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 powder according to the improved Hummers method [24, 27]. In detail, graphite powder (2.0 g) was slowly added into a solution consisting of concentrated H$_2$SO$_4$ (10.0 mL) and P$_2$O$_5$ (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 H$_2$SO$_4$ (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. KMnO$_4$ (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% H$_2$O$_2$ 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 ($\Phi$) 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]:

\[
QY = QY_s \frac{I}{I_R} \frac{A_s}{A_R} \frac{\eta^2}{\eta_R^2} \quad (1)
\]

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 \( \eta \) and \( \eta_R \) 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 μg 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 µg/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 Ru$^{3+}$ with different concentrations

(Here $C_{Ru^{3+}}$ 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 Ru$^{3+}$, and the corresponding UV-vis absorption intensity increased with increasing Ru$^{3+}$ concentration, confirming the formation of Si-GQDs/Ru$^{3+}$ complex.)
Figure S4 The time-resolved fluorescence decay curves

(Here the concentration of Si-GQDs was 1.8 µg/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 µg/mL), Si-GQDs (1.8 µg/mL) /Ru$^{3+}$ (1.0 ng/mL), and Si-GQDs (1.8 µg/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.
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 Ru\(^{3+}\), and \(F_0, F\) are the fluorescence intensities of Si-GQDs at 440 nm in the absence and presence of Ru\(^{3+}\), respectively. Quenching data are presented as plots of \(F_0/F\) 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 0.0299K, respectively, with the correlation coefficients \((R^2)\) 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/Ru\textsuperscript{3+} with addition of different TCS concentrations
Figure S7 The UV-vis absorption spectra of TCS (a and b), Si-GQDs (c), and Si-GQDs/Ru$^{3+}$ 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 µg/mL (c); the concentration of TCS in Si-GQDs/Ru$^{3+}$ system was 0.4 (d), 2.0 (e), 3.0 (f), and 4.0 ng mL$^{-1}$ (g), respectively; and the concentration of Ru$^{3+}$ was 1.0 µM in Si-GQDs/Ru$^{3+}$ system. The absorbance of TCS at low levels (a and b) was very poor in the range of 220 to 600 nM).