Synthesize of nitrogen doped carbon quantum dots by the hydrothermal method and its application for detection of iodide anion using paper based smart phone detection system.

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Abstract

The purpose of this research is to design a Whatman paper based sensor for quantitative measurement of iodide anion by its quenching effect on the fluorescence intensity of the nitrogen doped carbon quantum dots (N-doped CQDs) using a smart phone as a detection system. In this project, N-doped CQDs were synthesized by a hydrothermal method using citric acid as a source of carbon and hexamethylenediamine as a source of nitrogen. In order to characterize of the synthesized N-doped CQDs, Fourier transform infrared spectrophotometry (FT-IR), Energy-dispersive X-ray spectroscopy (EDX) and dynamic light scattering (DLS) was used. After designing of the paper based sensor, an aliquot of the mixture of the N-doped CQDs:Glue (glue roles as the stabilizing agent) was injected on the hydrophilic zone of the paper and then by injection of different concentrations of iodide anion, the reduction of the fluorescence intensity was measured using the smart phone camera. By optimizing the critical parameters affecting the quenching efficiency of the N-doped CQDs including the size of the hydrophilic zone, the volume ratio of the N-doped CQDs:Glue, type of the Whatman filter paper and the pH of sample solution, the proposed method was used for determination of iodide ion. The results show that two calibration curves in the ranges of 1-10 and 15-200 mmol L$^{-1}$ iodide were obtained for determination of iodide anion. Also, the detection limit (LOD) of 3 mmol L$^{-1}$ and the relative standard deviation (RSD) in the range of 2.6-2.9 % were obtained for the iodide anion in the
The range of 50-150 mmol L\(^{-1}\). The main advantages of the proposed method are rapidity, inexpensiveness, simplicity, availability and no need of expert for operation.

**Key word:** iodine, sensor paper, nitrogen doped carbon quantum dots, fluorescence method, Software Photoshop.

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1. Introduction

Iodine (I) is one of the essential elements for the human body so that it is requires for synthesis of thyroid hormones to prevent the disease goiter and also improvement of the nervous system\(^1\). Iodine presence in different oxidation forms such as iodide (I\(^{-}\)), iodate (IO\(_3^{-}\)) and periodate (IO\(_4^{-}\)) anions. Iodide, one of the most common forms of iodine, is added to the human dietary to compensate the deficiency of human body due to its cheaper and high solubility. Different analytical tools including, UV-Vis spectrophotometry\(^2\)-\(^4\), electrochemical methods\(^5\)-\(^8\), chromatographic methods\(^9\),\(^10\), capillary electrophoresis\(^11\) and inductively coupled plasma-mass spectrometry\(^12\) were used for determination of iodine species.

Carbon quantum dots (CQDs) as a class of carbon based materials have been used for detection of wide range of materials including organic molecules\(^13\), anions\(^14\),\(^15\) and cations\(^16\)-\(^18\) due to their fluorescence properties, cheapness and ease of synthesis. Recently, paper based devices as the miniaturized analytical platforms were used for the wide range of analytes\(^19\). The main advantages of these analytical tools are availability, low usage of the samples, non-toxicity and also, rapidity. Up to now, different detections systems were coupled with the paper based devices such as colorimetric\(^20\), electrochemicals\(^21\), fluorescence\(^22\) and mass spectrometry\(^23\). Among them, colorimetric devices are most common which used naked eye, digital camera or smart phone for detection of the changes in the colors.

The aim of this paper is to design of the paper based fluorescence sensor device using smart phone as a detection system. The N-doped CQDs were prepared by the hydrothermal method using citric acid as a source of carbon and hexamethylenediamine as a source of nitrogen and then characterized by the Fourier transform-infrared spectrophotometry (FT-IR), Energy-dispersive X-ray spectroscopy (EDX) and dynamic light scattering (DLS). After injection of the
synthesized N-doped CQDs onto the hydrophilic zone of the Whatman paper, different concentrations of iodide anion were injected on it and the quenching of the fluorescence intensity were measured against blank signal using smart phone camera device. The obtained images were then analyzed by the Photoshop software (Magenta color). By optimizing of different parameters affecting the fluorescence quenching including the size of hydrophilic zone, volume ratio of the N-doped CQDs:Glue, type of Whatman filter paper and the pH of sample solution, the proposed method was used for determination of iodide ion in different real samples.

2. Experimental

2.1. Reagent

Deionized water was used for making of solutions. Citric acid (99.5%, Fluka, Swiss) and hexamethylenediamine (99.5%, Fluka, Swiss) were used as source of carbon and nitrogen, respectively to synthesize of the N-doped CQDs. Sodium iodide (99.0%, Fluka, Swiss) was used for the preparation of the standard solutions of iodide ion.

Sodium fluoride (NaF, 99.5%, Merck, Germany), sodium chloride (NaCl, 99.5%, Merck, Germany), sodium sulfate (Na₂SO₄, 99.7, Merck, Germany), sodium nitrate (NaNO₃, 99.0%, Merck, Germany), sodium acetate (CH₃COONa, 99.5, Fluka, Swiss) were studied as interfering ions. Sodium hydroxide (NaOH, 0.1 mol L⁻¹) and hydrochloric acid (HCl, 0.1 mol L⁻¹) were used for adjusting of pH values.

2.2. Instrument

An instrument RF-1501 spectrofluorometer (Shimadzu, Japan) and Agilent 8453 (USA) UV-Vis spectrophotometer were used for recording of the fluorescence, and UV-Vis spectrums of the synthesized CQDs, respectively. In order to characterize of the synthesized N-doped CQDs, the Fourier transform-infrared spectrophotometry (FT-IR, Thermo Nicolet, USA) model AVATAR 370 was used. Energy dispersive X-Ray spectroscopy (EDX) instrument was used for elemental analysis on the synthesized N-doped CQDs and particle size distribution analysis was performed using Cordouan, model Vasco, France instrument. An ultrasonic bath model CP104 (France) was used to disperse of the synthesized N-doped CQDs. Whatman paper No. 40, 41 and 42 (England) were used as the bed and Bourgois eyeliner (Paris, France) was used to create hydrophobic zone on the Whatman paper.

2.3. Synthesize of N-doped CQDs
Hydrothermal method was used for synthesize of the N-doped CQDs using the proposed method: 0.5 g citric acid (as a carbon source) was mixed with 0.055 g hexa-methylenediamine (as a nitrogen source) and heated at 180 °C for 5 h to obtain a brown mixture. The synthesize N-doped CQDs were dispersed in the solution of deionized water:propanol (1:5 volume ratio) and centrifuged at 5000 rpm. The resulting supernatant was removed and kept in the refrigerator at 7 °C for further analysis.

2.4. Preparation of paper-based sensor

For preparation of the paper-based sensor, the tape circles with 5 mm diameter were prepared and attached on the Whatman paper No. 41 and the remaining space was painted by the Bourgeois eyeliner. By heating of the prepared paper, the taped was easily removed and the hydrophilic surface established at the center of the Whatman No.41 paper with the hydrophobic zone at the sides of the paper (Fig. 1).

![Schematic of the paper-based sensor](image)

**Fig. 1. The schematic of the paper-based sensor with hydrophilic and hydrophobic zones.**

2.5. Analytical method

0.8 µL of the mixture of the N-doped CQDs:Glue (1:1 volume ratio) was injected onto the hydrophilic zone of the bed. After 5 min, the paper was submitted under the UV light and the fluorescence intensity was detected by the smart mobile phone camera. The obtained image was analyzed by the Photoshop software (Magenta color) and considered as the blank signal (Fblank). Then, 0.8 µL of the iodide anion at the optimum pH value (in the range of calibration curve) was injected onto the hydrophilic zone and submitted under the UV light. The obtained fluorescence intensity was measured similar to the blank samples and considered as the Fsample. Finally, the ratio of Fsample/Fblank was considered as the analytical response. Fig. 2 shows the analytical procedure for recording of the blank and sample signals.
3. Results and Discussion

3.1. Characterization of Nitrogen doped CQDs

The synthesized N-Doped CQDs was characterized by FT-IR spectrophotometry, EDX analysis and DLS methods. Fig. 3 shows the FT-IR spectrum of the synthesized N-Doped CQDs.
As it could be seen, the peaks at 1769 cm\(^{-1}\) and 3450 cm\(^{-1}\) are related to the stretching vibration of carbonyl and OH- groups, respectively. Additionally, the peak at 2950 cm\(^{-1}\) and 3300 cm\(^{-1}\) are related to the stretching vibration of C-H and N-H group of the synthesized N-Doped CQDs, respectively. Finally, the presence of the peaks at 1407 cm\(^{-1}\) and 1441 cm\(^{-1}\) which are related to the bending vibrations of N-H group clearly show that, N-doped CQDs was synthesized successfully. Elemental analysis was also performed on the synthesized N-doped CQDs and the obtained results which presented in the Fig. 4 show that the N peak in the structure of CQDs.

Fig. 4. The result of Energy-dispersive X-ray spectroscopy for the synthesized N-doped CQDs
Fig. 5 shows the DLS analysis on the sample solutions containing the synthesized N-doped CQDs. As it could be seen, in the absence of iodide anion (Fig. 5a), the average size of the synthesized N-doped CQDs is about 12 nm; however, in the presence of iodide anion (Fig. 5b), its average size was reaches to 600 nm. This phenomenon shows that the electrostatic attraction between iodide anions and the synthesized N-doped CQDs cause to the changes of the size of the synthesized N-doped CQDs and strongly confirmed that iodide anions attached on the surface of the synthesized N-doped CQDs. Also, the fluorescence spectrum of the synthesized N-doped CQDs was shown in the Fig. 6. As it could be seen, the excitation peaks in the range of 280-450 nm cause to the emission spectrum in the range of 390-575 nm with the maximum emission peak at the 460 nm.
3.2. Optimization of the parameters affecting the Fluorescence intensity

As described in analytical method, the obtained spectrum for the injection of different concentrations of iodide anion was presented in the Fig. 7. As it could be seen, by increasing of the iodide concentration, the fluorescence intensity decreases which related to the quenching effect \( \frac{F_S}{F_b} \) of iodide ion on the N-doped CQDs. To reach the maximum \( \frac{F_S}{F_b} \), different parameters affecting the quenching of the synthesized N-doped CQDs including pH of sample solution, volume ratio of N-doped CQDs:Glue, the size of hydrophilic zone, type of Whatman paper were investigated and optimized.

![Excitation-emission spectrum of the synthesized N-doped CQDs](image)

**Fig. 6. The excitation-emission spectrum of the synthesized N-doped CQDs**
3.2.1. The size of the hydrophilic zone

The size of the hydrophilic zone was studied by creation of the circles with different diameters in the range of 3-6 mm with the interval of 1 mm. The obtained $F_s/F_b$ are presented in the Table 1.

Table 1. The effect of hydrophilic zone on the quenching efficiency of N-doped CQDs.

| No. | Hydrophilic zone (mm) | Volume of N-CQDs (µL) | $F_s/F_b$ ratio |
|-----|-----------------------|-----------------------|----------------|
| 1   | 3                     | 0.30                  | 0.85           |
| 2   | 4                     | 0.60                  | 0.83           |
| 3   | 5                     | 0.80                  | 0.76           |
| 4   | 6                     | 1.0                   | 0.82           |

As it could be seen, the optimum $F_s/F_b$ was obtained for the 5 mm circle diameter. Therefore, 5 mm hydrophilic zone was selected as the optimum value.

3.2.2. Effect of N doped CQDs:Glue volume ratio

In this research, it was revealed that the injection of aqueous solution of N-doped CQDs onto the Whatman filter paper causes to its dispersion into the hydrophobic zone. To resolve it and in
order to stabilization of the synthesized N-doped CQDs onto the paper, glue stick was used as stabilizer. However, to ensure that its presence has no effect on the quenching of N-doped CQDs, different volume ratios of N doped CQDs:Glue in the ratio of 0-1 (v/v) were prepare and tested.

![Graph showing the effect of the volume ratio of Glue:N-CQDs on the quenching efficiency of sample solution.](image)

**Fig. 8.** The effect of the volume ratio of Glue:N-CQDs on the quenching efficiency of sample solution. Conditions: 50 mmol L⁻¹ I⁻¹, 5 mm hydrophilic zone, pH 7 and Whatman No. 41 as a bed.

The results in Fig. 8 show that, the mixture of N doped CQDs:Glue in the volumetric ratio of 1:1 has no effect on the quenching of the synthesized N-doped CQDs. Therefore the mixture of N doped CQDs:Glue with the volume ratio of 1:1 was considered as the optimum value.

### 3.2.3. Effect of type of Whatman paper

As described before, different types of Whatman paper, No. 40, No. 41 and No.42 were tested as the bed for injection of N-doped CQDs on it.
Fig. 9. The effect of type of Whatman paper on the quenching efficiency of sample solution. Conditions: 50 mmol L$^{-1}$ I$^{-}$, 5 mm hydrophilic zone, pH 7 and 1:1 volume ratio of Glue:N-CQDs.

The results in Fig. 9 show that Whatman No.41 provides the optimum quenching efficiency (minimum Fs/Fb). To explain this effect, the pore size of the Whatman papers must be considered. As regard as the Whatman No. 41 filter paper has the largest pore size; therefore by injection of the mixture of the N-doped CQDs:Glue onto the paper bed, it could be penetrate into the paper pores and react with iodide anion more effectively. However, for the other filter papers, due to their small pore size, the injected N doped CQDs:Glue can-not be penetrated effectively. Therefore due to their aggregation, iodide anion can-not be effectively reacting with the N-doped CQDs and the quenching efficiency decreases. As a result, a Whatman filter paper No. 41 was selected as the optimum bed.

3.2.4. Effect of pH

The effect of pH of sample solution on the quenching efficiency was studied in the range of 3-11. The results are presented in the Fig. 10. As it could be seen, the pH values in the range of 6-8 provide the optimum quenching efficiency. However, higher pH values of 8 and lower pH values of 5 cause to the reduction of the quenching efficiency. It could be explain that, at high pH
values (pH>8), the surface of the synthesized N-doped CQDs have negative charge and therefore the repulsive interaction among the negative charged N-doped CQDs and iodide anion prevent of its attraction on the surface of CQDs. However, at low pH values (pH<4), the positive functional groups in the structure of Whatman paper bed may attract the negative charged iodide anion and it could not effectively react with the N-doped CQDs. Therefore, for further experiments, pH 6-8 was selected as the optimum value.

![Graph showing the effect of pH on quenching efficiency](image)

Fig. 10. The effect of pH of sample solution on the quenching efficiency of sample solution. Conditions: 50 mmol L⁻¹ I⁻, 5 mm hydrophilic zone, Whatman No. 41 as a bed and 1:1 volume ratio of Glue:N-CQDs.

3.3. Effect of interfering ions
The effects of different anions with the concentration of 0.1 mol L\textsuperscript{-1} on the quenching efficiency of the analyte was studied by their injection on the paper bed containing the N-doped CQDs.

![Fig. 11. The effect of other ions on the quenching efficiency of the synthesized N-doped CQDs.](image)

**Fig. 11. The effect of other ions on the quenching efficiency of the synthesized N-doped CQDs.**

The results in Fig. 11 show that, no serious interfering anion was observed for determination of iodide in different water and salt samples. Zhang et al. explain that as the iodide ion is a large monatomic anion, making it a typical soft Lewis base that can readily change its spatial shape during interaction with hard Lewis acids\textsuperscript{15}. Therefore, in comparison to other harder bases it could be easily changes its spatial shape and interact with the self trapped electrons at the N-doped CQDs. Therefore, it is expected that iodide anion represent a selective behavior toward the synthesized N-doped CQDs.

### 3.4. Analytical Figures of Merit

Under the optimum conditions the proposed method was used for determination of iodide anion. The results show two calibration curves in the range of 1-10 mmol L\textsuperscript{-1} and 15-200 mmol L\textsuperscript{-1} for determination of iodide anion. Their equations are $Y = \ -0.013X + 1.0086$ (first linear range) and $Y = \ -0.0011X + 0.8598$ (second linear range) where $Y$ is the $F_s/F_b$ intensity and $X$ is the concentration of iodide in mmol L\textsuperscript{-1}. The limit of detection, $3S_b/m$, where $S_b$ is the standard deviation of the blank for five replicate analysis of the blank and $m$ is the slope of the calibration curve was 0.3 and 4.2 mmol L\textsuperscript{-1} for the first and second linear range, respectively. Also, the
relative standard deviation (RSD%) for the five replicate analysis of the solutions of 50, 100 and 150 mmol L\(^{-1}\) iodide anion was in the range of 2.6-2.9%.

### 3.5. Analysis of real samples

In order to check the applicability of the proposed paper based sensor; tap water and edible salts were analyzed and the obtained results are presented in Table 2.

| Sample                        | Added (mmol L\(^{-1}\)) | Found (mmol L\(^{-1}\)) | Recovery (%) |
|-------------------------------|-------------------------|--------------------------|--------------|
| Tap water (Mashhad, Iran)     | 0                       | 110                      | 100          |
|                               | 50                      | 160                      | 110.0        |
|                               | 100                     | 220                      | 120.0        |
|                               | 150                     | 290                      |              |
| Sea salt No. 1 (50 mg in 10 mL)| -                       | 170                      | 120.0        |
|                               | 50                      | 230                      | 130.0        |
|                               | 100                     | 300                      | 113.3        |
|                               | 150                     | 340                      |              |
| Sea salt No. 2 (50 mg in 10 mL)| -                       | 50                       | 100.0        |
|                               | 50                      | 100                      | 90.0         |
|                               | 100                     | 140                      | 73.3         |
|                               | 150                     | 160                      |              |

Also, spike test analyses were performed on the samples to check the validity of the obtained results. As it could be seen recovery values higher that 70% were obtained for determination of iodide anion in different real samples. The obtained results show that the proposed method could be successfully determining iodide anion in different real samples.

### 4. Conclusion

In this paper, paper-based N-doped CQDs sensor was designed and used for determination of iodide anion in different real samples. N-doped CQDs was synthesized by the hydrothermal method using citric acid as a carbon source and hexamethylenediamine as a nitrogen source. The synthesized N-doped CQDs was characterized by the FT-IR spectrophotometry, EDX analysis and DLS spectroscopy. The results show that the fluorescence intensity of the synthesized N-doped CQDs was reduced in the presence of iodide anion and the quenching efficiency (F\(_0\)/F\(_b\))
was dependent on the pH of iodide solution, hydrophilic zone, type of the Whatman filter paper and the volume ratio of N-doped CQDs:Glue. Also, based on the results, two calibration curves were determined for determination of iodide anion in the ranges of 1-10 mmol L\(^{-1}\) and 15-200 mmol L\(^{-1}\) iodide anion. Finally, the proposed method was successfully used for determination of iodide anion in different water and edible salt samples. The main advantages such as availability, ease of fabrication of paper-based sensor, non-toxicity, non-expensively, in situ analysis and high sensitivity makes it a unique technique for determination of iodide anion.

References

[1] R. Fuge, C. C. Johnson, Appl Geochem, 2015, 63, 282-302.
[2] S. Zaruba, A. B. Vishnikin, V. Andrch, Talanta, 2016, 149, 110-116.
[3] S. Zaruba, V. Bozóová, A. B. Vishnikin, Y. R. Bazel, J. Šandrejová, K. Gavazov, V. Andrch, Microchem J, 2017, 132, 59-68.
[4] N. Nunes, S. Valente, S. Ferraz, Maria Carmo Barreto, M.A.A. Pinheirode Carvalho, Algal Res, 2019, 42, 101613-101621.
[5] A. Machado, R.B.R. Mesquita, S. Oliveira, A. A. Bordalo, Talanta, 2017, 167, 688-694.
[6] N. Wang, F. Wang, Y. Liao, H. Liu, Y. Li, X. He, Anal Methods, 2017, 9, 3159-3165.
[7] M. Ghaedi, S. Y. Shajaripour Jaberi, S. Hajati, M. Montazerozohori, M. Zarr, A. Asfaram, L. Kumar Kumawat, V. K. Gupta, Electroanal, 2015, 27, 1516-1522.
[8] H. Cunha-Silva, M. Julia Arcos-Martinez, Cathodic stripping voltammetric determination of iodide using disposable sensors, Talanta, 2019, 199, 262-269.
[9] E. Sanz Rodriguez, A. N. Setiawan, S. Pope, R. P. Haddad, P. N. Nesterenko, B. Paull, Anal Methods, 2016, 8, 5587-5595.
[10] B. Michalke, H. Witte, J Trace Elem Med Biol, 2015, 29, 63-68.
[11] J. J. Xu, Y. X. Chang, J. Hao, M. An, Z. Tan, R. Yang, J. Cao, L. Q. Peng, Microchim Acta, 2016, 183, 2441-2447.
[12] D. Huynh, S. J. Zhao, R. Gibson, L. Palmer, B. Muhlhausler, J Trace Elem Med Biol, 2015, 29, 75-82.
[13] J. Hou, F. Zhang, X. Yan, L. Wang, J. Yan, H. Ding, L. Ding, Anal Chim Acta, 2015, 859, 72-78.
[14] F. Du, F. Zeng, Y. Ming, S. Wu, Microchim Acta, 2013, 180, 453-460.
[15] H. Zhang, Y. Li, X. Liu, P. Liu, Y. Wang, T. An, H. Yang, D. Jing, H. Zhao, Environ Sci Technol Lett, 2014, 1, 87-91.
[16] Y. Dong, R. Wang, G. Li, C. Chen, Y. Chi, G. Chen, Anal Chem, 2012, 84, 6220-6224.
[17] F. Yan, D. Kong, Y. Luo, Q. Ye, J. He, X. Guo, L. Chen, Microchim Acta, 2016, 183, 1611-1618.
[18] R. Zhang, W. Chen, Biosens Bioelectron, 2014, 55, 83-90.
[19] A. A. Martinez, S. T. Phillips, G. M. Whitesides, E. Carrilho, Anal Chem, 2010, 82, 3-10.
[20] A. Yakoh, P. Rattanarat, W. Siangproh, O. Chailapakul, Talanta, 2018, 178, 134-140.
[21] Z. Nie, C. A. Nijhuis, J. Gong, X. Chen, A. Kumachev, A. W. Martinez, M. Narovlyansky, G. M. Whitesides, Lab Chip, 2010, 10, 477-483.
[22] J. Chang, H. Li, T. Hou, F. Li, Biosens Bioelectron, 2016, 86, 971-977.
[23] S. Chen, Q. Wan, A. K. Badu-Tawiah, J Am Chem Soc, 2016, 138, 6356-6359.