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Porous carbon quantum dots: one step green synthesis via L-cysteine and application in metal ions detection[†]

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A bottom-up and wet-chemical method employing L-cysteine as precursor has been proved to be an effective strategy for producing fluorescent porous CQDs for the first time, which exhibits stable and strong photoluminescence, and quantum yield reaches 18.1%. Under optimum conditions, a good linear semilogarithmic correlation between the quenching efficiency (F_0/F) and the concentration of chromium ions even at 10⁻⁸ mol L⁻¹ was achieved, and the limit of detection is 1.491×10^{-9} mol L⁻¹. The quenching of the porous CQDs' fluorescence intensity by Cr⁶⁺ may result from the inner filter effect. The generality of this porous CQDs as probes for detection of chromium ions is good and can be readily rapid and efficiently employed in natural environment.

1. Introduction

In the past several decades, the semiconductorquantum dots (QDs) have been followed closely in their unique optical properties and their promising potential applications in bioimaging, sensing, biological labelling, etc ¹⁻⁴. However, the intrinsic toxicity and environmental hazard of heavy metals limited their practical applications.

Recently promising carbon-based quantum dots (CQDs), usually evidence carbon nanocrystals of less than 10 nm in size with different methods. Carbon quantum dots (CQDs) share the remarkably advantageous characteristics of semiconductor quantum dots (QDs) without the burden of essential

toxicity or elemental scarcity, not only exhibiting many alluring optical properties, such as photoluminescence, electrochemiluminescence (ECL) and photoinduced electron transfer, but also presenting some additional advantages over the heavy metal-containing semiconductor-based QDs, such as inertness, biocompatibility and low toxicity⁵. These CQDs can be facilitated without the requirement of rigorous, tanglesome, costly, tedious, or demanding preparation steps, neither for expensive instrument nor passivating agent, which render the procedure in unique and novel aspect to all the existing methods ⁶. As the report suggested that both the size and surface structure are key to the properties of CQDs ⁷⁻⁹. Up to date, many studies have been paid attention to the synthetic methods of

as two types, "bottom-up" approaches and "topdown" methods, respectively. It is exciting that bottom-up approaches such as the carbonization of small organic compounds (i.e. glucose and acetic acids) and natural source (i.e. coffee and orange juice) as the molecular precursors to synthesize CQDs¹⁰⁻¹³, while the top-down methods prepare CQDs from larger carbon materials, such as nanodiamonds, graphite, carbon nanotubes, carbon soots, graphite oxide, activate carbon, lampblack ¹⁴⁻ 21

Because of CQDs's fluorescence (FL) properties, they have also been used for different metal ion analytical applications. Lu et al.²² used fluorescent carbon dots as probes for sensitive and selective detection of mercury ions. CQDs also could be used as probes to detect copper ions ²³. Xu et al.²⁴ by ionic prepared **CQDs** liquid assisted electrochemical exfoliation of graphite electrode, and developed as photoluminescence (PL) and electrochemiluminescence (ECL) probes for efficient detecting $Ru(bpy)_3^{2+}$. Sun et al.²⁵ used onestep pyrolysis method based on citrate precursor to synthesised CODs and application for the determination of Fe³⁺.

In this work, L-cysteine as the molecular precursors facilitates one-step synthesis of porous CQDs through the green approach and application in chromium ions detection, shown in Figure 1. This is the first time that employing the L-cysteine as the reactants to fabricate CQDs without using strong

CQDs. The developed methods can be categorized acid and alkali, passivating reagent, organic agent and complicated pretreatment. Then stable and strong fluorescence intensity was achieved. Additionally, these **CQDs** resisted are photobleaching and stable in water for more than half a year without fluorescence intensity decrease or precipitation. Thus, the porous CODs could be a promising alternative of fluorescence probes for detection of metal ions in a satisfactory manner in natural environment. In order to improve its fluorescence properties and fluorescence quantum yield, the effect of preparation temperature, the amount of carbon source, double distilled water, diphosphorus pentoxide (P₂O₅) was investigated, respectively. Under optimum conditions, a good linear semilogarithmic correlation between the quenching efficiency (F_0/F) and the concentration of chromium ions even at 10⁻⁴ mol L⁻¹ was achieved, and the limit of detection is 1.491×10^{-9} mol L⁻¹. The quenching of the CQDs' fluorescence intensity by Cr⁶⁺ may result from the inner filter effect ²⁶ related to the specific UV-vis absorption of the groups at the surface CODs combination with Cr⁶⁺ ions. Moreover, the generality of this CQDs as probes for detection of chromium ions is good and can be readily rapid and efficiently employed in natural environment.

2. Experimental

2.1. Chemicals and materials

L-cysteine, L-Serine, L-Methionine, L-Alanine, L-Tryptophan, L-Arginine, L-Threonine and L-

CdI₂,

Journal Name Leucine were purchased from Sinopharm chemical reagent Co., LTD. Diphosphorus pentoxide was purchased from Shanghai Lingfeng chemical reagent Co., LTD. NaOH, MnSO₄, AlCl₃•6H₂O, K₂Cr₂O₇, KMnO₄, AgNO₃, SeO₂, NaCl, KCl, CuSO₄•5H₂O, FeCl₃•6H₂O, HgCl₂, Pb(OOCCH₃)₂•3H₂O, Zn(OOCCH₃)₂•2H₂O were acquired from Nanjing Chemical Reagent Co., LTD. Quinine sulfate dihydrate (only for fluorometric analysis) was purchased from Aladdin Chemistry

Co., LTD. All chemicals were used as received without further purification. Dialysis bag (MWCO: Nominal: 3500) was purchased from Shanghai Green Bird Science & Technology Development Co., LTD. All water used in the experiment was double distilled.



Fig. 1. Illustration of the synthesis of carbon quantum dots and application.

2.2. Instruments

The absorption spectrum and photoluminescence spectrum of CQDs were measured at room temperature. Absorption spectra were recorded by a UV-1800 spectrophotometer (Shimadzu, Japan). The photoluminescence spectra were collected by an RF-5301PC fluorescence spectrometer (Shimadzu, Japan). The infrared (IR) spectrum of dried CQDs was obtained on a FT-IR spectrophotometer (Shimadzu, Japan). The size and dispersivity of CQDs were determined by a JEOLJEM 2010FEF TEM (Japan), for which samples were dropped onto a copper grid.

2.3. Preparation of CQDs

Carbon quantum dots has been prepared by the following simple procedure: Briefly, a mixture of 0.27 g L-cysteine and 2 mL double distilled water was added to 2.5 g diphosphorus pentoxide (P_2O_5) in a round-bottom flask without stirring and put plug quickly, meanwhile keep temperature at 200 °C during reaction procedure about 3 min. The reaction mixture was quickly foamed by the heat and a brown sticky liquid was obtained. Then the product cooled to room-temperature. Finally, pH was adjusted to neutral with sodium hydroxide (NaOH), followed by centrifuging at 13000 rpm for 10 min to remove precipitate particles. To further purify the CQDs, the brown solution was then subjected to dialysis against double distilled water through a dialysis bag (MWCO = 3500kDa) for 24 h. A bright yellow aqueous solution was obtained and stored at roomtemperature for further use.

$$H_2O + \frac{n}{m} P_2O_5 \rightarrow \frac{1}{m} \left[\left(P_2O_5 \right)_n \cdot H_2O_m \right]$$
(1)

$$C_3H_7NQS \frac{P_2O_5, PPA}{\Delta} \rightarrow C_3H_3NS_{CQD_3} + 2H_2O$$
 (2)

A trace amount of double distilled water was acted on the system, and it quickly reacted with P2O5 (eq 1). This reaction is highly exothermic, and the released heat was utilized to carbonizing and vaporizing the mixture of L-cysteine within double distilled water. Then, the CQDs at continuous heat was obtained, as the boiling water was selfassembled by the carbonization reaction (eq 2). The self-engendered nanobubbles were produced to remove the excessive heat and utilized as the templates to synthesize CQDs with hollow interiors. Hence P₂O₅ as the dehydrating agent could accelerate the carbonization reaction and excess P₂O₅ reacted with water to produce polyphosphoric acid (PPA). PPA is the semihydrolyzed product of P_2O_5 and still maintains a strong dehydrating effect¹³.

2.4. Quantum yield measurements

The quantum yield of the CQDs was measured by following equation:

$$\Phi = \Phi_{\rm R} \times \frac{\rm I}{\rm I_{\rm R}} \times \frac{\rm A_{\rm R}}{\rm A} \times \frac{\eta^2}{\eta_{\rm R}^2} \tag{3}$$

Where Φ is the quantum yield, I is the measured integrated emission intensity, η is the refractive index, and A is the optical density. The subscript R refers to the reference fluorophore of known quantum yield. The quantum yield (Φ) of CQDs was calculated by comparing the integrated photoluminescence intensities and absorbency values (<0.05) of the carbon quantum dots samples with the references quininesulfate. The quinine sulfate (literature $\Phi = 0.54$) was dissolved in 0.1 M H_2SO_4 (refractive index (n) of 1.33) and the CQDs

was dissolved in distilled water (η =1.33).

2.5. Determination of chromium ions with CQDs

Two microlitres of CQDs solution was placed within 50 mL volumetric flask, and successively diluted with 0.2 M PBS (pH 7) buffer solution. 3.00 mL of the diluted solution was transferred into a quartz cell, and then titrated manually by successive addition of the different concentration of chromium ions standard sample solution with a microsyringe. The excitation wavelength was 391 nm and the fluorescent emission spectra were obtained by scanning the emission from 300 to 700 nm on the spectrofluorimeter using 5 nm/5 nm slit widths. The sensitivity and selectivity measurements were conducted in triplicate.

3. Results and discussion

3.1. Characterization

The TEM image of the porous CQDs showed much dispersion particles with average size of 15.6 nm and spherical shape (Fig. 2). In the process of automatic synthesis, the mixture was composed of numerous particles because of the boiling of water, the carbon nanoparticles were linked with each other to form the agglomerated particles. As shown in the red mark of TEM image, they seem to have multiple voids either inside the particles or on the surface. We can see clearly the agglomerated particle was forming from the nanoparticles. Although their intrinsic mechanism of fluorescence is not yet clearly understood, the as-prepared fluorescent porous **CQDs** exhibited diverse potential

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applications in metal ions detection and fluorescencenm. Despite the accurate emitting mechanism ofimaging in our work.fluorescence and chemical construction were still



Fig.2. TEM image and the corresponding particle size distribution histograms of the products.

The UV-vis absorption spectrum of CQDs aqueous solution revealed the absorption band started at 520 nm. The fluorescence spectra of CODs were measured with the excitation wavelength from 370 to 405 nm by a 5 nm increment. The photograph of the dispersion under UV lamp (365 nm) exhibits a blue color (inset), further revealing that the resultant CQDs exhibit blue fluorescence. The corresponding spectra are given in Fig. 3. It can be seen that the fluorescence intensity gradually increased with the excitation wavelength between 370 and 390 nm, while decrease from 395 to 405 nm. However, stable and strong PL emission peak was obtained at 461 nm when excited at 390 nm, which indicated that fluorescent substances or structures dominate the fluorescence of the CQDs in this excitation range. Moreover, the excitation wavelength varied from 370 to 405 nm and the fluorescence emission spectra nearly created at 461

fluorescence and chemical construction were still not absolutely clear, the fluorescence behavior observed clearly pointed towards the presence of different types of fluorophores within the particles. which had different double bond-conjugation extents, different maximum excitation and emission wavelengths ²⁷, size-dependent optical properties ²⁸. Meanwhile, the FTIR spectrum was characterized to obtain further structural insights about the CQDs, the characteristic absorption bands of O-H at 3560 cm⁻¹, the stretching vibration bands of C–O at 1000 and 870 cm⁻¹ indicate the presence of oxygencontaining functional groups. Furthermore, a broad absorption around the range of 2750 - 3450 cm⁻¹ and two sharp peaks at 1540 and 1650 cm⁻¹ are assigned to the vibration and deformation bands of N-H, suggesting the existence of amino-containing functional groups. In addition, two peaks at 2620 and 680 cm⁻¹ ascribed to stretching vibration band of S-H and S-C, respectively, indicate the containing of sulfur-containing functional groups (Fig.4). According to equation (3), the quantum yield of synthesis CQDs by the present method (CQDs-1) was calculated as 18.1%, shown in the table 1. As a reference, we prepared CQDs at room-temperature and the quantum yield was not beyond 6.2% (CQDs-2). The fluorescence was found to be enhanced more than 3-fold under high reaction temperature, which indicating that reaction temperature (200°C) is the key factor of the quantum yield. Our approach is greener than reported approaches to the preparation

of CQDs ^{5, 29}.

 Table 1. The quantum yields of porous CQDs

Substance	Integrated emission intensity (I)	Abs. at 391 nm	Refractive index (η)	Quantum yield of solvent (\$D)
Quinine	89413.586	0.027	1.33	0.54
sulfate				(known)
CQDs-1	45409.591	0.041	1.33	0.1806
CQDs-2	17601.595	0.046	1.33	0.0624



Fig.3. UV-vis absorption (black line) and PL emissionspectra of the aqueous dispersion of the CQDs and excitation wavelength range from 370 to 405 nm. Inset: the photograph of CQDs dispersion under UV light (365 nm).



Fig.4. FT-IR spectrum of L-cysteine (a) and porous CQDs (b).

3.2. Optimization and application

3.2.1. Effect of solution pH values

The effect of pH on the fluorescence intensity of CQDs was investigated (Fig. 5). Different pH values of as-prepared CQDs which is strong acid - hydrosoluble was achieved by adding the various amounts of solid sodium hydroxide (NaOH). It is seen that the PL intensity increased in range of the pH value from 2.0 to 7.0 while between 8.0 and 13.0 resulted in decrease, which indicated that the fluorescence intensity of CQDs strongly depends on the pH value. Such observations are alike to those of **CQDs** modified with hydroxyl and carboxylic/carbonyl moieties^{18, 30}. Furthemore, fluorescence intensity of CQDs had slightly changed at the range of pH 6.0~8.0, thus, the stability of CQDs to pH could be a superiority for the application in medicine, biology and natural environment.



Fig.5. The effect of solution pH value (2,3,4,5,6,7,8,9,10,11,12 and 13, respectively) on fluorescence of CQDs.

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3.2.2. Effect of ionic strength

To confirm the stability of CQDs under high ionic strength environments, their PL intensities were measured in a solution of 0.2 M PBS (pH 7.0) containing different concentrations of NaCl (Fig.6). As can be seen, it was almost a straight line except the symbol at 0 mM without NaCl aqueous solution. The injection of 300 mM concentration of NaCl caused only a slight change in the PL intensity,which reveals that CQDs are stable even under high ionic strength conditions.



Fig.6. The NaCl concentration (0, 10, 50, 100, 200, 300 mM) on CQDs fluorescence.

3.2.3. Effect of coexisting ions

Considering that the free hexavalent chromium is not existing in the environment, we compared the fluorescence quenching of CQDs caused by $Cr_2O_7^{2-}$ and CrO_4^{2-} , and discovered that their quenching levels are similar, so we demonstrated the Cr^{6+} was the key factor leading to fluorescence quenching(Fig.S1-S2 in the ESI[†]). As shown in

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Figure 7, besides Cr^{6+} , the effects of 11 cations including Ag⁺, Al³⁺, Cd²⁺, Cu²⁺, Fe³⁺, Hg²⁺, Mn²⁺, Pb^{2+} , Se^{4+} , Zn^{2+} and K^+ , on the FL response of CQDs were investigated. The fluorescence of CQDs was insensitive to most cations at 1.0×10^{-4} mol L⁻¹, but only Cr⁶⁺ could effectively quench the fluorescence intensity approached to a half level in a solution of 0.2 M PBS (pH 7.0). On the other hand, the different anions in metal salts should be investigated as well. Therefore, we examined the FL intensity of CQDs affected by the Cl⁻, SO₄²⁻, NO₃⁻, OH⁻, I⁻ and CH₃COO⁻, respectively. As a result, these anions have no influence on FL intensity of CQDs (Fig.8). In addition, there was no obvious variation of fluorescence signals in the presence of all possible interference ions (the concentration of each ion in the mixture was 10^{-4} M) (Fig. S3 in the ESI⁺). This interesting phenomenon impelled us to further investigate the effect factors on the quenching and the possibility to apply CQDs for chromium ions sensing. UV-vis absorption spectra and FL spectra were investigated shown in Figure 9, the UV-vis spectra results showed that the CODs have a long absorption bands from 520 nm, but the line A showed us that the addition of Cr⁶⁺ into the CODs solution gives rise to two new obviously UV-vis absorption bands centered at 252 and 368 nm. The UV-vis absorption spectra of Cr⁶⁺ solution have not absorption above 240 nm. Thus, the two new absorption bands can be attributed to the structure that formed from the combination of Cr⁶⁺ ions with the groups at the surface of CQDs. Furthermore, the

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absorption band started from 520 to 270 nm has partial overlap with the excitation and emission spectra of the CQDs. The emission spectra of CQDs with increasing concentration of chromium ions were recorded (Fig. 10) under the optimal condition. The quenching efficiency (F_0/F) and the concentration of Cr^{6+} in the range from 10 to 5×10^5 nM does not fit a linear, as shown in Fig.11. In consideration of oxidizability of K₂Cr₂O₇, we selected KMnO₄ as reference and prepared series of concentration of 0.1, 1, 10 and 100 µM, respectively (Fig. 12). As can be seen, adding various concentration of KMnO₄ into the solution of CQDs in 0.2 M PBS (pH 7.0), almost did not caused any decrease in FL intensity. On the other hand, that various concentration of K₂Cr₂O₇(0.1, 1, 10 and 100 µM) added into CQDs solution leaded to FL intensity obviously decrease. Thus, the quenching of CQDs solution does not result from oxidizability of $K_2Cr_2O_7$. It is regarded that absorption of excitation and/or emission radiation by a sample reduces fluorescence intensity and results in a nonlinear relationship between the observed fluorescence intensity and the concentration of the fluorophore; i.e., FL can be guenched by the so-called inner filter effect ²⁶. As discussed above, the quenching of the CQDs' fluorescence intensity by Cr⁶⁺ may result from the inner filter effect related to the specific UVvis absorption of the groups at the surface of CQDs combination with Cr⁶⁺ ions. There is almost linear semilogarithmic correlation between the quenching efficiency (F₀/F) and the concentration of Cr^{6+} (see

 $Log(F_0/F) = 1279.6C + 0.024 R^2 = 0.9978$ (4)

Where F_0 and F are the FL intensities of CQDs in the absence and presence of Cr^{6+} and C represents the concentration of Cr^{6+} . The limit of detection (LOD) is defined by the equation $LOD=3\sigma/k$, where σ is the standard deviation of blank measurements (n=11) and k is the slope of calibration graph. Here LOD of Cr^{6+} ion was 1.491×10^{-9} mol L⁻¹. These results show that the CQDs with strong FL activity have very promising application in the detection of Cr^{6+} .



Fig.7. Metal ions effects on fluorescence of CQDs in a solution of 0.2 M PBS (pH 7.0).The concentration of the ions was 1.0×10^{-4} mol L⁻¹.

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Fig.8. Anions effects on fluorescence of CQDs in a solution of 0.2 M PBS (pH 7.0).The concentration of the ions was 1.0×10^{-4} mol L⁻¹.



Fig.9. UV absorption spectra (A, B) and FL spectra excitation spectra(E, F) and emission spectra(C, D) of CQDs solution in the absence (B, C, E) and presence (A, D, F) of 100 μ M Cr⁶⁺.



Fig.10. FL response of CQDs upon addition of various concentration of chromium ions (from top to bottom, 0, 0.01, 0.1, 1, 10, 20, 30, 100, 200, 300, 400, and 500 μ M) in a pH 7 PBS solution. Inset: semilogarithmic plot of F_0/F of CQDs vs the concentration of Cr⁶⁺



Fig.11. The quenching efficiency (F_0/F) plot of Cr⁶⁺ concentration dependence of the fluorescence intensity of CQDs.

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Fig.12. FL response of CQDs upon addition of various concentration of KMnO₄ and $K_2Cr_2O_7$ (0.1, 1, 10 and 100 μ M) in a pH 7 PBS solution, respectively.

3.2.4. Application

The proposed method of CQDs for detecting Cr⁶⁺ in real water samples was explored by lake water samples obtained from the Lake Thai of Wuxi, Jiangsu province, China. The samples under filtered and centrifuged of preprocessing were spiked with containing standard solutions different concentration of Cr⁶⁺. The present approach provides a linear response to Cr⁶⁺ ions in spiked samples at concentrations over the range from 0 to 2.5 μ M (log(F₀/F)=33713C+0.001, R²=0.9991) and the result of concentration of Cr⁶⁺ ions in different area of Lake Thai (n=5) was (1.563±0.053)×10-9 mol L⁻¹. In spite of the interference from numerous minerals and organics existing in lake water, this sensing system can still be applicated in fresh lake water to detecting and satisfying the practical Cr⁶⁺ ions in real samples. These results imply that the

CQDs is likely to be capable of practically useful Cr^{6+} ions detection upon further development.

We also applied the CQDs as fluorescent ink for text encryption. Interestingly, the word written with ink was invisible under daylight (Fig. 13a), whereas cyan fluorescent "CQDs" clearly observed under UV light (Fig. 13b). Hence, these photographs strongly depicted that fluorescent CQDs described here could play a role in text encryption and anticounterfeit techniques.

Benefited from their large-scale synthesis and low toxicity, CQDs were further loaded on commercial silica powder to obtain fluorescent powder. As shown in Fig. 13c (under daylight) and Fig. 13d (under UV light), fluorescent-response power (beaker 1) followed by adsorption of the CQDs shifted as non-fluorescent silica powder (beaker 2). Significantly, the fluorescent powder obtained here has been preserved for more than three months without obvious changes, indicating that it may provide the possibility for matching the requirement of commercial scale.

In addition, it was also found that other amino acids may serve as the carbon precursor for synthesizing fluorescent CQDs. Therefore, other types of amino acids (L-Serine, L-Methionine, L-Alanine, L-Tryptophan, L-Arginine, L-Threonine and L-Leucine) have been applied to test the possibility of producing fluorescent CQDs. As shown in Fig. 13, the corresponding photographs under daylight (e) and UV light (f) proved that different levels of emitted fluorescence displayed Journal Name

together with varying carbon precursors, suggesting that this simple method may be widely involved in synthesizing different CQDs towards specific demands originated from amino acids.

Fig.13. CQDs as fluorescent ink for text marked "CQDs" on paper under daylight (a) and UV light (b); photographs of silica powder loaded with (1) and without (2) CQDs under daylight(c) and UV light(d); photographs of fluorescent CQDs solution prepared by a series of amino acids from left to right including L-Serine, L-Methionine, L-Alanine, L-Tryptophan, L-Arginine, L-Threonine and L-Leucine under daylight (e) and UV light (f).

4. Conclusions

Our present study allows offer a straightforward and facile strategy to prepare high-quality CQDs even through various methods upward scalability of CODs. which exhibit stable and strong photoluminescence. Significantly, the porous CQDs described here were further employed for preparing fluorescent powder and ink towards commercial applications, and other types of amino acids have been proved to serve as carbon precursors to produce fluorescent CQDs. Under optimum porous conditions, а good linear semilogarithmic correlation between the quenching efficiency (F_0/F) and the concentration of chromium ions, and the limit of detection is part-per-billion level. The quenching of the CODs' fluorescence intensity by Cr⁶⁺ may result from the inner filter effect related to the specific UV-vis absorption of the groups at the surface of CQDs combination with Cr⁶⁺ ions, compared with KMnO₄ the quenching of CQDs solution is not result in oxidizability of K₂Cr₂O₇. The CQDs' FL-based sensing system shows many including rapid detection, high advantages, sensitivity, good selectivity, wide linear response range, and low cost, and has been demonstrated to have promising applications in the detection of chromium ions in environmental water samples.

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[†] Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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Graphical abstract

A bottom-up and wet-chemical method employing L-cysteine as precursor has been proved to be an effective strategy for producing fluorescent porous CQDs. In comparison with the previous methods, this method bears several unique merits, such as clean, cheap, convenient and potential advancement for large-scale industrialization. This one-step "green" process without the requirement of rigorous preparation steps. Neither expensive instruments nor passivating agents was needed for the synthesis of CQDs, which render the procedure unique and novel to all the existing methods. It suggests these CQDs thus obtained are well water-soluble and exhibit strong fluorescence. In this work, these porous CQDs have been proved as a sensitive and selective probe for the detection of chromium ions. Moreover, we believe that the as-prepared CQDs can be one of the most promising candidates for fluorescence marker, biomedical imaging, bio-sensors and drug delivery.