PHENOLIC HYDROXYL GROUP-CARBON DOTS AS A FLUORESCENT PROBE FOR THE DETECTION OF HYDROGEN PEROXIDE AND GLUCOSE IN MILK

Y. Wei, L. Li, Ch. Ma, Y. Wu, Ch. Zhu, H. Gao, J. Gu, Y. Xiong, X. Li, Z. Wang, G. Wang, S. Guo, G. Chen*

School of Science at Jiangnan University, Wuxi, China;
Jiangsu Provincial Research Center of Light Industrial Optoelectronic Engineering and Technology, Wuxi, China; e-mail: jncgq@jiangnan.edu.cn

In order to directly detect the concentration of glucose in milk, carbon dots (CDs) rich in phenolic hydroxyl groups were synthesized in one step as a fluorescent probe. We presented a new glucose oxidase (GOx)-mediated strategy to detect glucose, which allowed the quantitative analysis of hydrogen peroxide (H_2O_2) and glucose. Furthermore, it was possible to detect H_2O_2 and glucose directly in complex systems such as milk. The result in milk showed that the fluorescence of the CDs was quenched by H_2O_2 with the concentration range from 1 to 100 μM linearly, and the correlation coefficient was 0.977 with a detection limit of 0.175 μM. Similarly, a linear correlation was built between the fluorescence of the CDs and the concentration of glucose in the range from 10 to 100 μM with a correlation coefficient of 0.968 and a detection limit of 0.686 μM. The recovery rate was 97.30–101.05%, which showed high sensitivity in the detection of glucose in milk. As far as we know, this was the first time that CDs were used as a fluorescent probe to detect glucose in milk directly, which removed the step of pretreating milk and provided a supplement and extension for the detection of glucose in fluorescent spectroscopy.

Keywords: *carbon dots, fluorescent probe, detect, hydrogen peroxide, glucose, milk.*

ФЛУОРЕСЦЕНТНЫЙ ЗОНД НА ОСНОВЕ УГЛЕРОДНЫХ ТОЧЕК С ФЕНОЛЬНО-ГИДРОКСИЛЬНЫМИ ГРУППАМИ ДЛЯ ОБНАРУЖЕНИЯ ПЕРЕКИСИ ВОДОРОДА И ГЛЮКОЗЫ В МОЛОКЕ

Y. Wei, L. Li, Ch. Ma, Y. Wu, Ch. Zhu, H. Gao, J. Gu, Y. Xiong, X. Li, Z. Wang, G. Wang, S. Guo, G. Chen*

УДК 535.372:547.455.623

Научная школа Университета Цзяннань, Уси, Китай;
Исследовательский центр оптоэлектронной техники и технологий провинции Цзянсу, Уси, Китай; e-mail: jncgq@jiangnan.edu.cn

(Поступила 24 мая 2021)

Для определения концентрации глюкозы в молоке синтезированы богатые фенольно-гидроксильными группами углеродные точки. Представлена методика определения глюкозы, опосредованная глюкозооксидазой, которая позволяет проводить количественный анализ перекиси водорода (H_2O_2) и глюкозы. Можно определять H_2O_2 и глюкозу непосредственно в сложных системах, таких как молоко. Показано, что в диапазоне концентраций H_2O_2 1—100 мкМ флуоресценция углеродных точек тушится линейно с коэффициентом корреляции 0.977 и пределом обнаружения 0.175 мкМ. Аналогично построена линейная корреляция между флуоресценцией углеродных точек и концентрацией глюкозы в диапазоне 10—100 мкМ с коэффициентом корреляции 0.968 и пределом обнаружения 0.686 мкМ. Степень восстановления 97.30—101.05 % свидетельствует о высокой чувствительности определения глюкозы в молоке. Данный метод стал первым случаем, когда углеродные точки использовались в качестве флуоресцентного зонда для непосредственного обнаружения глюкозы

в молоке, что исключает этап его предварительной обработки и обеспечивает расширение возможностей использования флуоресцентной спектроскопии.

Ключевые слова: *углеродные точки, флуоресцентный зонд, детектор, перекись водорода, глюкоза, молоко.*

Introduction. Glucose is the most important monosaccharide in nature; thus, so it has been widely distributed all over the world. It is also a kind of aldehyde rich in hydroxide radicals. Glucose plays an important role in the field of biology [1], because it is the energy source and metabolic intermediate of living cells, namely, the main energy supply substance of organisms. Moreover, it has great significance in the process of life activities as it is the primary source of energy needed by all living organisms to support life activities. A large number of medical studies have shown that excessive intake of sugar weakens the immune system, leading to obesity, arteriosclerosis, hypertension, and diabetes [2]. Glucose is often used as the main raw and auxiliary material in the food industry, and it is also one of the main ingredients in most foods. In recent years, in order to reduce costs and make more profits, some businesses have adulterated food with saccharides. On the one hand, sugar sweeteners cost less than other sweeteners, and they are not easily identified. On the other hand, they are used to conceal the density change of food after introducing other additives [3]. For example, the methods of adulterating fresh milk include adding nitrogen compounds, which are commonly used to increase the protein content in the Kjeldahl method, adding preservatives to extend the shelf life of dairy products, adding diluting water to make additional volume and glucose to conceal the density change of the dairy product caused by adulteration [4]. Therefore, the quantitative detection of glucose in food is of great significance in protecting the health of ordinary people and saving the lives of patients. At the same time, the application of the fluorescent probe to detect glucose has a certain meaning for promoting the development of fluorescent spectroscopy detection, expanding and supplementing the existing detection methods.

At present, researchers have made some achievements in the detection of common carbohydrates, such as titrimetric analysis, chromatography, high-performance liquid chromatography, capillary electrophoresis, and enzymatic methods [5–7]. However, these methods have their own defects, such as high operating costs, the need for time and skilled operators, the lack of specificity or selectivity, and low detection accuracy. In addition, the complex detection environment causes great interference with the detection results; thus, it is necessary to introduce a fluorescent probe. In order to better meet the detection indicators, the fluorescent analytical method has become a research hotspot of many scholars [8–12]. Carbon dots have widely been used in heavy metal ions, photocatalysis, LED, and sensing because of its simple synthesis, low cost, low toxicity, biocompatibility, and high specificity [13–18].

Carbon dots was prepared by a solvothermal method and first used as a fluorescent probe for the selective detection of H_2O_2 and glucose in milk that had no need for pretreatment. The result showed that the fluorescence of the CDs was quenched by H_2O_2 within the concentration range 1–100 μM linearly. Glucose could be oxidized by glucose oxidase to produce H_2O_2; therefore, the concentration of glucose could be detected by the concentration of H_2O_2 coming from enzymolysis. According to this regulation, an environmentally friendly and sensitive sensor for the detection of glucose was established. The experimental results indicated that the proposed method had a good linear relationship between the fluorescence of the CDs and the concentration of glucose within the range 10 to 100 μM.

Materials and methods. Phloroglucinol, glucose, fructose, sucrose, maltose, hydrogen peroxide (30%), concentrated hydrochloric acid (HCl), nitric acid, sodium hydroxide (NaOH), dibasic sodium phosphate (Na_2HPO_4), sodium dihydrogen phosphate (NaH_2PO_4), alanine, ibuprofen, L-histidine, biuret, D-phenylalanine, L-lysine, DL-serine, L-tyrosine, L-phenylalanine, DL-tryptophan, glycine, DL-aspartic acid, L-valine, sodium chloride (NaC1), magnesium chloride ($MgC1_2$), and calcium chloride ($CaCl_2$) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Beijing, China). Glucose oxidase (GOx) was purchased from Aladdin (Beijing, China). Milk was purchased from Bright Dairy Co., Ltd (Shanghai, China). All reagents used were of analytical grade. All reagents used deionized water purified by the Labonova purification system (18 MΩ/cm). All glass instruments and quartz cuvettes were soaked in dilute nitric acid and cleaned with deionized water.

The fluorescent spectra of all samples were measured by Edinburgh integrated steady-state transient fluorescence spectrometer FS5, and the absorption spectra were measured by a UV-2600 ultraviolet spectrophotometer (Shimadzu, Japan). All solid reagents were weighed with a METTLER TOLEDO instrument microelectronic balance (Shanghai, China). The JEOL 2100F microscope operating (Peabody, MA, USA)

was utilized to obtain the transmission electron microscopy (TEM) photograph. The Fourier-transform infrared (FTIR) spectra were gathered by the Nicolet iS5 spectrometer (Waltham, MA, USA).

Carbon dots was prepared by phloroglucinol and ethanol according to the previous method with some modifications [19]. Briefly, 200 mg phloroglucinol, 40 mL ethanol, and concentrated hydrochloric acid (2 mL) as a catalyst were added into a 100-mL autoclave lined with tetrafluoroethylene and heated at 220°C for 2 h. The reaction product was concentrated to 1/4 of the former volume by a vacuum evaporator after cooling to 20°C. Then, the concentrated solution was purified by the column chromatography with an eluent mixed with methanol and dichloromethane. At last, the purified solution was prepared into a powder by a freeze-dryer for further use.

Procedures for H_2O_2 detection: At first, a milk solution with different concentrations of hydrogen peroxide was prepared. After that, the pH value of the solution was adjusted to 5.5 by the phosphate buffer, which respectively consisted of Na_2HPO_4 and NaH_2PO_4 with a concentration of 0.1 M, and adjusted by the diluted HCl and 0.1 M NaOH solution. Then 1 mL of 1 mg/mL CDs was added to 2 mL of the *d*-solution. At last, we measured the fluorescent intensity of the system at 510 nm and defined the blank's fluorescent intensity as F_0, and the others as F.

Glucose detection procedure: A milk solution with different concentrations of glucose and glucose oxidase was prepared. The pH value of the solution was adjusted to 5.5 with the phosphate buffer. After that, the mixed solution was incubated in an oil bath at 30°C for 40 min. 1 mL of (1 mg/mL) CDs was added to 2 mL of the mixed solution, then the mixed solution was cooled to room temperature. Finally, the fluorescent intensity of the system was measured, and the results were recorded in the same way as above.

Results and discussion. *Characterization of CDs.* The CDs were characterized by TEM, X-ray diffraction (XRD), FTIR, fluorescent spectroscopy, and UV-Vis absorption spectrophotometry. The absorption and photoluminescence spectrum of the CDs were provided in Fig. 1a. The photoluminescence spectrum of the CDs indicated an emission peak at 510 nm within the excitation of 460 nm. There were two obvious absorption peaks at wavelengths of 270 and 430 nm, which may be related to the π-π^* transition of sp^2 hybridization and the n-π^* broadened absorption bands of C=O transitions respectively [19]. Figure 1b showed that the lattice spacing of the carbon dots was 0.21 nm. According to Fig. 1c, the XRD patterns of the CDs illustrated a narrow (002) peak centered at around 24°, which confirmed the graphene structure of the CDs with high crystallinity [19, 20]. As shown in Fig. 1d, besides, the strong stretching vibration bands of O-H, C=C,

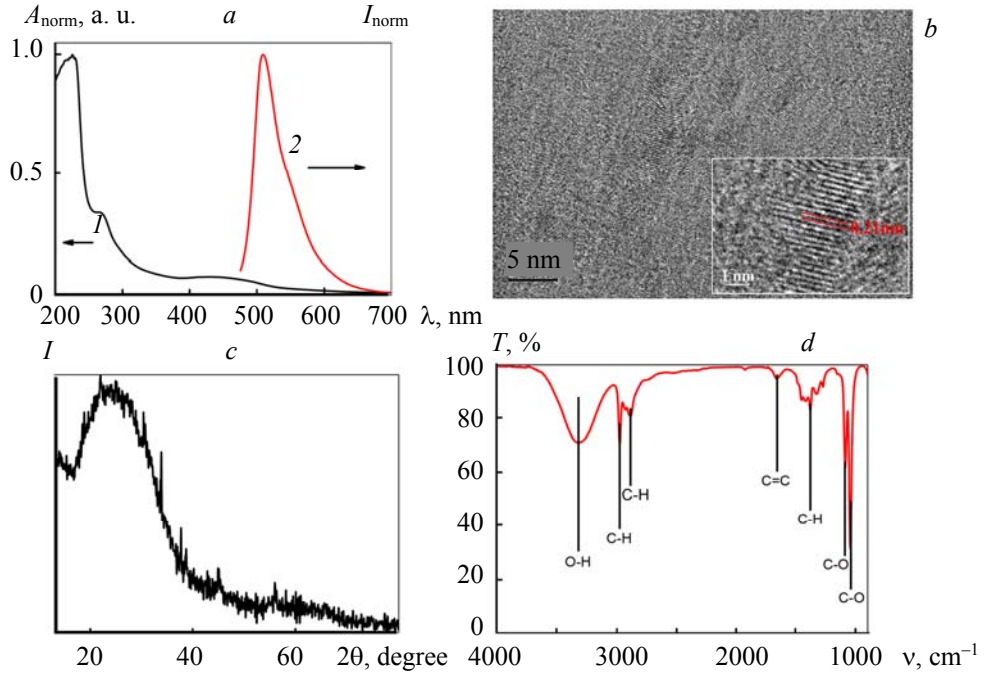

Fig. 1. (a) The absorption spectrum (1), fluorescent emission spectrum (2) of CDs, (b) the TEM image of CDs, (c) the XRD spectrum of CDs, (d) the FTIR spectrum of the CDs.

and C-O belonging to the CDs were observed at 3317, 1660, and 1087 cm^{-1}, respectively. The strong stretching vibration bands of C-H (antisymmetric), C-H (symmetric), and C-O existing in ethanol were also observed at 2972, 2883, and 1044 cm^{-1}, respectively. The bending vibration bands of C-H in ethanol were observed at 1378 cm^{-1}.

Reaction mechanism. Figure 2 depicted that the fluorescent emission peak of CDs was at 510 nm under the excitation at 460 nm. After adding H_2O_2, H_2O_2 oxidized the phenolic hydroxyl groups of the CDs, causing the fluorescence of the CDs to be quenched at 510 nm. By the same principle, glucose could be oxidized by the GOx to generate H_2O_2, which allowed glucose to be detected by the CDs.

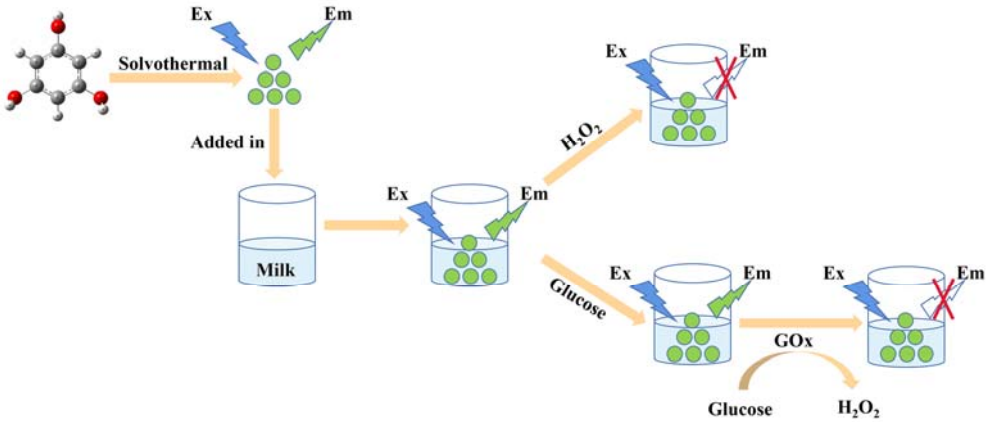

Fig. 2. Schematic illustration of detecting H_2O_2 and glucose in milk directly with carbon dots as the fluorescent probe.

Detection of hydrogen peroxide in milk. Phloroglucinol has a highly conjugated structure. Therefore, the CDs synthesized by phloroglucinol as a precursor have similar properties. The strong electron-pushing effect of the hydroxyl group increases the electron cloud density of the benzene ring and makes the hydrogen atoms on the phenolic hydroxyl group more reactive, which is the reason why the phenolic hydroxyl group is easier to oxidize and has strong reductivity. The CDs rich in phenolic hydroxyl groups also have reductivity and can react with hydrogen peroxide, resulting in the fluorescence quenching of the CDs.

First, we measured the reaction time of the CDs and H_2O_2, as shown in Fig. 3. The fluorescent intensity of the reaction system reached stability after 10 min and remained unchanged basically for 10–90 min, which also indicated that the method was rapid and stable for this detection. Hence, the reaction time was selected as 10 min. Milk solutions with different concentrations of H_2O_2 were prepared: 0 (blank), 1, 5, 10, 20, 40, 60, 80, 100, 200, 400, 600, and 800 μM, and 1 mM, 2, 4, 6, 10, and 20 mM. The pH of the mixed solution was adjusted to 5.5 by the phosphate buffer. Then, the CDs were added to the mixture. The fluorescent emission spectra of the CDs in every mixed solution were obtained under the excitation wavelength of 460 nm (Fig. 4). The fluorescent peak of the CDs was 510 nm, but in the graph, we found that a new peak at 560 nm appeared in the fluorescent spectra. Although it did not affect the detection of H_2O_2, we still detected the milk solution and some common substances in milk (Fig. 5). The result confirmed that the new peak at 560 nm was caused by casein in the milk, and it was the Raman peak of casein.

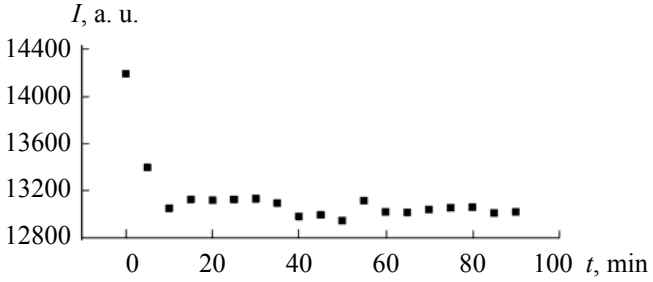

Fig. 3. Reaction time between the hydrogen peroxide and the glucose.

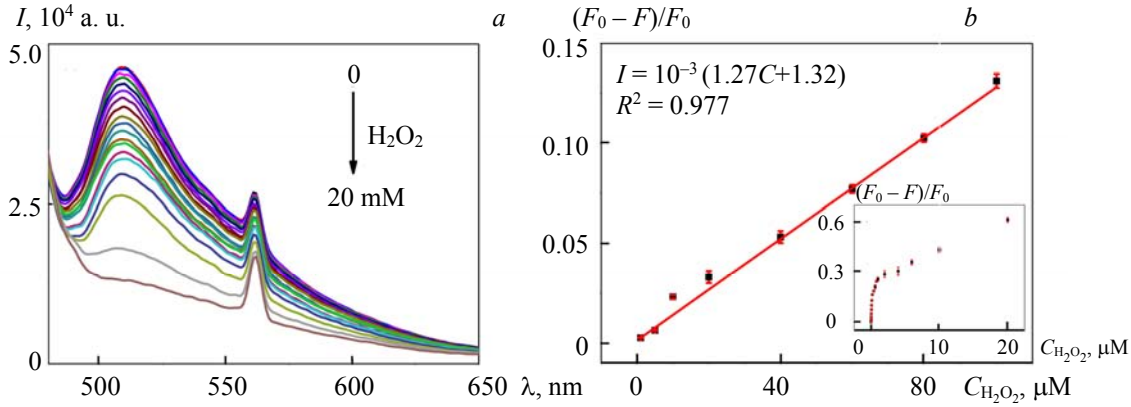

Fig. 4. (a) The fluorescent emission spectra of CDs in the detection of H_2O_2 (λ_{ex} = 460 nm), (b) the linear range between the quenching ratio of the fluorescent peak of the CDs and the concentration of H_2O_2. The inset describes the relationship of the quenching ratio changing with the concentration of H_2O_2.

In Figure 4b, the inset graph showed the quenching ratio of the fluorescent peak changing by the concentration of H_2O_2. It could be seen that the quenching ratio of the fluorescent peak of the CDs increased rapidly when the concentration of H_2O_2 increased gradually. It indicated that there was a strong quenching relationship between H_2O_2 and the CDs. The system had a higher sensitivity when the concentration of H_2O_2 was between 0 and 1 mM. The increase in the quenching ratio tended to be flat when the concentration of H_2O_2 was between 1 and 20 mM, which illustrated that most CDs in the solution had been almost bounded by H_2O_2 at this time. From Fig. 4b we knew that the CDs, as a fluorescent probe, were quite suitable for the detection of H_2O_2. A linear range was established when the concentration of H_2O_2 was between 1 and 100 μM, and the linear regression equation was $I = 1.27\times10^{-3}C+1.32\times10^{-3}$. By calculation, the correlation coefficient (R^2) was 0.977, and the limit of detection (LOD) was 0.175 μM.

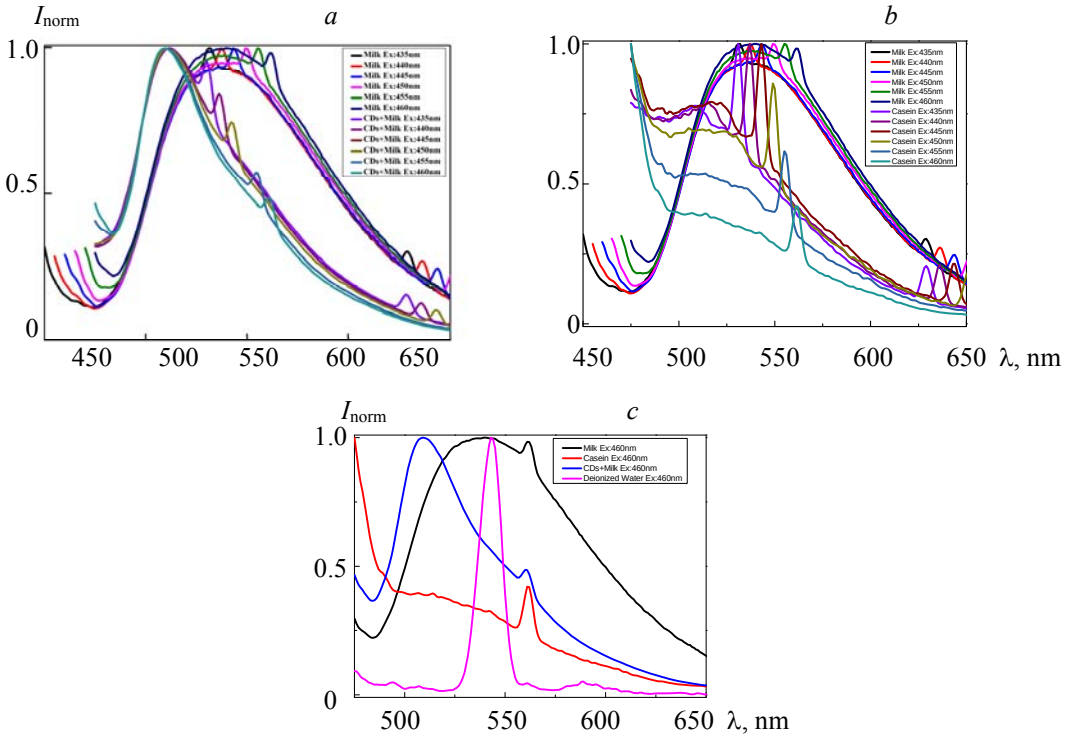

Fig. 5. (a) The normalized fluorescence spectra of milk and CDs mixed with milk at five different excitation wavelengths, (b) the normalized fluorescence spectra of milk and casein at five different excitation wavelengths, (c) the normalized fluorescence spectra of milk, CDs mixed with milk, casein and deionized water, λ_{ex} = 460 nm.

Detection of glucose in milk based on CDs. H_2O_2 is one of the most important intermediary materials, participating in many biological processes. Various kinds of substrates produced H_2O_2 by the catalytic oxidation of the respective O_2-dependent oxidases. H_2O_2 is the main product of the GOx-catalyzed reaction. Thus, the sensitive detection of H_2O_2 based on CDs made the determination of glucose possible [21–28].

The GOx obtained from Aladdin was known to have a pH value of 5–7 and a temperature of 30–50°C. Therefore, we first measured the optimal incubation conditions of the GOx in the system. The buffer solution with different pH values of 5, 5.5, 6, 6.5, and 7 were prepared by the phosphate buffer, HCl, and NaOH. We added the same concentration of glucose and GOx to five samples of the milk solution as the experimental groups. To the other five control groups we added the same concentration of glucose and the same volume of ultrapure water instead of the GOx. The pH value of the experimental groups and the control groups were adjusted from 5 to 7 by the phosphate buffer. Then, the oil bath was used to incubate the ten samples under 40°C for 40 min. To ten samples we added the same amount of the CD solution; the fluorescent peak intensity of the control groups was recorded as F_0, and the fluorescent peak intensity of the experimental groups were recorded as F. F/F_0, which represented the changes in the fluorescent intensity of the CDs under five different pH conditions. Figure 6a showed that the optimal pH value of GOx participating in the reaction was 5.5.

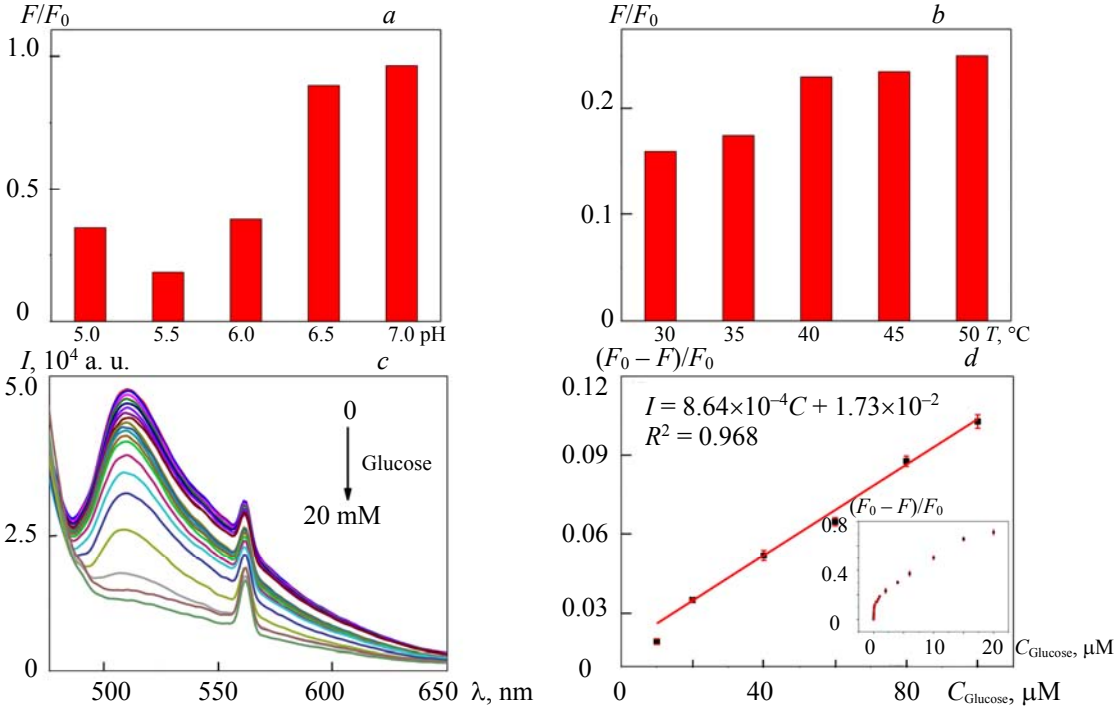

Fig. 6. (a) The pH activity of GOx in the system, (b) the temperature activity of GOx in the system, (c) the fluorescent emission spectra of CDs in the system in the detection of glucose (λ_{ex} = 460 nm), (d) the linear range between the quenching ratio of the fluorescent peak of the CDs and the concentration of glucose. The inset describes the relationship of the quenching ratio changing with the concentration of glucose.

Five experimental groups and five control groups were designed to explore the optimal temperature activity of GOx. The same concentrations of glucose and GOx were added to five samples of the milk solution as the experimental groups. To the other five we added the same concentration of glucose and the same volume of ultrapure water instead of the GOx. Each experimental group and control group were incubated respectively at 30, 35, 40, 45, and 50°C, heating for 40 min in the oil bath. Then, the same amount of the CD solution was added to the ten samples. The fluorescent peak intensity of the control groups was recorded as F_0, and the fluorescent peak intensity of the experimental groups was recorded as F. F/F_0, which represented the changes in the fluorescent intensity of the CDs under five different temperature conditions. Figure 6b indicated that the optimal temperature for GOx to participate in the reaction was 30°C.

Finally, the milk solutions with different concentrations of glucose were prepared: 0 (blank), 1, 5, 10, 20, 40, 60, 80, 100, 200, 400, 600, 800 μM, and 1, 2, 4, 6, 10, 15, and 20 mM. Then, the GOx was added, and the pH value of the mixed solutions was adjusted to 5.5 by the phosphate buffer. Next, the mixed solutions were incubated in the oil bath at 30°C for 40 min. Glucose was decomposed by oxidation into H_2O_2. After that, the CD solutions were added to the system and participated in the reaction for more than 10 min. Then, the fluorescent spectra of the blank sample were measured, and the fluorescent intensity of the peak F_0 was obtained. The fluorescent intensity of other samples was recorded as F, and the quenching ratio of the CDs $(F_0 - F)/F_0$ was calculated. Figure 6c showed the result of detecting the concentration of glucose. It indicated that there was a strong quenching relationship between glucose and the CDs. The quenching ratio of the fluorescent peak rose with the increase in the glucose concentration. In Fig. 6d, the inset graph illustrated high sensitivity when the concentration of glucose was 0–1 mM. The increase in the quenching ratio tended to be flat when the concentration of glucose was 1–20 mM. It could be seen from Fig. 6d that CDs, as a fluorescent probe, had good performance for detecting the concentration of glucose in milk. A linear range was established when the concentration of glucose was between 10 and 100 μM, and the linear regression equation was $I = 8.64\times10^{-4}C + 1.73\times10^{-2}$. The R^2 was 0.968, and the LOD was 0.68 μM by calculation.

To prove the repeatability and accuracy of this experimental model. A standard addition experiment of glucose was carried out in new milk samples. The predicted concentration of glucose was calculated by a linear equation. The results were shown in Table 1. All results were the average value of five measurements. The recovery rate of glucose was 97.30–101.05%, and the relative standard deviation (RSD) was less than 1.62%, which confirmed that the method was reliable for the quantitative detection of glucose. Table 2 was a comparison between this work and other methods of glucose detection. The data indicated that this fluorescent probe was fast, accurate, and sensitive to the detection of glucose. This work could detect glucose in milk directly and avoided the pretreatment of milk, which was the most important improvement compared with other methods.

TABLE 1. The Detection of Glucose

Spiked glucose, μM	Measured values, μM, $n = 5$	Recoveries%, $n = 5$	RSD%, $n = 5$
10	9.73	97.30	1.62
20	20.21	101.05	1.27
40	40.09	100.23	1.15

TABLE 2. Comparison of Different Detection Methods

Detection method	The linear range	LOD	Environment	Reference
GQDs/AgNPs	–	1.60 μM	Water	[29]
Lamb-CDs	10–300 μM	2.9 μM	Water	[30]
B-doped CDs	8–80 mM	8 mM	Water	[31]
(R-CDs)-TMB	0.01–0.40 mM	2 μM	Serum	[32]
HPAEC-PAD	–	0.25 mg/100 g	Milk	[33]
HPLC	0.1–4.0 g/100 mL	–	Milk	[34]
Phloroglucinol CDs	10–100 μM	0.69 μM	Milk	This work

Selectivity. For proving the specific response of the fluorescent probe to H_2O_2, common amino acids (200–400 μM), metal salts ions (1–10 mM), common sugars (5 mM), and GOx were used to interfere with the reaction system, and the results were shown in Fig. 7. We found that the interference had little effect on the fluorescent probe of the CDs, and the effects of fluorescent intensity were all within ±6%, which indicated that the probe had high selectivity to H_2O_2. The result was obtained by calculating three separate sets of the measured values.

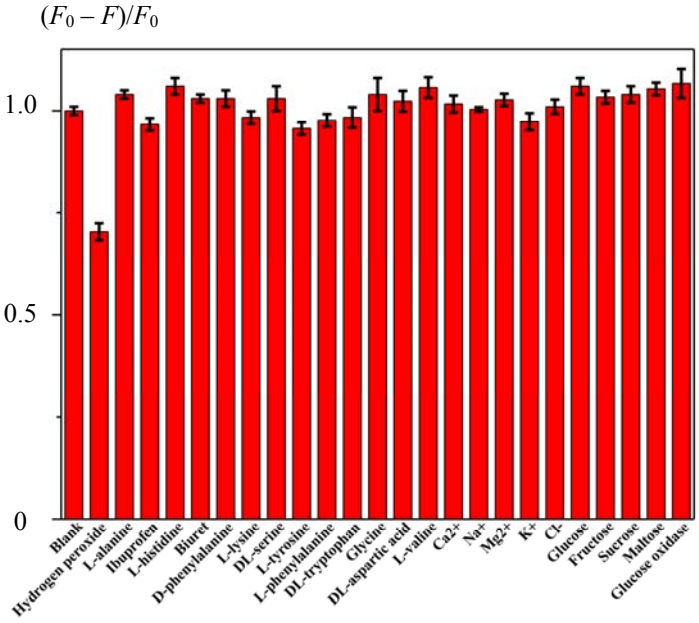

Fig. 7. Anti-interference experiment of CDs.

Conclusions. Water-soluble CDs were briefly compounded using a solvothermal method with the precursor of phloroglucinol. The prepared CDs had superb fluorescent characteristics and high stability. The CDs rich in phenolic hydroxyl groups had a certain degree of reducibility and could react with hydrogen peroxide, resulting in the fluorescent quenching of the CDs. Glucose could be oxidized by GOx to produce H_2O_2. On the basis of this process, an environmentally friendly and high-sensitivity sensor for the detection of glucose was established. According to our investigation, the detection of H_2O_2 and glucose in milk directly by using CDs as the fluorescent probe has not been reported yet. Compared with other works, the method reported in this paper for the direct detection of H_2O_2 and glucose in milk has the advantages of environmental friendliness, lower LOD, lower degree of interference of impurities, and omission of milk pretreatment steps. In general, this work established a rapid, sensitive, and accurate method for the detection of glucose based on fluorescent spectroscopy, which could be used as a supplement and expansion for the detection method of glucose in fluorescent spectroscopy.

Acknowledgments. The authors are greatly thankful to the National Key Research and Development Program of China (2018YFC1604204-3), the Key Research and Development Program of Jiangsu Province (No. BE2020756), the National First-Class Discipline Program of Food Science and Technology (JUFSTR20180302), and the Jiangsu Province Post Doctor Fund (2019K241) for financial support.

REFERENCES

1. A. Galant, R. Kaufman, J. Wilson, *Food Chem*., **188**, 149–160 (2015).
2. S. Kiran, R. Misra, *J. Biomed. Mater. Res. A*, **103**, 2888–2897 (2015).
3. C. F. Nascimento, P. M. Santos, E. R. Pereira-Filho, F. R. P. Rocha, *Food Chem*., **221**, 1232–1244 (2017).
4. Y. Wu, Y. Zhang, *Food & Chem. Toxic*., **56**, 325–335 (2013).
5. J. Ma, X. Hou, B. Zhang, Y. Wang, L. He, *J. Pharm. Biomed. Anal.*, **91**, 24–31 (2014).
6. S. Carballo, F. A. Zingarello, S. E. Maestre, J. L. Todolí, M. S. Prats, *Int. J. Food Sci. Technol*., **49**, 146–152 (2014).
7. M. P. Gangola, S. Jaiswal, Y. P. Khedikar, R. N. Chibbar, *Food Chem*., **154**, 127–133 (2014).
8. Q. Zhao, C. Zhou, Q. Yang, Z. Chu, N. Jia, *Microchim. Acta*, **186**, 1–8 (2019).
9. C. Peng, C. Liu, Z. Xie, *Anal. Methods*, **7**, 9749–9752 (2015).
10. S. Kiran, R. Misra, *Mater. Technol*., **30**, 1753555714Y.000 (2015).
11. Y. Ngo, W. M. Choi, J. S. Chung, S. H. Hur, *Sensors Act*., **B282**, 36–44 (2019).
12. P. Shen, Y. Xia, *Anal. Chem*., **86**, 5323–5329 (2014).

13. S. T. Yang, L. Cao, P. G. Luo, F. Lu, Y. P. Sun, *J. Am. Chem. Soc*., **131**, 11308–11309 (2009).
14. A. Iqbal, K. Iqbal, L. Xu, B. Li, D. Gong, X. Liu, Y. Guo, W. Liu, W. Qin, H. Guo, *Sensors Act. B: Chem*., **255**, 1130–1138 (2018).
15. R. Atchudan, T. N. J. I. Edison, K. R. Aseer, S. Perumal, N. Karthik, Y. R. Lee, *Biosens. Bioelectron*., **99**, 303–311 (2018).
16. R. Wang, K. Q. Lu, Z. R. Tang, Y. J. Xu, *J. Mater. Chem. A*, **5**, 3717–3734 (2017).
17. A. Kumar, A. R. Chowdhuri, D. Laha, T. K. Mahto, P. Karmakar, S. K. Sahu, *Sensors Act. B: Chem*., **242**, 679–686 (2017).
18. Y. Hou, H. Liu, Z. Li, H. Zhang, L. Wei, M. Yu, *Anal. Methods*, **12**, 2835–2840 (2020).
19. F. Yuan, T. Yuan, L. Sui, Z. Wang, Z. Xi, Y. Li, X. Li, L. Fan, Z. Tan, A. Chen, *Nat. Commun*., **9**, 2249 (2018).
20. F. Yuan, Z. Wang, X. Li, Y. Li, Z. Tan, L. Fan, S. Yang, *Adv. Mater*., **29**, 1604436 (2017).
21. Y. Huan, Q. Fei, H. Shan, B. Wang, H. Xu, G. Feng, *Analyst*., **140**, 1655–1661 (2015).
22. Y. Wu, Y. Gao, J. Du, *Talanta*, **197**, 599–604 (2019).
23. Y. Nerthigan, A. K. Sharma, S. Pandey, K. H. Sharma, M. S. Khan, D. R. Hang, H. F. Wu, *Microchim. Acta*, **185**, 65 (2018).
24. M. J. Cho, S. Y. Park, *Sensors Act. B*, **282**, 719–729 (2019).
25. C.-S. Chu, M.-W. Hsieh, Z.-R. Su, *Opt. Mater. Express*, **6**, 759–766 (2016).
26. M. Tang, B. Zhu, Y. Wang, H. Wu, Z. Su, *Microchim. Acta*, **186**, 604–610 (2019).
27. J. Wei, L. Qiang, J. Ren, X. Ren, F. Tang, X. Meng, *Anal. Methods*, **6**, 1922–1927 (2014).
28. W. Hou, X. Liu, Q. Lu, M. Liu, Y. Zhang, S. Yao, *Colloids Surf. B: Biointerface*, **162**, 118–125 (2017).
29. J. L. Ma, B. C. Yin, X. Wu, B. C. Ye, *Anal. Chem*., **89**, 1323–1328 (2017).
30. H. Wang, Y. Xie, S. Liu, S. Cong, Y. Song, X. Xu, M. Tan, *J. Agric. Food Chem*., **65**, 7553–7559 (2017).
31. X. Shan, L. Chai, J. Ma, Z. Qian, J. Chen, F. Hui, *Analyst*., **139**, 2322–2325 (2014).
32. Y. Long, X. Wang, D. Shen, H. Zheng, *Talanta*, **159**, 122–126 (2016).
33. L. Monti, S. Negri, A. Meucci, A. Stroppa, A. Galli, G. Contarini, *Food Chem*., **220**, 18–24 (2017).
34. Y. H. Zhang, W. Zhao, Y. Y. Duan, D. P. Cao, J. Fang, W. N. Chen, *China Food Addit*., **1**, 137–140 (2016).