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Synthesis of Fluorescent Carbon Nanoparticles and Selective Detection of Fe^{3+} in Tap Water

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ABSTRACT

In this work, we report a simple method to synthesized Carbon nanoparticles (CNP) from sucrose by using sulphuric acid at room temperature. The CNP is characterized with UV-visible, FT-IR, powder X-ray diffraction and transmission electron microscopy (TEM). The particle sizes of the CNP are in the range 10 nm to 30 nm with mean size of 19.82 nm. The CNP show bright blue fluorescence, sensitive to pH and strong stability towards NaCl concentration. The fluorescence of the CNP is found to be independent of excitation wavelength. Moreover, we have demonstrated the capability of CNP for selective Fe^{3+} ions detection in aqueous medium, tap water to minimum detection limit of 10 nM. The linear range dependent of Fe^{3+} concentration is 1 µM to 25 µM. Therefore, this fluorescent CNP may used for detection Fe^{3+} ions in water system and biological samples.

Keywords: Carbon nanoparticles, blue fluorescence, pH sensor, Fe^{3+} sensor

I. INTRODUCTION

Quantum dots (QDs) such as CdS, CdSe etc are successfully applied in bio-sensing, bio-imaging, light emitting diodes, solar cells but it is harmful to our environment and affects living cells [1]. On the other hand, carbon nanoparticles (CNP) are new class of carbon based nanomaterials discovered in 2004 while purifying single wall nanotube [2]. CNP has the advantages of high fluorescence, good stability, water solubility, biocompatibility, and nontoxicity, making them suitable materials for replacing QDs. Due to their unique structural, optical and biochemical features, these carbon nanomaterials is suitable to be used in photocatalysis, bioimaging, chemical sensing, fluorescent markers and optical sensors [3]. The CNP are synthesized by two approaches, (1) top-down and (2) bottom-up approaches. The first route involves the breaking of larger graphitic materials into smaller carbon nanoparticles via physical or chemical approaches such as include arc-discharge single walled carbon nanotubes, laser ablation and electrochemical oxidation [4].On the other hand second approach is synthesis for CNP from a variety of molecular precursors by chemical synthesis or carbonization; for example, methods include chemical or thermal oxidation of suitable chemical precursors, ultrasonic treatment and microwave pyrolysis [5]. However, expensive precursors, harsh reaction conditions, time-consuming purification processes, low fluorescent quantum yield and difficulties in large-scale production still remain a challenge [6]. Therefore, the development of an economical, facile and simple synthetic route to produce strong fluorescent CNP on a large scale for practical application is still essential.

Iron is the most important transition metal ions for organisms and biological systems play various vital roles in biological processes such as oxygen transport and exchange, DNA and RNA synthesis and enzymatic reactions at the cellular level [7]. However, present of excess iron may generate various disorders such as Alzheimer's, diabetes and hemochromatosis [8]. In view of this, various analytical techniques such as high pressure liquid chromatography [9], atomic spectroscopy and inductively coupled plasma-atomic emission spectrometry [10] have been currently used for detecting Fe^{3+} ion in environmental and biological samples. However, all these techniques require costly instrumentation and also required skilled person [11]. On the other hand due to simple, fast and cost effective nature, fluorescence method has been recently used by few groups for sensing Fe^{3+}, for example, Chen group synthesized nitrogen and sulphur doped carbon dots from garlic and applied for detection of Fe^{3+} ion [12]. Miao and co-workers developed fluorescent Fe^{3+} sensor for water samples using carbon NCs [13]. Yang and co-authors reported an efficient method to synthesis CQDs from honey and used for detecting Fe^{3+} [14].

Herein, a blue fluorescent carbon nanoparticle is synthesized by using sulphuric acid at room temperature. The CNP has been effectively used for selective detection of Fe^{3+} ions in aqueous medium out of other metal ions by fluorescence quenching process. The minimum detection limit of Fe^{3+} is 10 nm (1 ppb) which is lesser than WHO permitted limit 0.3 ppm. By using this fluorescence CNP, it was able detect Fe^{3+} in real tap water samples.

II. METHODS AND MATERIAL

A. Materials

Sucrose, sulphuric acid, manganese sulphate, mercury chloride, silver nitrate, copper sulphate, lead acetate, zinc sulphate, cobalt chloride, sodium chloride, ferric chloride, aluminum sulphate were received from Merck Specialities Private Limited, India. Double distilled water is used throughout the experiment.

B. Methods

1) Preparation of carbon nanoparticles (CNP)

1 mL of sulphuric acid is added to 1 g of sucrose taken in a 100 mL beaker. The mixture is stirred for 1 h to obtain black CNP solid product and excess acid is decant off. The product is than dissolved in water is used for further experiments.

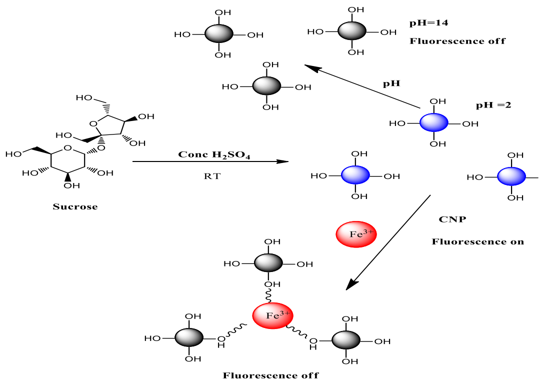
2) Fluorescent sensing of metal ions

10 mg of CNP was dissolved in 10 mL of water. For the quenching experiment 100 μL of CNP solution was diluted with 1mL water and different concentrations of Fe^{3+} was mixed and kept for 5 min in static conditions for reactions to occur. After 5 min fluorescence of mixture solution were recorded with excitation wavelength 360 nm at room temperature.

The selectivity of CNP towards Fe^{3+} are compared for others transition metals such as Al^{3+},Cu^{2+}, Mn^{2+}, Na^{+}, Ag^{+}, Pb^{2+}, Co^{2+}, $Hg^{2+}$and Zn^{2+} under identical conditions. The concentrations of Fe^{3+} and other ions were fixed as10 μL, 40 μM. In order to study the sensitivity of Fe^{3+} in aqueous medium, the CNP solution was mixed with Fe^{3+} or other metal ions and kept in static condition for 5 min. After 5 min fluorescence emission spectra was recorded with excitation wavelength at room temperature.

C. Material characterizations

The Powder XRD patterns of the Sample were recorded from 10° to 80° 2θ on X'Pert Pro Advanced X-ray diffraction measurement system with CuK_α radiation (λ =1.54 Å) at room temperature. UV 1800 spectrophotometer (SHIMADZU, Japan) was used for recording UV-VIS absorption (200 to 1000 nm). FT-IR spectra was recorded in SHIMADZU IR Affinity, in the range from (500 to 4000) cm^{-1} with KBr pellets. Fluorescence measurements were carried out with Hitachi F-2500 spectrophotometer (Hitachi, Japan). The morphologies of the samples were observed by JEM-2100 microscope (Japan, JEOL) with an accelerating voltage of 200 kV.



Scheme 1. Synthetic scheme of CNP and mechanism of detection of Fe^{3+} and pH sensivity.

III. RESULTS AND DISCUSSION

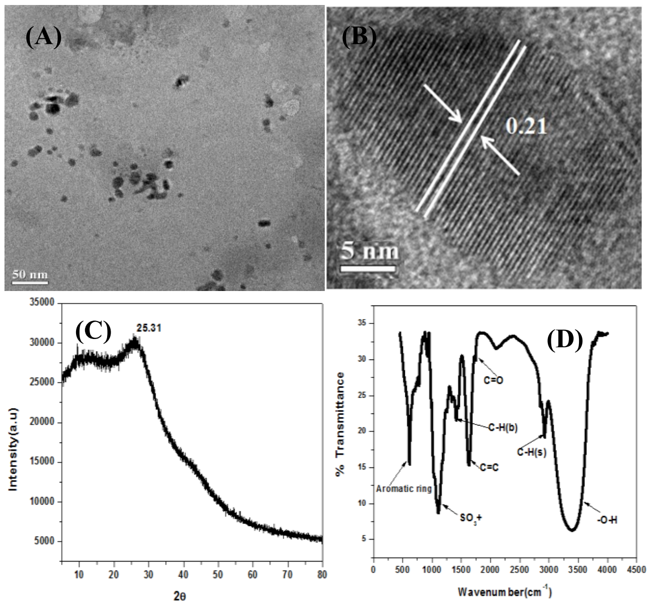


Figure 1. (A) TEM images of CNP (B) HRTEM of CNP (C) PXRD of CNP (B) FT-IR of CNP

The scheme for synthesis of CNP is shown in scheme 1. On reaction of sucrose with sulphuric acid results in dehydrolysis to form carbon materials which further oxidized to form the final carbon nanoparticles. Morphology of CNP is studied with TEM and high resolution TEM imaging. From the TEM images in Figure 1A and B, it can be seen that the as-prepared CNP are irregular in shape with particle size ranging from 10-30 nm with average size of about 19.82 nm. The inter layer lattice spacing is determined to be 0.21 nm, which indicates the graphitic nature of the CNP. (Figure 1B) The powder X-ray diffraction (XRD) pattern of CNP is shown in Figure 1C. The peak at 25.31 2θ value corresponds to the 002 graphitic plane of the CNP which is similar to reported for carbon materials (3.26 A) [15].

The FT-IR spectrum of CNP is shown in the Figure 1D. The intense bands at 1092.57 cm^{-1} and 1630.27 cm^{-1} respectively correspond to SO_3^+ and –C=C– stretching vibrations. The two bands at 1417.37 cm^{-1} and 2940.69 cm^{-1} can be attributed to –C-H bending and stretching mode respectively. The characteristic peak at 610 cm^{-1} is assigned to the present of aromatic rings and a broad band at 3388 $cm^{-1}$to the stretching mode of –OH groups which make them highly soluble in water.

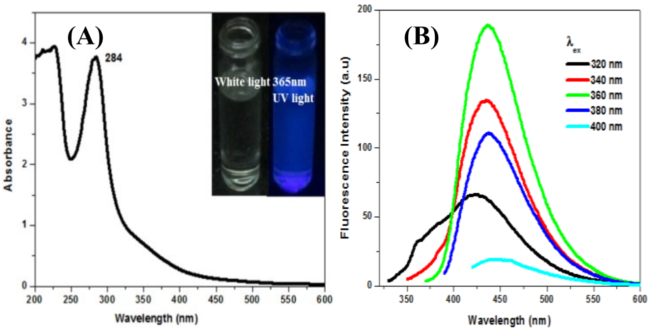


Figure 2. (A) UV–visible spectrum of CNP (inset: CNP in water under day light and 365nm UV light lamp) (B) Fluorescence of CNP with variation of excitation wavelength

D. Optical properties

The optical property of the as-obtained CNP is confirmed by the UV-visible and fluorescence spectroscopy. As shown in Figure 2A, UV-visible spectrum indicate a characteristic absorption peak at 284 nm for the CNPs which are assign to be π-π^* of –C=C– in the heterocyclic ring [16]. The fluorescence spectra show that the emission peak at 436 nm when excited at 360 nm wavelength as shown in the Figure 2B. The digital picture of the aqueous dispersions further shows that the obtained CNP are water-soluble (colourless) and exhibit strong blue fluorescence under 365 nm UV light (Figure 2 A, inset). The fluorescence emission peak is found to be independent on variation of excitation wavelength. When the exctation wavelength is varied from 320 nm to 400 nm, no shift of the emission peak centre is observed at 436 nm (Figure 2B).

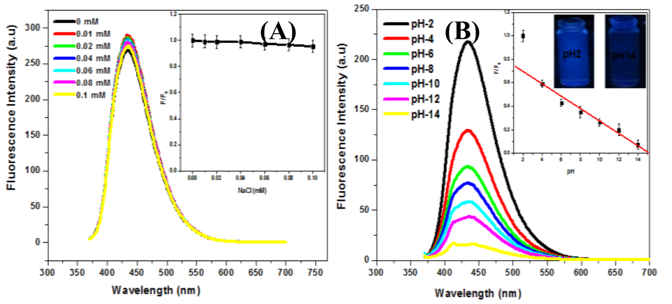


Figure 3. (A) Effect of CNP on NaCl concentration (B) Fluorescence of CNP with variation of pH

E. Effect of pH and salt concentration

Moreover, the CNP are well dispersed in water, display resistance to change in ionic strength of the solution. The ionic strength (NaCl) dependence of CNP is depicted in Figure 3A. It is observed that the fluorescence from CNP is stable up to high concentration NaCl, 0.1M. The sensitivity of fluorescence of CNP towards changing pH is shown in Figure 3B and scheme 1. The fluorescence intensity of the CNP decrease with increase in pH from 2 to 14. At acidic, CNP fluorescence is highest and variation of pH to basic condition results in decrease in fluorescence intensity. Aggregation of CNP by intermolecular or intramolecular hydrogen bonding in basic condition may be assigned as the cause of this observation. Therefore, this CNP may be a suitable materials to be used as fluorescence pH sensors in biological environment.

F. Fluorescence sensing experiments

The CNP can be suitably act as metal ion sensor based on fluorescence quenching behaviour. CNP on interaction with different metal ions such as Cu^{2+}, Fe^{3+}, Pb^{2+}, Al^{3+}, Co^{2+}, Zn^{2+}, Na^{+}, Mn^{2+}, Ag^{+} and Hg^{2+}, exhibit fluorescence quenching selectively with Fe^{3+}. Figure 4A and B, depicts the quenching of fluorescence from CNP in presence of Fe^{3+} while no such effect is seen for the remaining other metal ions. Visual observation of the process is shown in Figure 4C, showing the photograph of fluorescence from CNP after addition of 10 μL of 40 μM metal ions,Cu^{2+}, Fe^{3+}, Pb^{2+}, Al^{3+}, Co^{2+}, Zn^{2+}, Na^{+}, Mn^{2+}, Ag^{+} and Hg^{2+} with fixed concentration (under 365 nm UV lamp). It indicates that Fe^{3+}ions can bind to CNP by the –OH functional groups leading to electron donation from CNP to vacant orbitals of Fe^{3+} ions forming non fluorescent metal complexes as shown in scheme 1 [17].

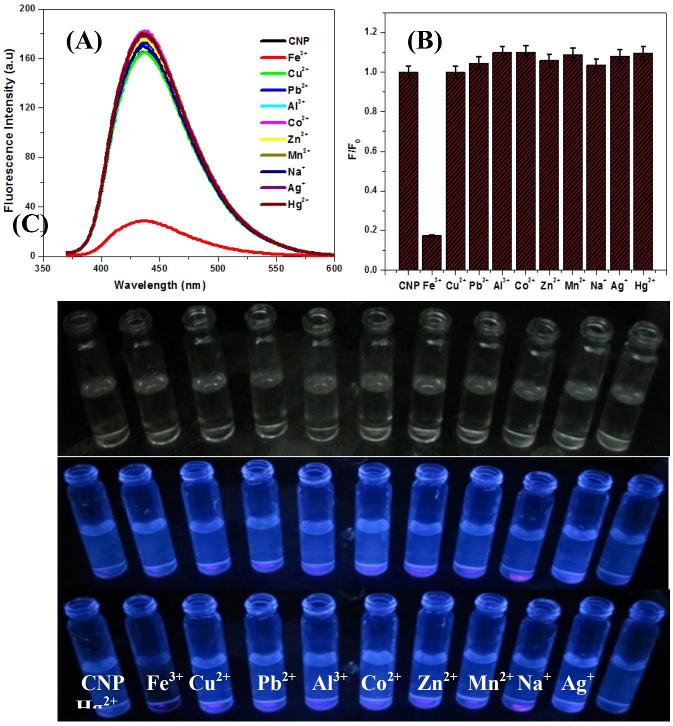


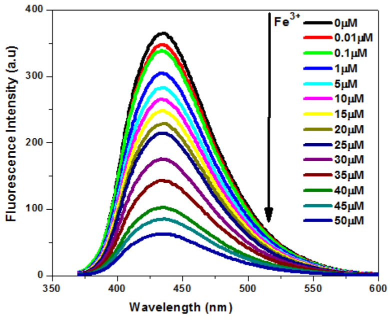
Figure 4. (A) Fluorescence spectra of CNP in presence of different metal ions (B) corresponding bar diagram (C) Photograph of fluorescence sensing experiment of CNP for different metal ions (upper bar under day light, middle bar under 365nm UV lamp and lower bar under 365nm UV lamp after addition of metal ions (10 μL, 40 μM)

G. Determination of minimum detection limit

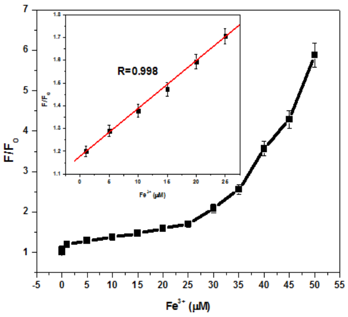
In order to determine the minimum detection limit of Fe^{3+} ions, we have performed the concentration dependent study as shown in the Figure 5. With the increase concentration of Fe^{3+}ions from 0.01 µM to 50 µM, the fluorescence intensity of CNP at 436 nm decreases gradually as observed from the Figure 5A. The detection limit is found to be 10 nM (1 ppb) which must lesser than permitted limit of Fe^{3+} (0.3 ppm) ions in drinking water [5]. A plot of F/F_0 (where, F_0= Fluorescence intensity of CNP; F= Fluorescence intensity of CNP in presence of different concentrations of Fe^{3+}) vs Fe^{3+} concentration (quencher concentration) shows linear pattern (inset) as we observed from Figure 5 B. With the variation of concentrations of the quencher (Fe^{3+}) the fluorescence intensity of CNP decreases with increase in concentrations of the quencher. The fluorescence quenching of CNP by the quencher (Fe^{3+}) is described by the following (1) [18].

$$F_0/ F = 1+K_S [Q] \text{ ------------ } (1)$$

F_0= Fluorescence intensity of CNP; F= Fluorescence intensity of CNP in presence of Fe^{3+}). K_S is the ground state stability constant. [Q]= quencher (Fe^{3+}). The linear range is 1 µM-20 µM.



(A)



(B)

Figure 5. (A) Fluorescence emission responses of CNP aqueous solution on addition of Fe^{3+} ions on excitation at fixed 360 nm wavelength (B) Plot of F_o/F vs Fe^{3+} concentration. (With different 0-50 µM conc of Fe^{3+} ions

H. Application in tap water samples

To test the applicability in real samples, the CNP is used for detection of Fe^{3+}in tap water samples by standard addition method [19]. The water samples were spiked to CNP solution and fluorescence measurements is carried out. The recoveries of $Fe^{3+}$are found to be in the range of 104.0 to 112.0% with relative standard deviation (RSD) less than 3%, which indicates that the CNP have the capability to detect Fe^{3+}in real samples as shown in Table 1. Therefore,CNP can be used for detection of Fe^{3+} ions in aqueous medium, which is also suitable for real samples.

Table 1

Sample	Added (Fe^{3+}) (µM)	Found (Fe^{3+}) (µM)	RSD (n=3)	Recovery (%)
1	1.0	1.12	1.54	112.0
2	3.0	3.17	1.62	105.6
3	6.0	6.24	2.31	104.0

IV. CONCLUSIONS

In summary, we have developed facile method for preparing highly fluorescent CNP from sucrose by using sulphuric acid at room temperature. The obtained CNP possess blue fluorescence, pH sensitivity and strong stability towards NaCl concentration. The CNP is used for sensitive and selective detection of Fe^{3+} ions in aqueous medium by fluorescence quenching process. The minimum detection limit of Fe^{3+} ions with the CNP is 10 nM (1 ppb) which is much lesser than WHO standard limit 0.3 ppm. Moreover, the spectroscopic studies indicates the mechanism of Fe^{3+} detection with CNP is due its capability of binding Fe^{3+} by the –OH functional groups, leading to electron donation from CNP to vacant orbitals of Fe^{3+} ions forming non fluorescent metal complexes at ground state. This fluorescent CNP is also suitable for detection Fe^{3+} ions in real tap water samples.

V. ACKNOWLEDGEMENTS

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VI. REFERENCES

[1]. Yong, L. Z., Lei, W., Heng, C. Z., Yang, L., Hai,Y. W., Zhen, H. K., Shuit,T. Lee.: Graphitic carbon quantum dots as a fluorescent sensing platform for highly efficient detection of Fe3+ ions. RSC Adv. 3 (2013) 3733-3738

[2]. Jiong, L., Jia X. Y., Junzhong, W., Ailian, L., Shuai, W., Kian, P. L.: One-Pot Synthesis of Fluorescent Carbon Nanoribbons, Nanoparticles, and Graphene by the Exfoliation of Graphite in Ionic Liquids. ACS Nano. 3 (2009) 2367-2375

[3]. Sheila, N. B., Gary A. B.: Luminescent Carbon Nanodots: Emergent Nanolights. Angew. Chem. Int. Ed. 49 (2010) 6726 - 6744

[4]. Yang, L., Yanan, L., Soo, J. P., Yifan, Z., Taewoo, K., Suhyeong, C., Mira, P., Hak, Y. K.: One-step synthesis of robust nitrogen-doped carbon dots: acid-evoked fluorescence enhancement and their application in Fe3+ detection. J. Mater. Chem. A. 3 (2015) 17747-17754

[5]. Xiaojuan, G., Wenjing, L., Man, C. P., Qin, H., Xin, W., Shaomin, S., Chuan, D., Martin, M. F. C.: Facile synthesis of nitrogen-doped carbon dots for Fe3+ sensing and cellular imaging, Analytica Chimica Acta. 861 (2015) 74-84

[6]. Raji, A., Thomas N. J. I. E., Dasagrandhi, C., Suguna, P., Jae, J. S., Yong, R. L.: Facile green synthesis of nitrogen-doped carbon dots using Chionanthus retusus fruit extract and investigation of their suitability for metal ion sensing and biological applications. Sensors and Actuators B. 246 (2017) 497-509

[7]. Soumen, C., Triveni, K. M., Angshuman, R. C., Balaram, D., Sumanta, k. S.: One step synthesis of functionalized carbon dots for the ultrasensitive detection of Escherichia coli and iron (III). Sensors and Actuators B. 245 (2017) 835-844

[8]. Jigna, R. B., Sanjay, J., Rakesh, K. S., Suresh, K. K.: Synthesis of Water Dispersible Fluorescent Carbon Nanocrystals from Syzygium cumini Fruits for the Detection of Fe3+ Ion in Water and Biological Samples and Imaging of Fusarium avenaceum Cells. J Fluoresc. 27 (2017) 125-134

[9]. Ghaedi, M., Shokrollahi, A., Kianfar, A. H., Mirsadeghi, A. S., Pourfarokhi, A., Soylak, M.: The determination of some heavy metals in food samples by flame atomic absorption spectrometry after their separation-preconcentration on bissalicyl aldehyde, 1,3 propandiimine (BSPDI) loaded on activated carbon. J Hazard Mater 154 (2008) 128-134

[10]. Pomazal, K., Prohaska, C., Steffan, I., Reich, G., Huber, J. F. K.: Determination of Cu, Fe, Mn, and Zn in blood fractions by SECHPLC-ICP-AES coupling. Analyst 124 (1999) 657-663

[11]. Chen, Y., Wu, Y., Weng, B., Wang, B., Li, C.: Facile synthesis of nitrogen and sulfur co-doped carbon dots and application for Fe (III) ions detection and cell imaging. Sensors Actuators B. 223 (2015) 689-696

[12]. Miao, P., Tang, Y., Hanab, K., Wang, B.: Facile synthesis of carbon nanodots from ethanol and their application in ferric (III) ion assay. J Mater Chem A 3 (2015)15068-15073

[13]. Yang, X., Zhuo, Y., Zhu, S., Luo, Y., Feng, Y., Dou, Y.: Novel and green synthesis of high-fluorescent carbon dots originated from honey for sensing and imaging. Biosens. Bioelectron. 60 (2014) 292-298

[14]. Haipeng, L., Tao, Y., Chengde, M.: Fluorescent Carbon Nanoparticles Derived from Candle Soot. Angew. Chem. Int. Ed. 46 (2007) 6473 - 6475

[15]. Zhi, Y., Minghan, X., Yun, L., Fengjiao, H., Feng, G., Yanjie, S., Hao, W., Yafei, Z.: Nitrogen-doped, carbon-rich, highly photoluminescent carbon dots from ammonium citrate. Nanoscale. 6 (2014) 1890-1895

[16]. Qian, Q. S., Yu, H. Li., Yang, X., Yue, W., Xue, B. Y., Xi, W. H.: High-yield and high-solubility nitrogen-doped carbon dots: formation, fluorescence mechanism and imaging application RSC Adv. 4 (2014) 1563-1566

[17]. Pengfei, L., Yixin. Y., Huimin, Z., Jin, Z., Zengyuan, P., Kelong, A., Yibing, C., Qufu, W.: Synthesis of novel nitrogen-doped carbon dots for highly selective detection of iron ion. Nanotechnology. 28 (2017)165502-165512

[18]. Valeur, B.: Molecular fluorescence (Wiley Hoboken NJ). p.85, (2001)

[19]. Lia, Z., Wang, Y., Nia, Y and Kokot S A rapid and label-free dual detection of Hg (II) and cysteine with the use of fluorescence switching of graphene quantum dots Sensors and Actuators B 207 (2015) 490-497