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Short communication

Highly luminescent organosilane-functionalized carbon dots as a nanosensor for sensitive and selective detection of quercetin in aqueous solution

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ABSTRACT

The organosilane-functionalized carbon dots (SiCDs) were synthesized using citric acid with *N*-(*b*-aminoethyl)-*g*-aminopropyl methyldimethoxy silane (AEAPMS). The as-synthesized SiCDs were characterized by IR, TEM, XPS, NMR and fluorescence. The SiCDs showed a strong emission at 455 nm with excitation at 365 nm. The SiCDs exhibited analytical potential as sensing probes for quercetin (QCT) determination. pH effect, temperature effect, interferences, and analytical performance of the method were investigated. It suggested that SiCDs exhibited high sensitivity and selectivity toward QCT: the linear ranges of SiCDs were estimated to be 0–40 μM while the limit of detection (LOD) was calculated to be 79 nM.

Flavonoids (or bioflavonoids) are a class of plant secondary metabolites, which found in fruits, vegetables and some beverages [1]. Commonly all the three cycles are substituted by hydroxyl groups or methoxy groups and discrete derivatives differ in the stage of substitution and oxidation [2]. Quercetin (3,3′,4′,5,7-pentahydroxyflavone, QCT) is one of the most common flavonols present in nature that has attracted the attention from many researchers [3–5]. It is known to exhibit anticancer, antiallergy, antiviral, antimutagenic, cardiovascular protection, cataract prevention, and lipid peroxidation inhibitory effects. The biological actions have been attributed to their antioxidant properties, because of their ability to scavenge free radicals and the influence on the intracellular redox status [6,7]. Therefore, the determination of quercetin is significant in biochemistry, clinical medicine and natural pharmaceutical chemistry. Hitherto, numerous analytical methods have been employed for the quantification of QCT include electrophoresis with a diode array detector, electroanalytical methods, high-performance liquid chromatography, electrochemical methods, fluorescence detection and so on [8–15]. The fluorescence detection attracted the most attention because of its high sensitivity and local observation by fluorescence imaging spectroscopy [16,17]. However, the traditional QCT fluorescence probes have several shortages, for example, the sensitivity to QCT is not enough; the detection of QCT is susceptible to interference from other flavonoids; last but most important, commonly used fluorescent molecules and quantum dots have cytotoxicity, which limit their applications in biology. Therefore, it is quite demanding to develop low/non-toxic optical sensing materials with a simple preparation process for selective and sensitive detection of QCT.

Carbon dots (CDs), a new member of the quantumsized carbon analogues, have shown great potential in biological, medical and environmental applications due to their fascinating photoluminescent properties and the ability to serve as nontoxic substitutes for traditional heavy-metal-based quantum dots [18–23]. Due to the spatial confinement in the CDs nanostructures, their radiative recombination rates get enhanced and nonradiative recombination rates are suppressed, making their fluorescence efficiency greatly improved [24,25]. Moreover, CDs have also been widely used in analytical chemistry for the determination of metal ions as well as other inorganic ions, such as Cu^{2+}, Hg^{2+}, Fe^{3+}, NO^{2-} and F^{-} [26–32]. However, research on the application of CDs in organic compounds remains limited. To our knowledge, the determination of flavonoid molecule using CDs as probes has not been previously reported [33].

In this communication, we investigated for the first time the fluorescence interactions between the methyldimethoxy silane functionalized CDs (SiCDs) and QCT in detail and have found QCT can selectively and sensitively detect QCT in aqueous solution. On this basis, a rapid, selective, and sensitive sensing method based on the SiCDs fluorescence probe has been developed for the

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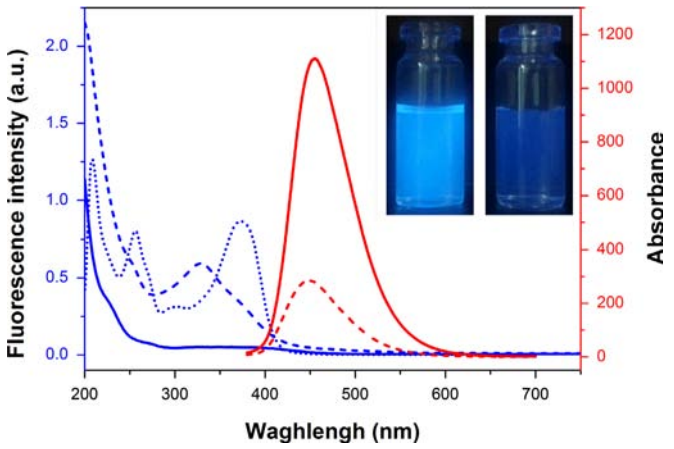

Fig. 1. UV absorption spectra (blue lines) and fluorescence spectra (red lines) of 50 μg mL^{-1} SiCDs solution in the absence (solid lines) and presence (dashed lines) of 40 μM QCT, and the UV absorption spectrum of 40 μM QCT (blue dot line). The inset shows the photos of 50 μg mL^{-1} SiCDs solutions in the absence (left) and presence (right) of 40 μM QCT illuminated by UV light of 365 nm. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

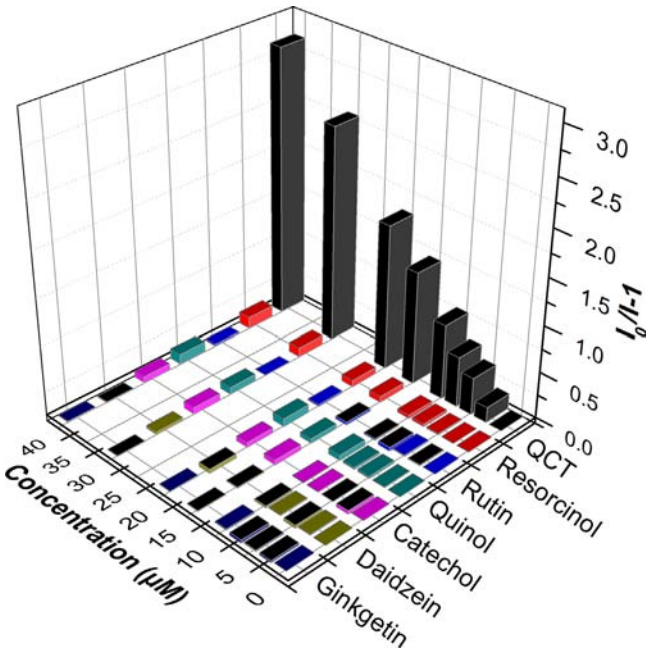

Fig. 2. Quenching efficiencies of QCT and common interferents to the emission of the SiCDs in aqueous solution at different concentrations.

detection of trace QCT in water. A linear range of F_{455} versus QCT concentration was obtained within 0–40 μM, while the limit of detection of 79 nM was obtained.

SiCDs synthesized by the previously reported method [34,35]. The basic procedures include the decomposition and pyrolysis of anhydrous citric acid, accompanied by the formation of gas and condensable vapors together with the surface passivation reaction of the amine groups of *N*-(β-aminoethyl)-γ-aminopropyl methyldimethoxy silane (AEAPMS) with the carboxyl groups driven from the pyrolyzed species [36]. SiCDs were characterized by spectroscopic and microscopic methods (see Figs. S1 and S2 in ESI†). The quantum yield of the resultant ultrasmall (~1.7 nm) SiCDs is as high as 55% (see Figs. S1a and S3 in ESI†). SiCDs dispersed in water emit blue light under 365 nm UV light illumination (Fig. 1 inset).

This strong emission can be attributable to the surface passivation of methyldimethoxy silane group, because it introduces a new kind of surface state and makes electrons be able to facilitate a high yield of radiative recombination [37–39]. The UV–vis absorption spectra show that SiCDs feature two peaks at around 250 nm and 345 nm (Fig. 1). The peak centered about 345 nm due to the trapping of excited state energy by the surface states leads to strong emission [40,41].

It was generally considered that fluorescence from carbon dots can be quenched efficiently by either electron acceptor or electron donor molecules in solution [42]. However, SiCDs are insensitive to most heavy metal-ions, anions and organic moleculars but show high sensitivity and selectivity to QCT. The selectivity of SiCDs fluorescence sensing system was estimated. As shown in Fig. 2, upon the addition of these flavonoids to the SiCDs in aqueous solution, only QCT caused the remarkable fluorescence quenching, while electron-rich phenolic compounds, quinol, resorcinol and catechol, quenched the emission intensity only to a small extent. Besides flavonoids and phenolic compounds, the effects of 20 other kinds of cations, anions and small molecules, including Al^{3+}, Cd^{2+}, Ce^{3+}, Fe^{3+}, Co^{2+}, Cu^{2+}, Hg^{2+}, K^{+}, Na^{+}, La^{3+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, Ag^{+}, Au^{+}, Au^{3+} NO_2^-, SO_3^-, methyl sulfonate and phthalate, on the fluorescence response of SiCDs were investigated (Fig. S4 in ESI†). Fluorescence intensity of SiCDs was quenched 25% as soon as Hg^{2+} (40 μM) was added, due to the stronger affinity constants between Hg^{2+} and carboxylic groups on the surface of SiCDs. However, it obviously has little significance for the detection of QCT. All these observations indicate that the present fluorescent sensing probe exhibits high selectivity toward the QCT detection. The interference of various ions was also investigated. Fig. S5 (ESI†) shows the fluorescence response of the SiCDs toward QCT in the presence of competitive ions. Clearly, these potentially interfering ions do not interfere with QCT bindings with SiCDs as well as the subsequent fluorescence quenching.

For sensitivity study, different concentrations of QCT were investigated in the deionized water. The fluorescence shows continuous quenching with the addition of QCT, but has no effect on the fluorescence wavelength. Besides, the addition of QCT into the SiCDs solution gives rise to a new UV absorption band centered at 328 nm, but the typical absorption peak of QCT at 371 nm was not observed. Upon addition of increasing concentrations of QCT (0–40 μM) to the solution of SiCDs (5×10^{-5} g mL^{-1}), a new absorption band centered at 328 nm appeared with increasing intensity (Fig. 3b). The absorbance of the mixed solution was found to increase linear relationship with the concentration of QCT in range of 0–40 μM (Eq. (1)). The fluorescence sensing behavior of SiCDs for QCT was also explored. Fig. 3a shows a gradual decrease in fluorescent intensity at emission peaks with increasing QCT concentration, suggesting that this system is sensitive to QCT concentration. In the range of 0–40 μM QCT, the relative fluorescent intensity (I_0/I) of SiCDs could be described by the Stern–Volmer plot with a perfect linear behavior (Eq. (2)).

$$A = 0.01355C + 0.052\left(R^2 = 0.99921\right) \quad (1)$$

$$\frac{I_0}{I} = 0.0744C + 1\left(R^2 = 0.99581\right) \quad (2)$$

where I_0 and I are the fluorescence intensity of SiCDs in the absence and presence of QCT and C represents the concentration of QCT. Herein, we calculated the detection limit of 79 nM, respectively, which suggest that this kind of CDs with strong fluorescence activity have very promising application in the detection of QCT. Table 1 summarized the detection limit, linear range and recovery with different methods for the determination of quercetin. Our method was comparable with chemiluminescence sensor [43], resonance Rayleigh scattering [44] electrochemical detection [45] and other fluorescence detection [46].

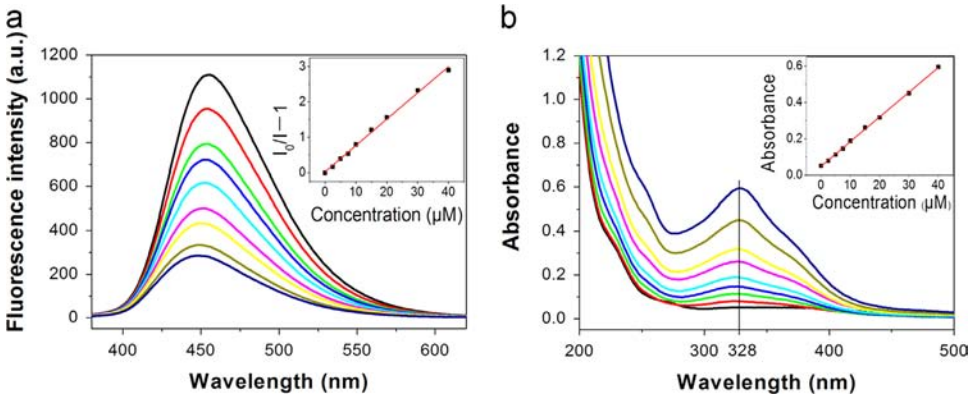

Fig. 3. Fluorescence (a) and absorption (b) spectra of QCT (5×10^{-5} g mL^{-1}) in aqueous solution upon addition of different amounts of QCT (0–40 μM), λ_{ex}=360 nm. Inset: $I_0/I-1$ at 455 nm as a function of QCT concentration (a), absorption at 328 nm a function of QCT concentration (b).

Table 1
Detection of quercetin in samples with different methods.

Methods	Linear range (nM)	LOD (nM)	Recovery (%) (n=10)	Re.
FI-CL	1,400–160,000	930	96.0–101.2	43
Resonance rayleigh scattering	3,245–23,179	97.7	97.1–102.6	44
CE-ED	500–1000,000	225	96.84	45
Fluorescence detection	2,870–31,570	98.8	93.3–105.1	46
This methd	1,000–40,000	79	97.1–103.5	

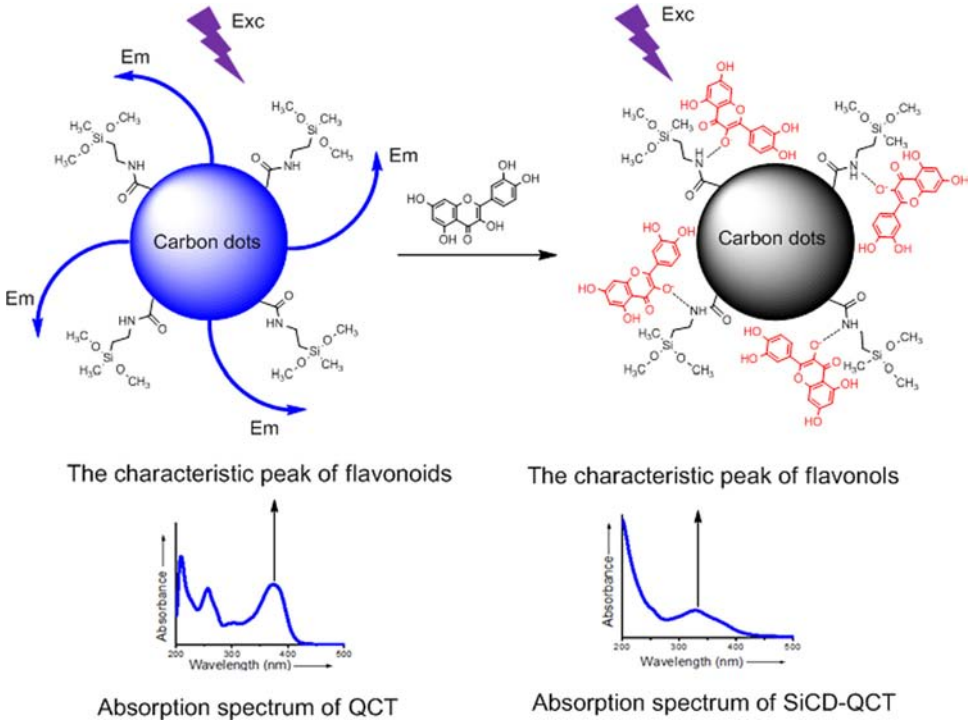

Fig. 4. The schematic illustration for QCT sensing based on the SiCDs fluorescence system.

Usually, the traditional fluorescent sensors could produce highly sensitive but not selective fluorescent quenching toward flavonoids. However, the SiCDs nanosensor herein shows highly selective recognition and detection for QCT in aqueous solution. It is probably because QCT complexed on the surface of SiCDs by electrostatic interaction. The response mechanism is shown in Fig. 4. The surface of SiCDs contains abundant basic groups, like amide and amino group. In 'hard and soft acids and bases theory' (HSAB), phenolic hydroxyl groups (Ar–OH) from QCT belong to soft acids [16]. The most acidic proton of QCT is that of the hydroxyl group on the C ring (3-hydroxychromone site) with a p*Ka* of 6.74 [47]. Therefore, QCT would link to the surface of SiCDs through electrostatic interaction between 3-hydroxyl of QCT and basic groups of SiCDs, and further promote the dissociation of 3-hydroxyl and quench the fluorescence of SiCDs. Fig. S6 (ESI†) explains the absorption titrations of QCT with SiCDs in water under neutral conditions. On addition of

SiCDs (20–150 μg L^{-1}), the absorbance at 371 nm decreased and that at wavelengths below 328 nm increased with an isosbestic point appearing at 358 nm. It is because the dissociation of 3-hydroxyl of QCT will make the absorption peak of cinnamoyl moieties blueshift and coincide with absorption peak of flavonoid [48]. Without strong alkaline conditions, the degree of dissociation promoted by the complexation between QCT and SiCDs and increased linearly with SiCDs added. The quenching efficiency of QCT at different temperatures also supported the conclusion (Fig. S7 in ESI†). It decreased as the temperature increased, showed the interaction between CDs and QCT is the static quenching mechanism.

The pH value of the solution is another key factor that affects the sensing system, because the initial fluorescence intensity (in the absence of QCT) and the quenched fluorescence intensity (in the presence of QCT) of SiCDs are both pH-dependent. Fig. S8 (ESI†) is clear that the fluorescence quenching efficiency is at the pH value of 3 is higher, when the concentrations of QCT are above 50 μM. At other pH values, a change in pH has little effect on the fluorescence quenching efficiency. Both the high pH value and the low pH value will promote the hydrolysis of methyldimethoxy silane group, and reduce steric hindrance of the complexation of QCT and SiCDs. However, silanol is prone to copolymerization in the alkaline medium, which would weaken the quenching effect of QCT. Note that the relative fluorescent intensity versus concentration of QCT can be described by the Stern–Volmer plot with a perfect linear behavior in the weak acidic and neutral conditions. Therefore, the pH value of 7 was chosen because it is closer to physiological conditions.

The sensing capability of SiCDs for detecting QCT was evaluated in real water samples collected from Haihe River. The water sample was spiked with standard solutions containing different concentration of QCT. The present approach provides a linear response to QCT in spiked samples at concentrations over the range from 0 to 40 μM ($I_0/I = -0.03259C - 0.03638$, $R^2 = 0.972$) (Fig. S9in ESI†). It is seen that numerous minerals and organics existing in river water caused little interference with the detection of QCT.

In conclusion, we have demonstrated a simple and low toxicity method to use water-soluble methyldimethoxy silane functionalized carbon dots as a highly sensitive and selective nanosensor for the trace detection of QCT in aqueous solution. The response detection mechanism is that QCT complexed on the surface of SiCDs by electrostatic interaction between 3-hydroxyl of QCT and basic groups on the surface of SiCDs. The electrostatic interaction will quench the fluorescence of SiCDs and gives rise to a new absorption peak at 328 nm. The linear range of SiCDs was estimated to be 0–40 μM while the limit of detection (LOD) was calculated to be 79 nM. In addition, this nanosensor for QCT shows outstanding selectivity over other flavonoids and phenolic compounds, suggesting it provides us a simple and effective approach for imaging QCT in vivo and in vitro.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2014.12.029.

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