 \quad (\text{S2})$$

$$\text{Ln}(y_t - y_0) = A1 - x/\tau \quad (\text{S3})$$

3.3 Critical distance (R_c)

The quenching mechanism of Mn⁴⁺ concentration in KSF:yMn⁴⁺ is explored by the

critical distance (R_c) between Mn^{4+} ions. The Eq. (S4)^[39] is use to calculated the R_c .

$$R_c \approx 2 \left[\frac{3V}{4\pi x_c N} \right]^{1/3} \quad (S4)$$

Where V , x_c , and N are the unit cell volume of the sample, the critical concentration of Mn^{4+} and the number of sites that activators can substitute per unit, respectively.

3.4 Multipolar interaction type

Eq. (S5)^[31,41] is used to estimate the multipolar interaction type for the sample.

$$\frac{I}{x} = k [1 + \beta(x)^{\theta/3}]^{-1} \quad (S5)$$

Where I is the PL intensity of the sample, x is the Mn^{4+} concentration ($x \geq x_c$). The β and k are constants for the same test condition. When θ are 6, 8 and 10, the corresponding mechanisms are the dipole-dipole, dipole–quadrupole, and quadrupole–quadrupole interactions, respectively.

3.5 Negative thermal quenching behaviors of the anti-Stokes and the Stokes transitions

Negative thermal quenching behaviors of the anti-Stokes and the Stokes transitions can be expressed with Eqs. (S6-S7).^[36]

$$W_s(T) = D \cdot \frac{\exp\left(\frac{\hbar\omega}{kT}\right)}{\exp\left(\frac{\hbar\omega}{kT}\right) - 1} \quad (S6)$$

$$W_a(T) = D \cdot \frac{1}{\exp\left(\frac{\hbar\omega}{kT}\right) - 1}$$

(S7)

Here, k , T , D and $\hbar\omega$ are the Boltzmann constant, temperature, the proportional coefficient and the coupled vibronic mode, respectively.

3.6 ΔE (chromaticity shift)

ΔE (chromaticity shift) at different temperatures is calculate with Eq. (S8)^[42,43].

$$\Delta E = \sqrt{(u'_t - u'_0)^2 + (v'_t - v'_0)^2 + (w'_t + w'_0)^2} \quad (\text{S8})$$

Where $v' = 9y/(3 - 2x + 12y)$, $u' = 4x/(3 - 2x + 12y)$, $w' = 1 - u' - v'$. v' and u' are the chromaticity coordinates in $u' \cdot v'$ uniform color space. x and y are the chromaticity coordinates, and 0 and t are the chromaticity shift at room temperature and a given temperature, respectively.

3.7 Activation energy (E_a) of the luminescent thermal quenching

Eq. (S9) is applied to calculate the E_a of the luminescent thermal quenching. Eq. (S10) can be transformed from Eq. (S9).^[44,45]

$$I_T = \frac{I_0}{1 + A \exp\left(-\frac{E_a}{k_B T}\right)} \quad (\text{S9})$$

$$\text{Ln}\left(\frac{I_0}{I_T} - 1\right) = \text{Ln}A - \frac{E_a}{k_B T} \quad (\text{S10})$$

Here, I_0 and I_T are the initial emission intensity and the intensity at different temperatures, respectively. A and k_B are a constant and the Boltzmann constant (8.617×10^{-5} eV/K), respectively.