




PAPER

Bright green fluorescence of microwave irradiation-synthesized Cdots as sensitive probe of iron (III)

RECEIVED
31 May 2019REVISED
7 July 2019ACCEPTED FOR PUBLICATION
29 July 2019PUBLISHED
7 August 2019I W L Lewa¹, H Sutanto^{1,2} , A Subagio¹, I Marhaendrajaya¹ and H Sugito¹¹ Department of Physics, Diponegoro University, Jl. Prof. Soedarto, SH, Semarang-50275, Indonesia² Central Laboratory of Research and Services Diponegoro University (CORES DU), Jl. Prof. Soedarto, SH, Semarang-50275, IndonesiaE-mail: herisutanto@fisika.undip.ac.id**Keywords:** Cdots, bio imaging, bright Green fluorescence, microwave irradiation

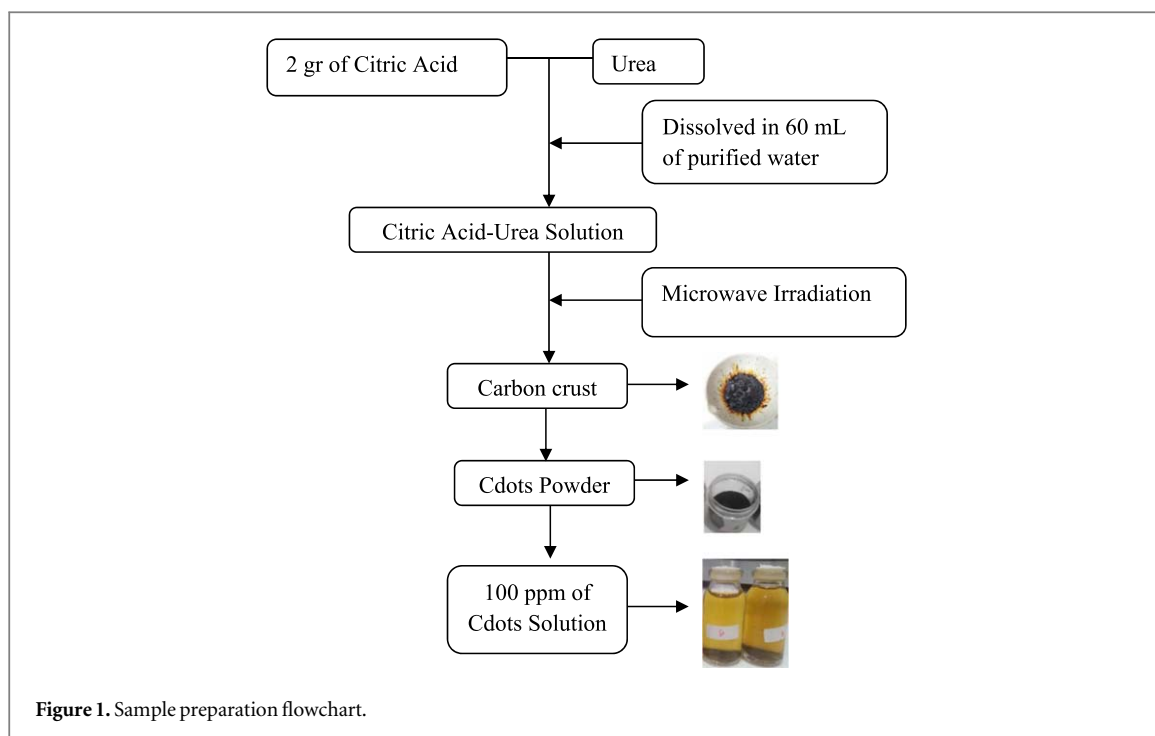
Abstract

Carbon nanodots (Cdots) are very attractive materials due to their fluorescence and great potential in various fields. One field that still needs to be developed is heavy metal ion detector. In this study, a simple and cost efficient fluorescent detector of Fe^{3+} was built. This material was synthesized by microwave irradiation method using citric acid and urea with purified water as the solvent to get the optimal concentration of urea in order to produce bright green fluorescence. Synthesized Cdots with optimal concentration of urea emit bright green fluorescence under UV light radiation. This bright green fluorescence was then used to detect Fe^{3+} . The fluorescence of this solution was quenched with the addition of Fe^{3+} due to transfer charges and exciton recombination. Optical characterization was carried out using UV-vis spectrophotometer, and fluorescence spectrophotometer. Results showed two absorption peaks on Cdots; at 330 nm and 410 nm. Fluorescence analysis was performed using a beam of 532 nm produced emission at a wavelength of 590 nm. In addition, structural characterization was performed using FTIR, SEM and EDX.

Introduction

Carbon nanodots (Cdots) are zero-dimensional carbon material with a dimension of less than 10 nm. Cdots were first discovered by Xu *et al* in 2004 from the purification process of carbon nanotubes [1]. Cdots are spherical [2], non toxic [3] and have high water solubility [4]. Cdots can be used in several application areas such as biomedicine [5], LED [6], energy related applications [7, 8], bioimaging [9], and sensors [10]. Cdots are very interesting material with their fluorescence properties [11] and one of the fields that is being developed using this is sensors. Cdots are the right material choice to replace the commonly used probes. Sensor applications typically use quantum dots semiconductor materials such as CdS [12]. However, CdS is toxic and is not easily degraded in the environment. Cdots are an alternative substitute material that are effective because they are not toxic, compatible, and easily soluble in water [12].

Cdots can be synthesized using several methods that are divided into two categories of top down and bottom up. The top down method breaks large molecules into smaller ones. This method includes laser ablation [13], electrochemistry [14] and arc discharge [15]. Meanwhile, the bottom up method, which is also known as the chemical method, is the preparation of a material from small-sized materials. This method includes pyrolysis [16], hydrothermal [17] and microwave [18]. Microwave irradiation is one of the most widely used methods because it can reach certain heat in shortly, efficiently, fast, easily, and inexpensively. Improving the fluorescence properties of this material is an important aspect that should be considered. Various methods can be used such for this purpose, including surface passivation [19]. Passivation process uses organic materials containing an amine group to improve fluorescence. Fluorescence is caused by a surface energy trap that can be modified to get the properties that are suitable for certain applications. Surface modification method is appropriate for sensing applications [20]. Based on research by Sun and coworkers, the surface passivation process of non-luminescent Cdots derived from polyethylene glycol polymers (PEG) shows strong luminescence [20]. By using microwave



irradiation, the passivation process can be carried out in one step, hence, microwave irradiation is the right method to synthesize Cdots [21].

Previous studies have proven that Cdots can be used to detect heavy metals with the turn on/turn off fluorescence mechanism. One study by Zhang *et al* synthesizes Cdots from melamine and g-C₃N₄ by heating them for 2 h to detect Pb²⁺ ions [22]. Another study by Kumar *et al* synthesizes Cdots using the hydrothermal method for 7 h to detect Hg²⁺ ions [23]. In this research, Cdots synthesis using microwave irradiation was carried out to obtain a material that has strong luminescence and can be used as a detector of Fe³⁺ heavy metal ions. The precursors used here were citric acid as a source of carbon and urea as passivation agents and distilled water as solvent. Variations of urea concentration were made in order to find the right formula to produce strong luminescence. Sensitivity tests for Fe³⁺ heavy metal ions were also carried out. Further characterization includes using UV–vis spectrophotometer to observe absorbance spectrum, fluorescent spectrometer to observe emission spectrum of Cdots and FTIR to observe functional groups contained in the synthesized material.

Material and methods

A synthesis procedure for Cdots can be seen in figure 1. Cdots were made of citric acid and urea using microwave irradiation method. Citric acid was used as a source of carbon, while urea was used as passivation agent with its amine group content. Purified water was used as solvent in the reaction. Two grams of citric acid were mixed with urea with varied concentration of 1 to 7 grams. The solvent for each solution was 60 ml of purified water. Once the solution is homogenized, it was then irradiated using a microwave with power 450 W for 30 min until a blackish brown crust is formed. The crust was then taken and mashed into powder. Afterwards, the Cdots powder was dissolved in purified water with a concentration 100 ppm. This solution was then characterized and analyzed to determine its properties.

Results and discussion

Cdots synthesis

The first step is synthesizing Cdots using microwave irradiation. The materials used were citric acid as a source of carbon and urea as a surface passivation agent. Physical processes occurring during synthesis are divided into 4 stages of dehydration, polymerization, carbonization and passivation²⁰. Dehydration reaction is the release of water content in the molecules that are reacting. The second step is polymerization. This is where reaction triggers spontaneous nucleation process that is followed by the formation of new longer bonds. The third step is carbonization in which inorganic carbon bonds are derived from citric acid²¹. The final step is surface passivation. This is where coating on the surface of Cdots by compounds of the amine functional groups

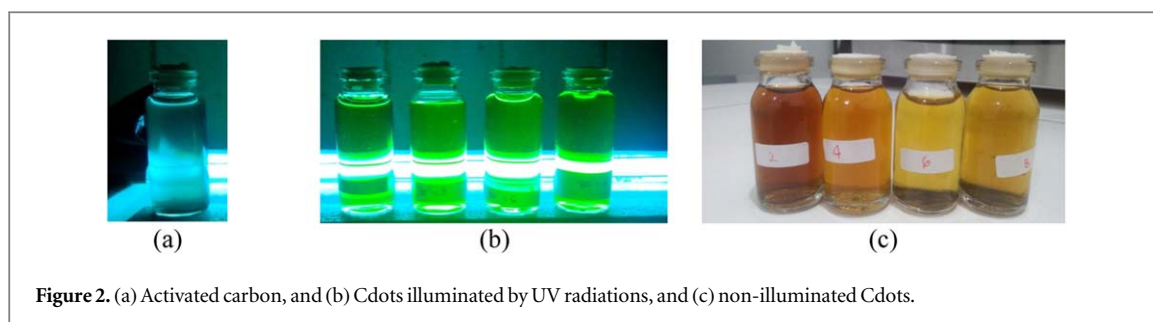


Figure 2. (a) Activated carbon, and (b) Cdots illuminated by UV radiations, and (c) non-illuminated Cdots.

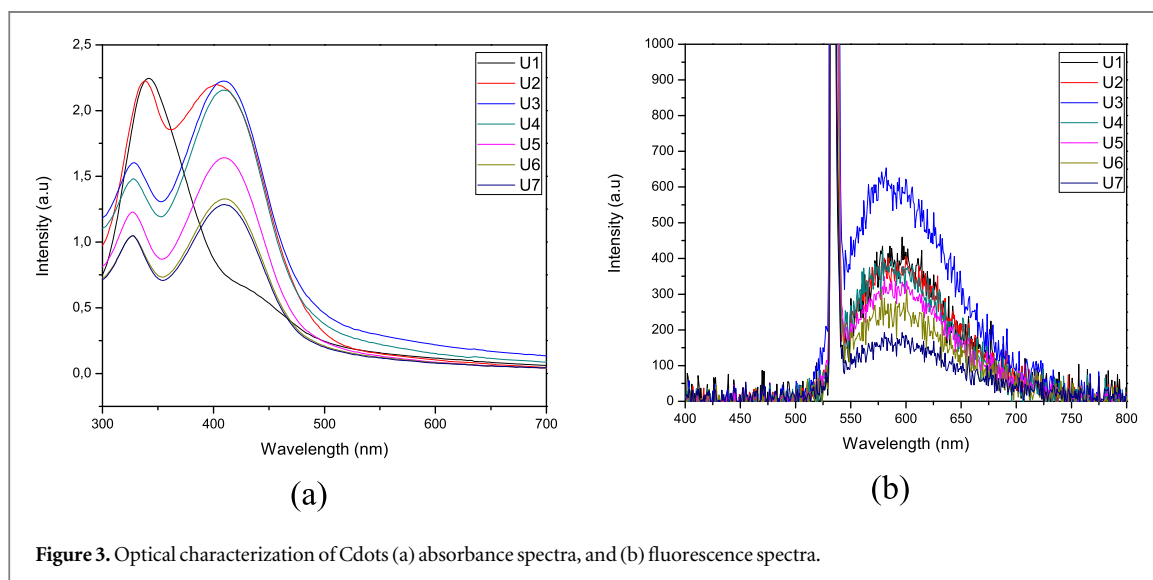


Figure 3. Optical characterization of Cdots (a) absorbance spectra, and (b) fluorescence spectra.

contained in urea takes place. Cdots surface without coating is not only exposed to contaminants, but also powerless because carbon and oxygen are endogenous to be able to react with organic molecules, hence, it can eliminate opto-electronic properties of Cdots. Therefore, coating is very important because it can maintain the stability of Cdots' physical properties and strengthen fluorescence. Surface passivation forms a thin insulating capping layer that can protect Cdots and increase their fluorescence. There are various types of polymers or organic molecules that can be used as passivation agents as long as they do not contain chromophores from visible light to UV and they do not emit the same wavelength, as this may affect the original luminescence of Cdots [24].

Results obtained in this synthesis process are black solids, which were then dissolved in purified water for further observation. Upon observation using UV radiation with a wavelength of 280–300 nm it appeared that the Cdots emit green luminescence, as shown in figure 2 below.

The figure shows that activated carbon (a) has no green luminescence, while Cdots produce green luminescence (b). This indicates change in optical properties when Cdots are changed into a quantum nano materials dimension.

Optical characterization

Optical characterization of Cdots was performed using UV-visible spectroscopy and fluorescence spectroscopy. Absorption spectra of synthesized Cdots (figure 3(a)) showed two absorption peaks; at 330 nm and 410 nm. These absorption peaks could be associated with $\pi \rightarrow \pi^*$ transition of C=C bond and $n \rightarrow \pi^*$ transition of C=O bond, respectively. These are transitions of carbonyl and oxygen containing compounds. These results corresponds to several study before [25, 26]. Figure 3(a) shows the effect of adding urea that causes a decrease in absorption intensity from the sample. This is possible as the more nitrogen levels contained in urea, the less Cdots absorption is because of lower levels of citric acid and more predominant nitrogen levels. Furthermore, surface functional groups also play an important role in determining the absorption wavelength of Cdots.

The fluorescence spectrum shows a peak at a wavelength of 590 nm. At a concentration of 1 gram, 2 g and 3 g of urea, there is an increase in fluorescence intensity. Fluorescence that occurs in Cdots is caused by the presence of surface passivation process by passivation agents. The passivation process results in surface energy trap that enables emission stability and hence, improved fluorescence of Cdots. This is because of the quantum

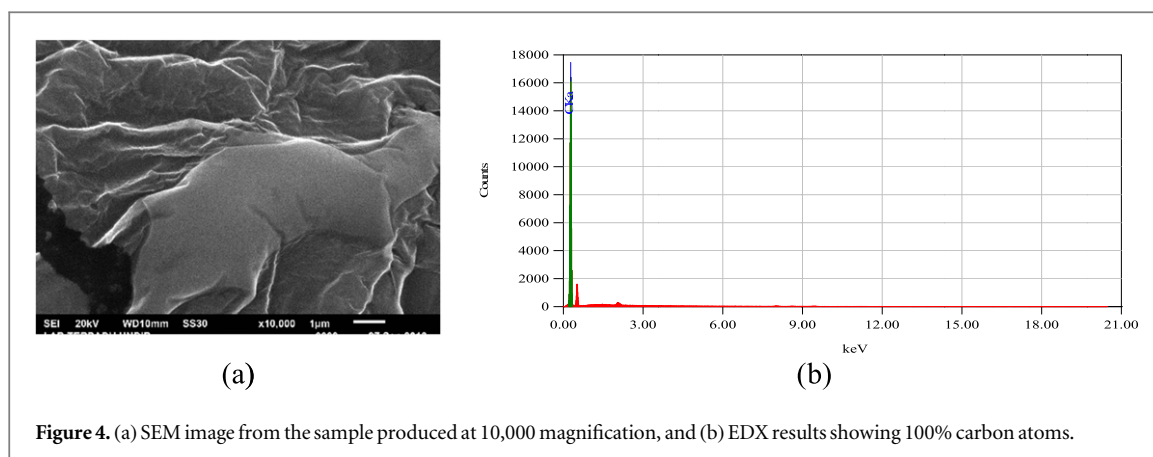


Figure 4. (a) SEM image from the sample produced at 10,000 magnification, and (b) EDX results showing 100% carbon atoms.

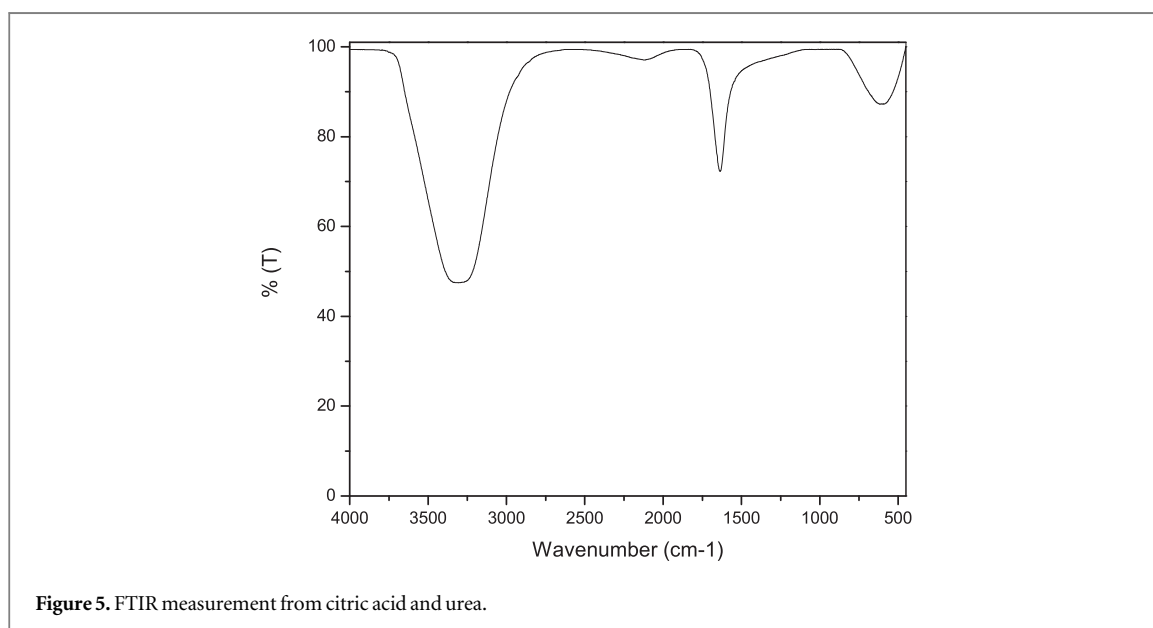


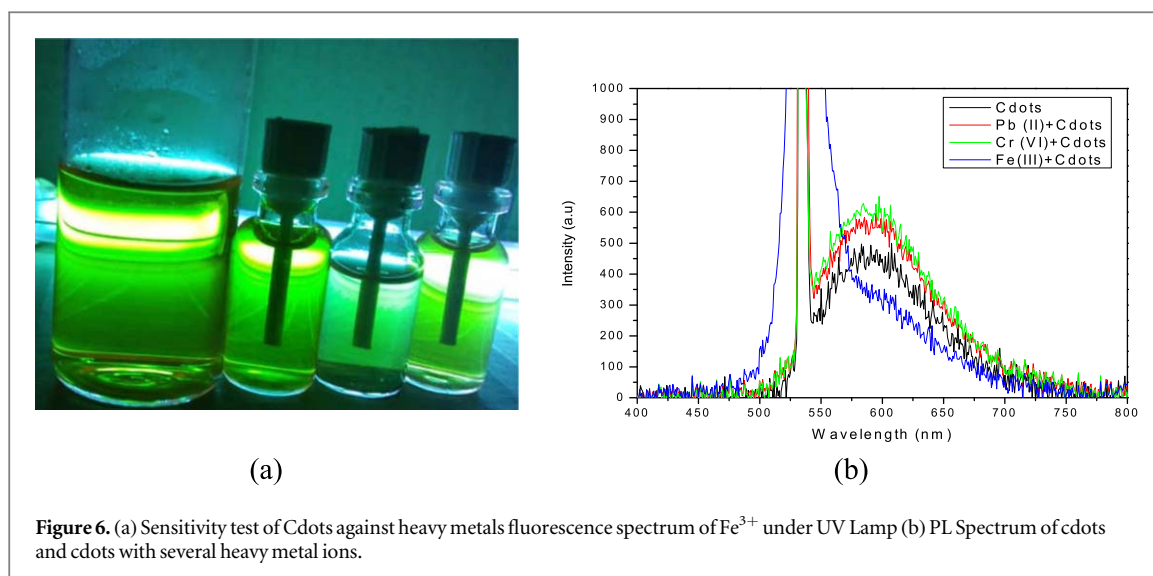
Figure 5. FTIR measurement from citric acid and urea.

confinement effect of the emission energy trap on particles, where the ratio between the surface and volume of particles affects passive particles [20]. Fluorescence intensity of Cdots saturated at a variation of 4 g urea kept on decreasing until the concentration reaches 7 g of urea. The reason is that at a concentration of 4 g, the level of urea is more dominant than citric acid as a carbon source. So it is estimated that the number of carbon bonds decreases and this results in reduced fluorescence intensity. The effect of concentration is very important for the fluorescent properties of Cdots. Emissions from strong surface energy levels are caused by changes in concentration [27].

Structural characterization

In addition to optical characterization, characterization using SEM, EDX and FTIR were also carried out. SEM is used to see the topography of this material. From figure 4(a) we can see that cdots are irregularly shaped with a rough surface. While previous research stated that cdots have spherical shape and uniform size [28]. This is because cdots tend to agglomerate and poses a problem for characterization. EDX used to analyze the elements that exist in the material. From figure 4(b) we can see that the material consists of 100% carbon element. Meanwhile, FTIR was used to determine the functional group of synthesized material.

FTIR analysis is used to determine the functional groups contained in Cdots [29]. From figure 5 we can see that cdots shows transmittance band at 3307 cm^{-1} correspond to O–H bond, $\text{C}\equiv\text{C}$ bond at 2111 cm^{-1} and transmittance band 1635 cm^{-1} correspond to C=O and C=C bonds. These results show the same results according to previous research explain that the functional group of Cdots contain O–H at wave numbers $3100\text{--}3400\text{ cm}^{-1}$ and function group C=O at $1600\text{--}1770\text{ cm}^{-1}$ [30]. Results of FTIR measurement show no significant differences with urea variation. Cdots will be more stable and hidrofily increases if there are O–H and N–H groups [31].



Fe³⁺ ions detection

The Fe³⁺ ions detection test was carried out to find out changes in fluorescence properties of Cdots when some heavy metal solutions were added. Observations show that Cdots fluorescence changes with the addition of heavy metals ions solution, as can be seen in figure 6.

It can be seen in figure 6(a) that when given a standard solution of Cr⁶⁺ and Pb²⁺ fluorescence of cdots remained constant. But it was different when Cdots were given a solution of Fe³⁺, as the fluorescence began to quench. This can be proven by observing PL spectrum shown in figure 6(b). It is easy to see in the spectrum that when compared to other metal ions, Fe³⁺ shows more quenched effect with decrease in the emission spectrum. Therefore, we can conclude that Cdots synthesized from citric acid and urea are sensitive to Fe³⁺ ion solutions. Quenched fluorescence of cdots are caused by several functional groups on their surface. These include hydroxyl and carboxyl groups that are capable to selectively respond to Fe³⁺ ions. The mechanism of this fluorescence turning off stems from charge transfer and controlled exciton recombination [26, 32].

Conclusions

A synthesis of Cdots has been successfully carried out using the microwave irradiation method of citric acid and urea via microwave irradiation process. The synthesized Cdots show bright green fluorescence and are sensitive to Fe³⁺ ions. Therefore, it can be concluded that the addition of urea increases fluorescence. Nonetheless, Cdots saturate at some point and have reduced the intensity. The most appropriate concentration of citric acid-urea that produce the strongest fluorescence is at a concentration 2:3. Cdots fluorescence is quenched upon administration of a standard solution of Fe³⁺ ion. This quenching mechanism is caused by the response of carboxyl and hydroxyl functional groups with Fe³⁺ ions that reside on the surface of Cdots.

Acknowledgments

The authors would like to thank Diponegoro University for funding this research in 2019.

ORCID iDs

H Sutanto  <https://orcid.org/0000-0003-3404-0337>

References

- [1] Xiaoyou Xu et al 2004 Electrophoretic analysis and purification of fluorescent single-walled carbon nanotube fragments *J. Am. Chem. Soc.* **126** 12736–7
- [2] De B and Karak N 2013 A green and facile approach for the synthesis of water soluble fluorescent carbon dots from banana juice *RSC Adv.* **3** 8286–90
- [3] Bhamore J R, Jha S, Park T J and Kailasa S K 2019 Green synthesis of multi-color emissive carbon dots from Manilkara zapota fruits for bioimaging of bacterial and fungal cells *J. Photochem. Photobiol. B Biol.* **191** 150–5

- [4] Zheng L, Chi Y, Dong Y, Lin J and Wang B 2009 Electrochemiluminescence of water-soluble carbon nanocrystals released electrochemically from graphite *J. Am. Chem. Soc.* **131** 4564–5
- [5] Jaleel J A and Pramod K 2018 Artful and multifaceted applications of carbon dot in biomedicine *J. Control. Release* **269** 302–21
- [6] Cui B et al 2017 The use of carbon quantum dots as fluorescent materials in white LEDs *Xinxing Tan Cailiao/New Carbon Mater.* **32** 385–401
- [7] Genc R et al 2017 High-Capacitance hybrid supercapacitor based on multi-colored fluorescent carbon-dots *Sci. Rep.* **7** 1–13
- [8] Li L, Wu G, Yang G, Peng J, Zhao J and Zhu J J 2013 Focusing on luminescent graphene quantum dots: current status and future perspectives *Nanoscale* **5** 4015–39
- [9] Zhang J and Yu S H 2016 Carbon dots: large-scale synthesis, sensing and bioimaging *Mater. Today* **19** 382–93
- [10] Ng S M 2019 *Carbon Dots as Optical Nanoprobes for Biosensors*. (Elsevier Inc)
- [11] Qu S, Wang X, Lu Q, Liu X and Wang L 2012 A biocompatible fluorescent ink based on water-soluble luminescent carbon nanodots *Angew. Chemie - Int. Ed.* **51** 12215–8
- [12] Das A and Snee P T 2016 Synthetic developments of nontoxic quantum dots *Chem. Phys. Chem.* **17** 598–617
- [13] Li X, Wang H, Shimizu Y, Pyatenko A, Kawaguchi K and Koshizaki N 2011 Preparation of carbon quantum dots with tunable photoluminescence by rapid laser passivation in ordinary organic solvents *Chem. Commun.* **47** 932–4
- [14] Ming H et al 2012 Large scale electrochemical synthesis of high quality carbon nanodots and their photocatalytic property *Dalt. Trans.* **41** 9526–31
- [15] Tuerhong M, XU Y and YIN X B 2017 Review on carbon dots and their applications *Chinese J. Anal. Chem.* **45** 139–50
- [16] Marpongahtun S, Gea Y, Muis, Andriyani T, Novita and Piliang A F 2018 Synthesis of carbon nanodots from cellulose nanocrystals oil palm empty fruit by pyrolysis method *J. Phys. Conf. Ser.* **1120** 1–6
- [17] Zhao S et al 2015 Green synthesis of bifunctional fluorescent carbon dots from garlic for cellular imaging and free radical scavenging *ACS Appl. Mater. Interfaces* **7** 17054–60
- [18] Liu X et al 2017 Carbon nanodots as a fluorescence sensor for rapid and sensitive detection of Cr(VI) and their multifunctional applications *Talanta* **165** 216–22
- [19] Zhai X et al 2012 Supporting information - highly luminescent carbon nanodots by microwave-assisted pyrolysis *Chem. Commun.* **48** 7955–7
- [20] Sun Y P et al 2006 Quantum-sized carbon dots for bright and colorful photoluminescence *J. Am. Chem. Soc.* **128** 7756–7
- [21] Guo C, Zhang X, Wang C, Lu J and Zhou X 2016 Rapid microwave synthesis of N-doped carbon nanodots with high fluorescence brightness for cell imaging and sensitive detection of iron (III) *Opt. Mater. (Amst.)* **64** 1–8
- [22] Zhang H, Huang Y, Zheng Y and Zhou J 2019 SC
- [23] Kumar G G, Kim A R, Annaraj J, Xavier S S J, Siva G and Yoo D J 2017 Sensitive and selective turn-off-on fluorescence detection of Hg²⁺ and cysteine using nitrogen doped carbon nanodots derived from citron and urine *Sensors Actuators B Chem.* **259** 1133–43
- [24] Dimos K 2015 Carbon quantum dots: surface passivation and functionalization *Curr. Org. Chem.* **20** 682–95
- [25] Zhang M et al 2012 Facile synthesis of water-soluble, highly fluorescent graphene quantum dots as a robust biological label for stem cells *J. Mater. Chem.* **22** 7461–7
- [26] Liu Y et al 2019 Nitrogen doped graphene quantum dots as a fluorescent probe for mercury(II) ions *Microchim. Acta* **186**
- [27] Jusuf B N, Sambudi N S, Isnaeni I and Samsuri S 2018 Microwave-assisted synthesis of carbon dots from eggshell membrane ashes by using sodium hydroxide and their usage for degradation of methylene blue *J. Environ. Chem. Eng.* **6** 7426–33
- [28] Devi S, Kaur A, Sarkar S, Vohra S and Tyagi S 2018 Synthesis and characterization of highly luminescent N-doped carbon quantum dots for metal ion sensing *Integr. Ferroelectr.* **186** 32–9
- [29] Hu B, Wang K, Wu L, Yu S H, Antonietti M and Titirici M M 2010 Engineering carbon materials from the hydrothermal carbonization process of biomass *Adv. Mater.* **22** 813–28
- [30] Liu H, Ye T and Mao C 2007 Fluorescent carbon nanoparticles derived from candle soot *Angew. Chemie - Int. Ed.* **46** 6473–5
- [31] (Saunders Golden Sunburst Series) Donald L. Pavia, Gary M. Lampman, George S. Kriz-Introduction to Spectroscopy -Brooks Cole (2000).pdf., Washington (US): Thomson Learning, Inc
- [32] Zhang Y L et al 2013 Graphitic carbon quantum dots as a fluorescent sensing platform for highly efficient detection of Fe³⁺ ions *RSC Adv.* **3** 3733–8