

Electronic Supplemental Material

Silicon doped graphene quantum dots combined with ruthenium(III) ions as a fluorescent probe for turn-on detection of triclosan

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GO preparation

Graphene oxide (GO) was synthesized from graphitic power according to the improved Hummers method [24, 27]. In detail, graphite powder (2.0 g) was slowly added into a solution consisting of concentrated H₂SO₄ (10.0 mL) and P₂O₅ (1.0 g) with stirring, and reacted at 80 °C for 6 h. After cooling to room temperature, deionized water (100 mL) was slowly added. The product was filtered and washed repetitiously using a 0.2 µm Nylon film to remove all traces of acid. The obtained production was transferred to a drying beaker and allowed to dry at 60 °C in a vacuum oven. For the oxidation step of the synthesis, concentrated H₂SO₄ (46 mL) was placed into a beaker flask and chilled to 0 °C using an ice bath. The pretreated graphite was then added to the acid and stirred. KMnO₄ (6.0 g) was added slowly and allowed to dissolve with the aid of stirring, while the temperature was closely monitored so as not to allow the mixture to go above 20 °C. The mixture was then allowed to react at 35 °C for 4 h after which deionized water (300 mL) was added, initially in 20 mL aliquots. After that, the mixture was stirred for 30 min at which time 100 mL of deionized water was added, and then 12 ml of 30% H₂O₂ was added to the mixture resulting in a brilliant yellow color along with bubbling. The mixture was allowed to settle for at least a day after which the clear supernatant was decanted. The remaining mixture was repeated centrifuged and washed with a total of 1 L of 10% HCl solution followed by 1 L of deionized water to remove the acid. The resulting GO was dried at 60 °C in a vacuum oven.

5.0 g GO was suspended in 200 mL deionized water and sonicated for 2.5 h, and then transferred to a 1000-mL volumetric flask. Subsequently, the aqueous GO suspension solution (5 mg mL⁻¹) was used to prepare all of the subsequent dispersions for the further use.

Quantum yield measurements

Fluorescence quantum yields (**QYs**) of Si-GQDs were evaluated by comparison of the wavelength integrated intensity of sample to that of the standard quinine sulfate. The optical density was kept below 0.05 to avoid inner filter effects. The following

equation (1) was used to calculate QY [26, 28]:

$$QY = QY_R \frac{I}{I_R} \frac{A_R}{A} \frac{\eta^2}{\eta_R^2} \quad (1)$$

In the above equation, QY and QY_R represent the quantum yield of the Si-GQDs and standard, I and I_R are the measured integrated intensity of the Si-GQDs and the standard, A and A_R signify the optical density, and η and η_R are the refractive index of the solvents used to dissolve the Si-GQDs and the standard, respectively.

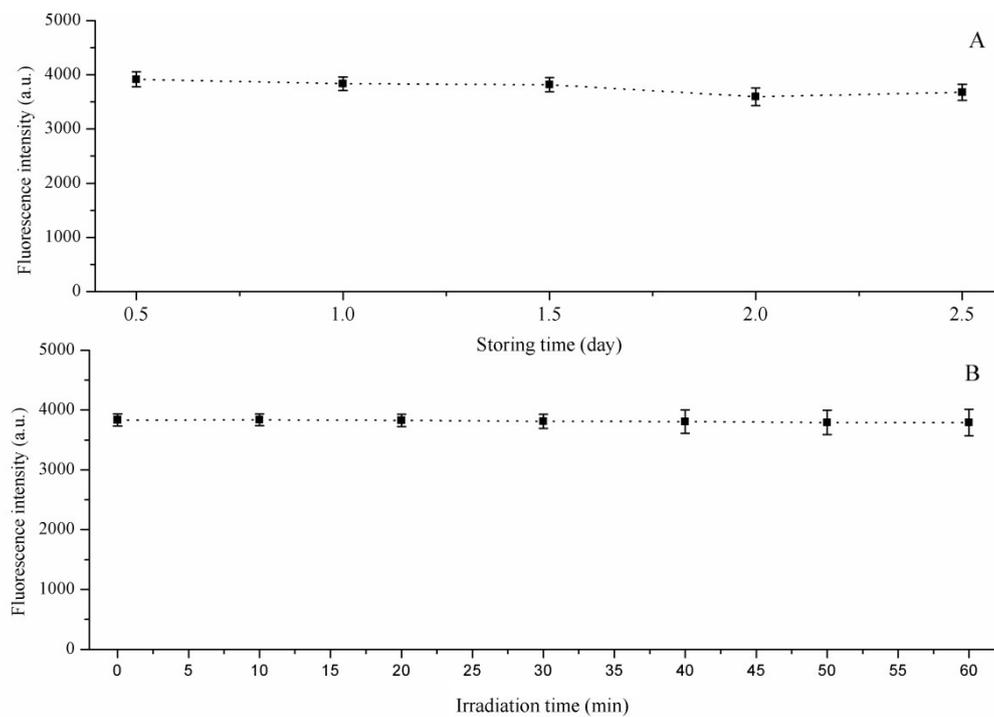


Figure S1 The change results of the fluorescence intensity of SI-GQDs during 2.5 months (A) and under the UV irradiation from 0 to 60 min (B), respectively. Here the concentration of Si-GQDs was $9.0 \mu\text{g mL}^{-1}$.

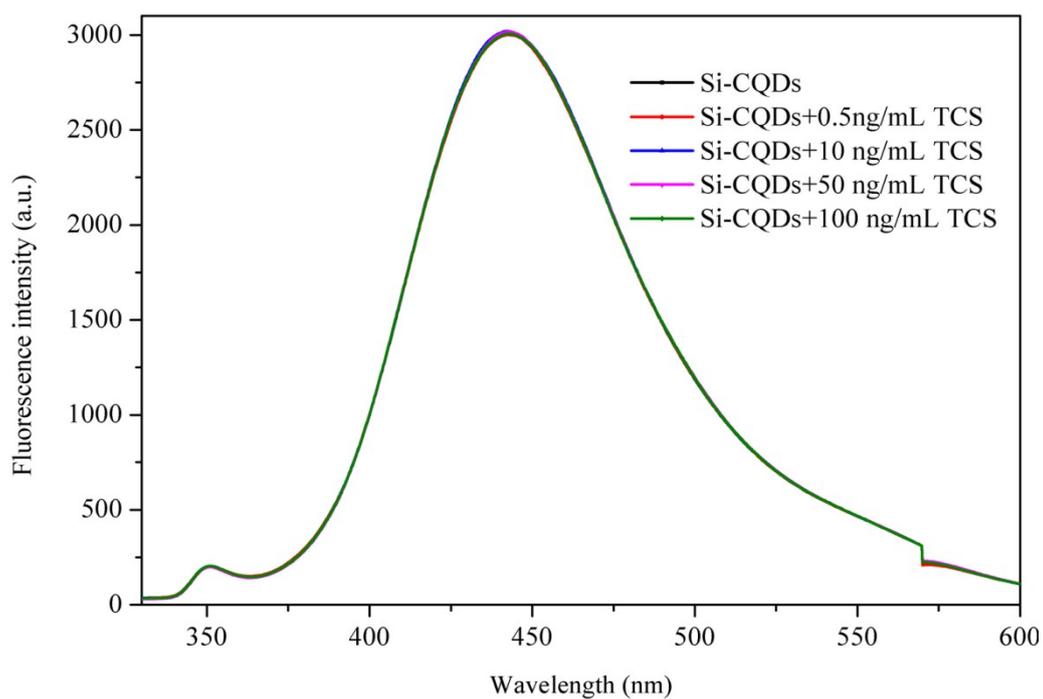


Figure S2 The fluorescence intensity of Si-GQDs in presence of TCS with different concentrations (Here the concentration of Si-GQDs was 9.0 $\mu\text{g/mL}$, the TCS concentration was 0, 0.5, 10, 50, and 100 ng/mL, respectively)

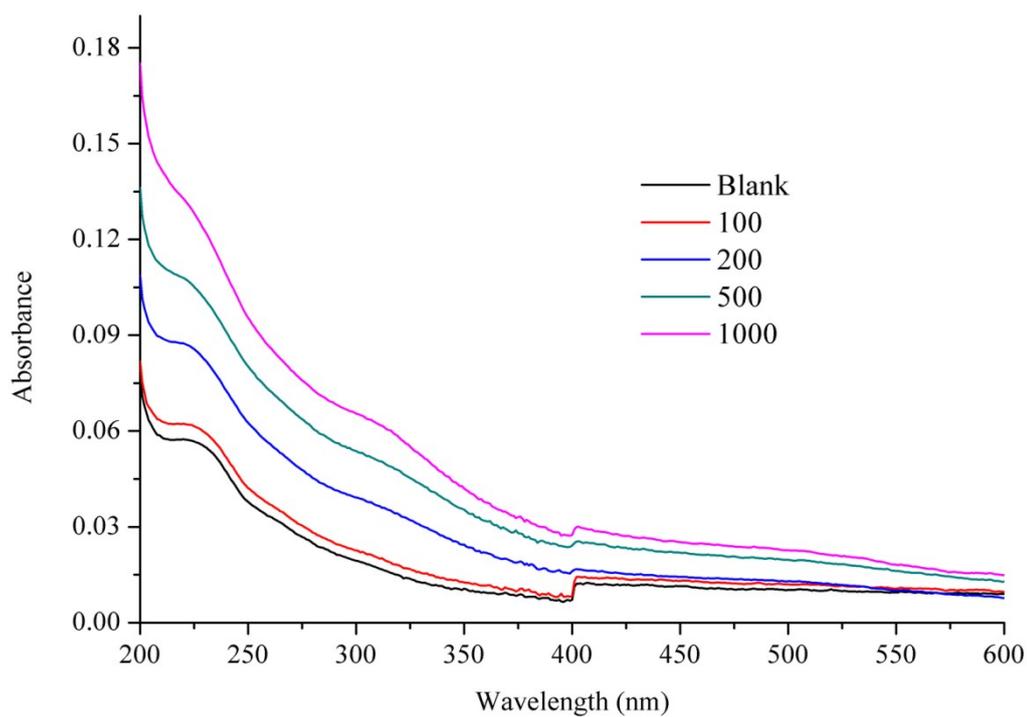


Figure S3 the UV-vis absorption spectra of the Si-GQDs in presence of Ru³⁺ with different concentrations

(Here $C_{\text{Ru}^{3+}}$ was 0, 100, 200, 500, and 1000 nM, respectively. A notable blue-shift of the absorption peak at 230 nm was observed in Si-GQDs solution after addition of Ru³⁺, and the corresponding UV-vis absorption intensity increased with increasing Ru³⁺ concentration, confirming the formation of Si-GQDs/Ru³⁺ complex.)

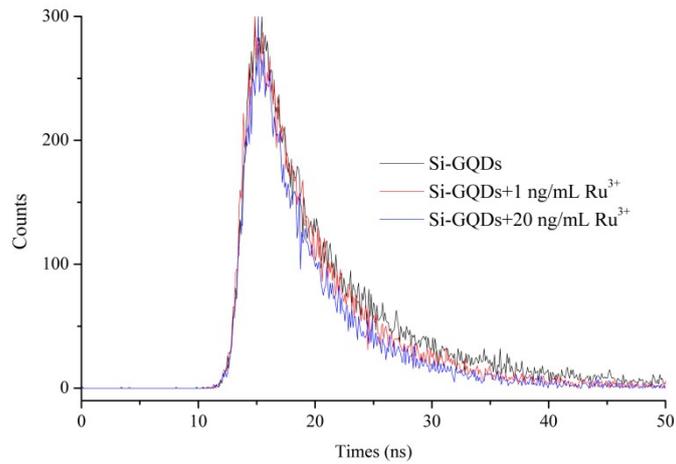


Figure S4 The time-resolved fluorescence decay curves

(Here the concentration of Si-GQDs was 1.8 $\mu\text{g/mL}$. The concentration of Ru^{3+} was 0, 1.0, and 20 ng/mL , respectively).

According to the results of the time-resolved fluorescence decay curves, the average lifetime of Si-GQDs (1.8 $\mu\text{g/mL}$), Si-GQDs (1.8 $\mu\text{g/mL}$) / Ru^{3+} (1.0 ng/mL), and Si-GQDs (1.8 $\mu\text{g/mL}$) / Ru^{3+} (20 ng/mL) was 6.71, 5.07, and 4.54 ns, respectively, with increase of Ru^{3+} concentration from 0 to 20 ng/mL .

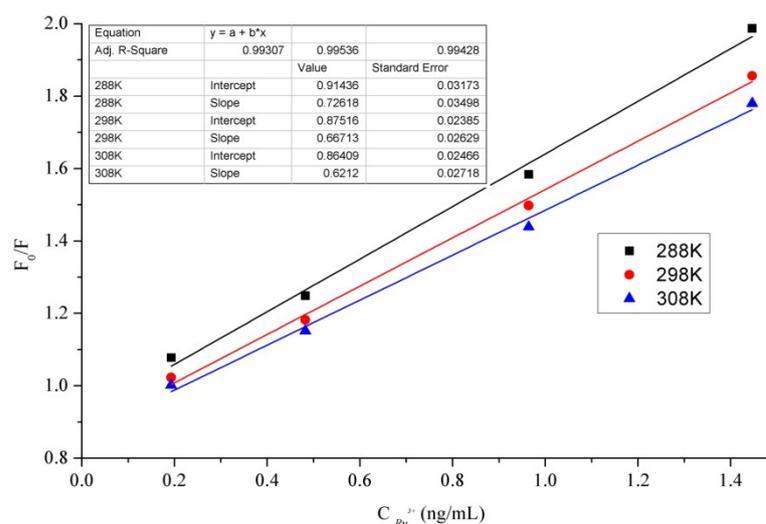


Figure S5 the Stern-Volmer curves of Ru³⁺ quenched Si-GQDs at different temperature (288, 298 and 308 K)

(Here C_{Si-GQDs} was 1.8 μg/mL, C_{Ru³⁺} was 0.19, 0.48, 0.96, and 1.45 μM, respectively)

Here, the Stern-Volmer equation was used to analyze the results of the fluorescence emission spectra of Si-GQDs in order to study the quenching mechanism. The Stern-Volmer equation was as following:

$$\frac{F_0}{F} = 1 + K_{SV}[Q]$$

Where K_{sv} is the Stern-Volmer quenching constant, [Q] is the concentration of quencher Ru³⁺, and F₀, F are the fluorescence intensities of Si-GQDs at 440 nm in the absence and presence of Ru³⁺, respectively. Quenching data are presented as plots of F₀/F versus [Q] in this work.

According to the calculated results by using Stern-Volmer equation, the Stern-Volmer constant (K_{sv}) was 0.7262 at 288 K, 0.6671 at 298K, and 0.6212 at 308K, respectively, with the correlation coefficients (R²) higher than 0.99. The K_{sv} values were decreased with increase of temperature from 288 to 308 K, which suggested that the quenching was a static quenching process [35].

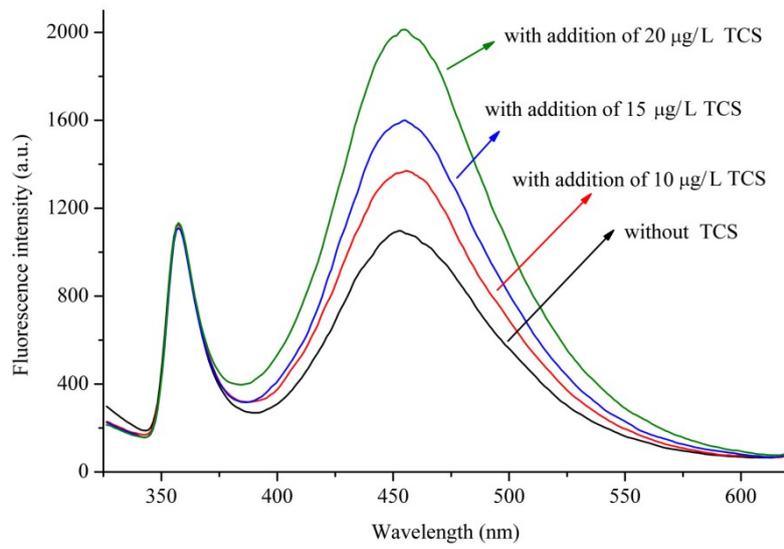


Figure S6 The fluorescence recovery of Si-GQDs/Ru³⁺ with addition of different TCS concentrations

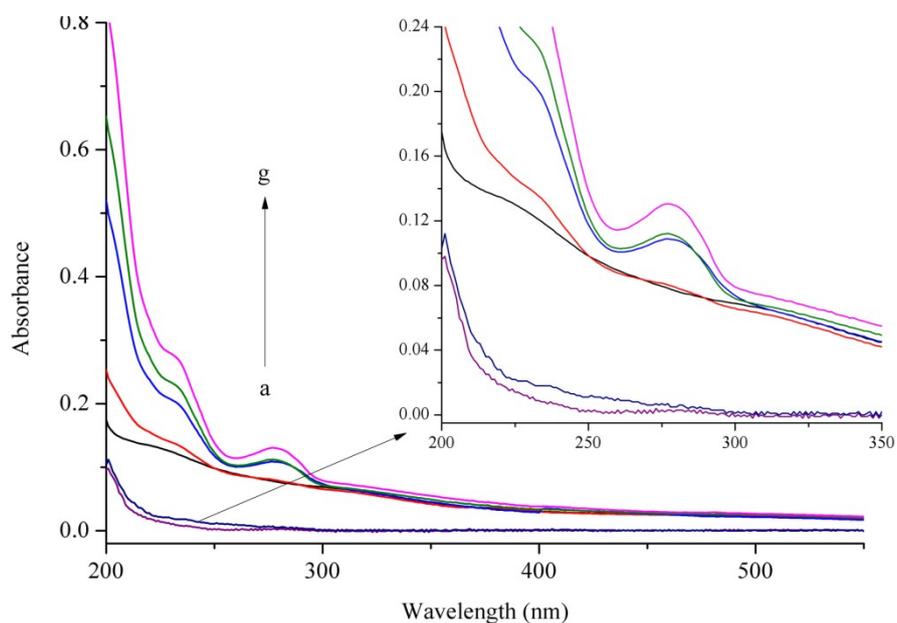


Figure S7 The UV-vis absorption spectra of TCS (a and b), Si-GQDs (c), and Si-GQDs/Ru³⁺ in the presence of TCS (d, e, f, and g)

(Here the concentration of TCS (C_{TCS}) was 2.0 (a) and 4.0 ng mL⁻¹ (b); the concentration of Si-GQDs was 1.8 μ g/mL (c); the concentration of TCS in Si-GQDs/Ru³⁺ system was 0.4 (d), 2.0 (e), 3.0 (f), and 4.0 ng mL⁻¹ (g), respectively; and the concentration of Ru³⁺ was 1.0 μ M in SI-GQDs/Ru³⁺ system. The absorbance of TCS at low levels (a and b) was very poor in the range of 220 to 600 nm).