Economically Viable Synthesis of Carbon dots and its Application

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ABSTRACT

Highly luminescent carbon dots (C-dots) were synthesized by the one-pot simple hydrothermal method directly from moringa oleifera leaf. C-dots were characterized with Fourier transform infrared spectrophotometry and Zeta. The carbon dots was further utilized as Nano nutrient for the growth of plants. The plant treated with C-dots nanoparticles showed significant growth against the non-treated plants.

Keywords: Carbon dots, Nano particles, green synthesis, plant treatment.

INTRODUCTION:

Carbon nanodots (CDs), discovered in the mid-2000s. One of the protagonists of carbon nanoscience. CDs are nanoparticles smaller than 10 nm typically composed by carbon, oxygen, nitrogen and hydrogen. Their most important hallmark is a bright fluorescence, tunable across the visible range, which has revolutionized the traditional paradigm of carbon as a black material unable to emit light. Their luminescence is accompanied by many additional benefits, such as low cost, ease of synthesis, high water solubility, biocompatibility, and non-toxicity, high sensitivity to the external environment, and marked electron donating and accepting capabilities. This combination of properties allows for using CDs in a very broad range of applications, across many different fields ranging from optoelectronics to sensing. In fact, the potential of CDs is evident

from the explosion of the number of studies, currently ranging in the thousands per year. From the practical point of view, the optical properties of CDs are somehow comparable, and often competitive, to fluorescent semiconductor quantum dots (QDs). Compared to them, luminescent CDs are superior in terms of aqueous solubility, high resistance to photo bleaching, low toxicity and good biocompatibility. In addition, they do not usually show blinking effects, they display strong absorption in the blue and UV ranges, and their reported QYs are steadily increasing, due to the progressive improvement of the synthesis procedures. From a structural viewpoint, CDs are a relatively wide family of nanomaterials with a range of possible structures and variable optical properties. Even graphene quantum dots (GQDs), which can be pictured as nanometer-size fragments of monolayer graphene, may probably be considered a special sub-type of CDs because they display very similar photophysics despite the twodimensional morphology. In all the synthesis approaches, the surface of CDs is passivated (during or after synthesis) by external agents, forming a layer of functional groups or molecules which bind to the carbonaceous core. The passivation layer should be considered as an integral part of the structure and function of CDs, which, in particular cases, can be as thick as a few nanometers. Thereby, depending on the specific surface structures, CDs can be hydrophilic or hydrophobic. As for the optical properties, different synthesis procedures yield subtypes of CDs capable of emitting fluorescence at different wavelengths. In fact, CDs can emit blue, green, or red light, and their fluorescence can be either independent of the excitation wavelength or more commonly "tunable", in the sense that the emission peak continuously shifts as a function of the excitation wavelength. Their fluorescence intensity can be sensitive to one particular ion in solution, or it can respond to a variety of interactions with other systems, such as carbon nanotubes (CNTs).

Carbon dots research is still in a developing phase despite thousands of studies have already been published on the subject, and several scientific open questions exist about their optical behavior, the fundamental nature of the electronic states, the key factors determining their bright fluorescence, and the relation between structure and emission. Therefore, a large effort is in progress to find the most effective ways to tailor CDs for specific applications. While several review papers have been already published on CDs focusing on different aspects of the field, this work specifically focuses on the most fundamental aspects of the photo physics and photochemistry of CDs, currently the subject of a large debate. In this application CDs are use as agriculture.

In view of these aspects we have worked on Green Synthesis of Carbon dots from <u>Moringa Oleifera leaves</u>, and further applied in agriculture to induce plant growth.

MATERIAL & METHOD: Collection of Sample:

Fresh Moringa Oleifera leaves were collected from Farm house. Leaves were washed thoroughly by water and were allowed to dry in air at Sun light.

Preparation of Moringa Oleifera Leaf Extract:

CDs were prepared by pyrolysis of leaves. In a typical run, 1 g of leaves was transferred into a crucible, and was pyrolyzed at 250 C for 2h at a heating respectively. After cooling down to room temperature, the dark black products were mechanically ground to fine powders. The as-prepared CD solutions derived from oriental plane leaves moringa oleifira leaves which are collected for further characterization and use.



1446

Fig: 1 Scheme of Carbon Nano particles

For the synthesis of zinc oxide nanoparticles by precipitation reaction process, 10 ml of Moringa Oleiferaleaf extract was mixed with 5 ml 5% NaOH solution. Then solutions were taken in a 250 ml beaker and kept stirring for 1 h. Then zinc acetate (2.1g in100ml water), ammonium carbonate (0.96g in 100ml) solutions were added drop wise into the beaker simultaneously with constant stirring. After the completion of reaction, the suspension was kept stirring for 1 h at room temperature. Finally, precipitate was filtered, washed with distilled water for several times. Then the precipitates were dried under hot air oven. Then zinc oxide nanoparticles were collected and stored in vacuum for further use.

RESULTS AND DISCUSSION:

FTIR Analysis

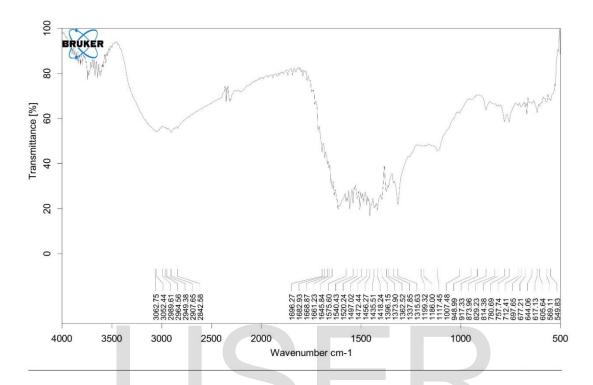


Figure: 2 FTIR spectra of synthesized carbon dots Nanoparticles

The carbon dot nanoparticle was subjected to FTIR analysis and the spectrum was recorded in the range from500 to 4000 cm⁻¹ and is shown in Figure. The peak at 3550 to 3200 cm⁻¹ is due to the presence of strong O-H alcohol group. The peak at 3200 to 2500cm⁻¹ is weak broad O-H group. The peak at 1696 cm⁻¹ strong C=O group. The peak is 1682 to 1645cm ⁻¹ denotes the weak C-H bending, At 1645 to 1600 cm⁻¹, the peak weak C=C stretching alkene group. The peak at 1550 to 1520 cm⁻¹ shows the presence of strong N-O. The peak at 1472 to 1418 cm⁻¹ is due to the presence of medium C-H bending alkane. The peak at 1396 to 1315 cm⁻¹ medium O-H bending. The peak at 1199 to 1117 cm⁻¹ indicates the presence of strong C=C bending alkene. The peaks at 945.51 to 814 cm⁻¹ shows presence of strong C=C bending alkene. The pic at

829 cm-1 Indicates medium C=C bending alkene, at 780 cm -1 indicates strong C-H bending The peak at 697 cm-1570 cm-1 and at 554.78 cm-1 shows presence of strong C-H bending, and it is due to the presence of FTIR many group present in carbon dot respectively.

FTIR Analysis

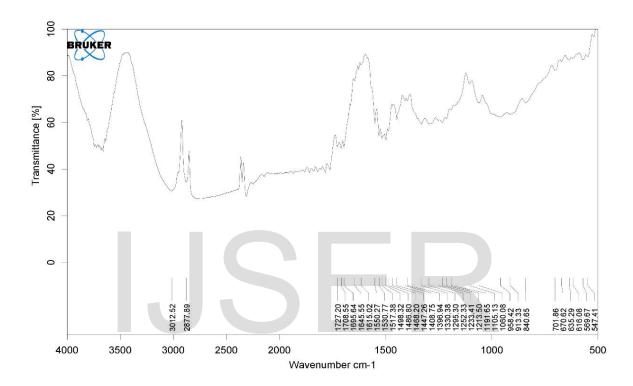


Figure: 3 FTIR spectra of moringa oleifira leaf powder

The moringa oleifira leaf was subjected to FTIR analysis and the spectrum was recorded in the range from500 to 4000 cm⁻¹ and is shown in Figure. The peak at 3550 to 3200 cm⁻¹ is due to the presence of strong O-H alcohol group. The peak at 3200 to 2500cm⁻¹ is weak broad O-H group. The peak at 1695 cm⁻¹ strong C=O group. The peak is 1727 to 1645cm⁻¹ denotes the weak C-H bending, At 1645 to 1610 cm⁻¹, the peak weak C=C stretching alkene group. The peak at 1550 to 1517 cm⁻¹ shows the presence of strong N-O. The peak at1480 to 1408 cm⁻¹ is due to the presence of medium C-H bending alkane. The peak at 1396

to 1330 cm-1 medium O-H bending. The peak at 1295 to 1230cm-1 is presence of strong C-O group. The peak at 1250 to 1230 cm-1 is presence of medium C-N stretching group. The peak at 1191 to 1105 cm-1 indicates the presence of strong C-O Stretching secondary alcohol. The peaks at 958 to 913 cm-1 shows presence of strong C=C bending alkene. The peak at 840 cm-1 Indicates medium C=C bending alkene, at 701 cm -1 indicates strong C-H bending The peak at 670 cm-1 570 cm-1 and at 547 cm-1 shows presence of strong C-H bending[49].

Particle size analysis

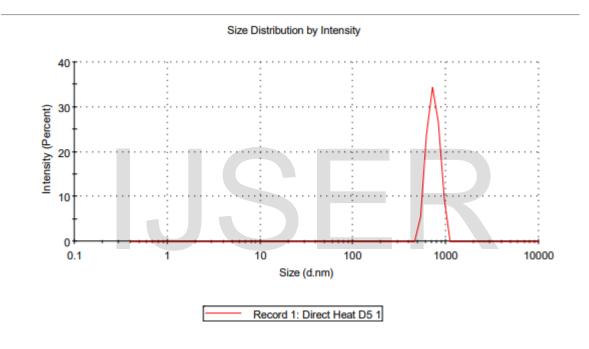


Figure: 4 Particle size analysis of carbon dots nanoparticles

The particle size distribution (PSD) curve of the synthesized carbon dots particles is given in figure. The PSD plot for sample carbon dots shows that all the particles are within the size range of 732 nm [50].

Effect on Plant growth

The carbon dots obtained by green synthesis method was applied to evaluate the growth of plants.

Initially soil was taken and mixed with cow dung and further carbon dots was added to the soil to check the improvement in growth of plants.

The growth of the plants was evaluated at regular intervals

Weekly growth analysis of Sorghum Plant

	Soil	Soil+Cow dung	Soil + Cowdung + carbon dots
Week :1	14.5cm	14.6cm	14.8cm
Week :2	30.1cm	30.5cm	31.5cm



Only soil

Soil + Cow dung

Soil + Cow dung + carbon dots

Fig: 5 Plant height measurement after 1st Week

Conclusion

Carbon dots have been synthesized by simple and eco-friendly method using leaf powder of moringa olefira. Characterization of particles formed shows the formation of the particle in the size range of around 732 nm. The green synthesis of carbon dots is much safer and environment friendly compared to chemical synthesis because it does not lead to formation of toxic by-products. The colloidal solution of carbon dots NPs are used as Nano nutrient and applied to soil along with Cow dung to the species of Sorghum pant i.e. common Indian wheat wherein we observed that the addition of carbon dots to soil resulted in significant increase in the growth of wheat plant.

4. References:

1. Sun, Y.; Zhou, B.; Lin, Y.; Wang, W.; Fernando, K.A.S.; Pathak, P.; Meziani, M.J.; Harruff, B.A.; Wang, X.; Wang, H.; et al. Quantum-Sized Carbon Dots for Bright and Colorful Photoluminescence. J. Am. Chem. Soc. **2006**, 128, 7756–7757.

2. Xu, X.; Ray, R.; Gu, Y.; Ploehn, H.J.; Gearheart, L.; Raker, K.; Scrivens, W.A. Electrophoretic Analysis and Purification of Fluorescent Single-Walled Carbon Nanotube Fragments. J. Am. Chem. Soc. **2004**, 126, 12736–12737.

3. Cayuela, A.; Soriano, M.L.; Carrillo-Carrion, C.; Valcarcel, M. Semiconductor and carbon-based fluorescent nanodots: The need for consistency. Chem. Commun. **2016**, 52, 1311–1326.

4. Li, H.; Kang, Z.; Liu, Y.; Lee, S.T. Carbon nanodots: Synthesis, properties and applications. J. Mater. Chem. **2012**, 22, 24230–24253.

5. Nguyen, V.; Si, J.; Yan, L.; Hou, X. Direct demonstration of photoluminescence originated from surfacefunctional groups in carbon nanodots. Carbon **2016**, 108, 268–273.

6. Pan, L.; Sun, S.; Zhang, A.; Jiang, K.; Zhang, L.; Dong, C.; Huang, Q.; Wu, A.; Lin, H. Truly Fluorescent Excitation-Dependent Carbon Dots and Their Applications in Multicolor Cellular Imaging and Multidimensional Sensing. Adv. Mater. **2015**, 27, 7782–7787.

7. Cayuela, A.; Soriano, M.L.; Valcàrcel, M. Photoluminescent carbon dot sensor for carboxylated multiwalled carbon nanotube detection in river water. Sens. Actuators **2015**, 207, 596–601.

8. Zhou, J.; Yang, Y.; Zhang, C.Y. A low-temperature solid-phase method to synthesize highly fluorescent carbon nitride dots with tunable emission. Chem. Commun. **2013**, 49, 8605–8607.

9. Rong, M.; Song, X.; Zhao, T.; Yao, Q.; Wang, Y.; Chen, X. Synthesis of highly fluorescent P,O-g-C3N4 nanodots for the label-free detection of Cu2+ and acetylcholinesterase activity. J. Mater. Chem. C **2015**, 3, 10916–10924.

10. Sciortino, A.; Mauro, N.; Buscarino, G.; Sciortino, L.; Popescu, R.; Schneider, R.; Giammona, G.; Gerthsen, D.; Cannas, M.; Messina, F. *b*-C3N4 Nanocrystals: Carbon Dots with Extraordinary Morphological, Structural, and Optical Homogeneity. Chem. Mater. **2018**, 30, 1695–1700.

11. Shinde, D.B.; Pillai, V.K. Electrochemical Preparation of Luminescent Graphene Quantum Dots from Multiwalled Carbon Nanotubes. Chem. Eur. J. **2012**, 18, 12522–12528.

12. Zhu, H.;Wang, X.; Li, Y.;Wang, Z.; Yang, F.; Yang, X. Microwave synthesis of fluorescent carbon nanoparticles with electrochemiluminescence properties. Chem. Commun. **2009**, 34, 5118–5120.

13. Papagiannouli, I.; Patanen, M.; Blanchet, V.; Bozek, J.D.; de Anda Villa, M.; Huttula, M.; Kokkonen, E.; Lamour, E.; Mevel, E.; Pelimanni, E.; et al. Depth Profiling of the Chemical Composition of Free-Standing Carbon Dots Using X-ray Photoelectron Spectroscopy. J. Phys. Chem. C **2018**, 122, 14889–14897.

14. Bourlinos, A.B.; Stassinopoulos, A.; Anglos, D.; Zboril, R.; Karakassides, M.; Giannelis, E.P. Surface Functionalized Carbogenic Quantum Dots. Small **2008**, 4, 455–458.

15. Panniello, A.; Di Mauro, A.E.; Fanizza, E.; Depalo, N.; Agostiano, A.; Curri, M.L.; Striccoli, M. Luminescent Oil-Soluble Carbon Dots toward White Light Emission: A Spectroscopic Study. J. Phys. Chem. C **2018**, 122, 839–849.

16. Zhou, J.; Booker, C.; Li, R.; Zhou, X.; Sham, T.K.; Sun, X.; Ding, Z. An Electrochemical Avenue to Blue Luminescent Nanocrystals from Multiwalled Carbon Nanotubes (MWCNTs). J. Am. Chem. Soc. **2007**, 129, 744–745.

17. Miao, X.; Yan, X.; Qu, D.; Li, D.; Tao, F.F.; Sun, Z. Red Emissive Sulfur, Nitrogen Codoped Carbon Dots and Their Application in Ion Detection and Theraonostics. ACS Appl. Mater. Interfaces **2017**, 9, 18549–18556.

18. Zhang, Y.; Hu, Y.; Lin, J.; Fan, Y.; Li, Y.; Lv, Y.; Liu, X. Excitation wavelength independence: Toward low-threshold amplified spontaneous emission from carbon nanodot. ACS Appl. Mater. Interfaces **2016**, 8, 25454–25460.

19. Gude, V.; Das, A.; Chatterjee, T.; Mandal, P.K. Molecular origin of photoluminescence of carbon dots: Aggregation-induced orange-red emission. Phys. Chem. Chem. Phys. **2016**, 18, 28274–28280.

20. Liu, S.; Tian, J.; Wang, L.; Zhang, Y.; Qin, X.; Luo, Y.; Asiri, A.M.; Al-Youbi, A.O.; Sun, X. Hydrothermal Treatment of Grass: A Low-Cost, Green Route to Nitrogen-Doped, Carbon-Rich, Photoluminescent Polymer Nanodots as an Effective Fluorescent Sensing Platform for Label-Free Detection of Cu(II) Ions. Adv. Mater. **2012**, 24, 2037–2041.

21. Huang, H.; Lv, J.J.; Zhou, D.L.; Bao, N.; Xu, Y.; Wang, A.J.; Feng, J.J. Onepot green synthesis of nitrogen-doped carbon nanoparticles as fluorescent probes for mercury ions. RSC Adv. **2013**, 3, 21691–21696.

22. Xu, Q.; Pu, P.; Zhao, J.; Dong, C.; Gao, C.; Chen, Y.; Chen, J.; Liu, Y.; Zhou, H. Preparation of highly photoluminescent sulfur-doped carbon dots for Fe(iii) detection. J. Mater. Chem. A **2015**, 3, 542–546.

23. Sciortino, A.; Cayuela, A.; Soriano, M.L.; Gelardi, F.M.; Cannas, M.; Valcarcel, M.; Messina, F. Different natures of surface electronic transitions of carbon nanoparticles. Phys. Chem. Chem. Phys. **2017**, 19, 22670–22677.

24. Wang, X.; Wang, S.T.; Lu, F.; Meziani, M.J.; Tian, L.; Sun, K.W.; Bloodgood, M.A.; Sun, Y.P. Bandgap-like strong fluorescence in functionalized carbon nanoparticles. Angew. Chem. Int. Ed. **2010**, 122, 5438–5442.

25. Vinci, J.C.; Ferrer, I.M.; Seedhouse, S.J.; Bourdon, A.K.; Reynard, J.M.; Foster, B.A.; Bright, F.V.; Colòn, L.A.Hidden properties of carbon dots revealsed after HPCL fractionation. J. Phys. Chem. Lett. **2013**, 4, 239–243.

26. Zhu, S.; Meng, Q.; Wang, L.; Zhang, J.; Song, Y.; Jin, H.; Zhang, K.; Sun, H.; Wang, H.; Yang, B. Highly Photoluminescent Carbon dots for multicolor patterning, sensors and bioimaging. Angew. Chem. Int. Ed. **2013**, 125, 4045–4049.

27. Hou, J.; Wang, W.; Zhou, T.; Wang, B.; Li, H.; Ding, L. Synthesis and Formation Mechanistic Investigation of Nitrogen- Doped Carbon-Dots with High Quantum Yield and Yellowish-Green Fluorescence. Nanoscale **2016**, 8, 11185–11193.

28. Qiao, Z.A.; Wang, Y.; Gao, Y.; Li, H.; Dai, T.; Liu, Y.; Huo, Q. Commercially activated carbon as the source for producing multicolor photoluminescent carbon dots by chemical oxidation. Chem. Commun. **2010**, 46, 8812–8814.

29. Liu, C.; Zhang, P.; Tian, F.; Li, W.; Li, F.; Liu, W. One-step synthesis of surface passivated carbon nanodots by microwave assisted pyrolysis for enhanced multicolor photoluminescence and bioimaging. J. Mater. Chem. **2011**, 21, 13163–13167.

30. Bourlinos, A.B.; Zbo^{*}ril, R.; Petr, J.; Bakandritsos, A.; Krysmann, M.; Giannelis, E.P. Luminescent Surface Quaternized Carbon Dots. Chem. Mater. **2012**, 24, 6–8.

31. Pan, D.; Zhang, J.; Li, Z.; Wu, C.; Yan, X.; Wu, M. Observation of pH, solvent-, spin-, and excitation-dependent blue photoluminescence from carbon nanoparticles. Chem. Commun. **2010**, 46, 3681–3683.

32. Kozák, O.; Datta, K.K.; Greplová, M.; Ranc, V.; Kašlík, J.; Zbo`ril, R. Surfactant-Derived Amphiphilic Carbon Dots with Tunable Photoluminescence. J. Phys. Chem. C **2013**, 117, 24991–24996.

33. Zhang, S.; Li, J.; Zeng, M.; Xu, J.; Wang, X.; Hu, W. Polymer nanodots of graphitic carbon nitride as effective fluorescent probes for the detection of Fe3+ and Cu2+ ions. Nanoscale **2014**, 6, 4157–4162.

34. Liu, M.; Xu, Y.; Niu, F.; Gooding, J.J.; Liu, J. Carbon quantum dots directly generated from electrochemical oxidation of graphite electrodes in alkaline alcohols and the applications for specific ferric ion detection and cell imaging. Analyst **2016**, 141, 2657–2664.

35. Wang, C.; Xu, Z.; Zhang, C. Polyethyleneimine-Functionalized Fluorescent Carbon Dots: Water Stability, pH Sensing, and Cellular Imaging. ChemNanoMat **2015**, 1, 122–127.

36. Cayuela, A.; Soriano, M.L.; Carriòn, M.C.; Valcàrcel, M. Functionalized carbon dots as sensors for gold nanoparticles in spiked samples: Formation of nanohybrids. Anal. Chim. Acta **2014**, 820, 133–138.

37. Zhou, D.; Li, D.; Jing, P.; Zhai, Y.; Shen, D.; Qu, S.; Rogach, A.L. Conquering Aggregation-Induced Solid-State Luminescence Quenching of Carbon Dots through a Carbon Dots-Triggered Silica Gelation Process. Chem. Mater. **2017**, 29, 1779–1787.

38. Chen, Y.; Zheng, M.; Xiao, Y.; Dong, H.; Zhang, H.; Zhuang, J.; Hu, H.; Lei, B.; Liu, Y. A Self-quenching-resistan Carbon-dot powder with tunable solid-state fluorescence and construction of dual-fluorescence morphologies for white light-emission. Adv. Mater. **2015**, 28, 312–318.

39. LeCroy, G.E.; Messina, F.; Sciortino, A.; Bunker, C.E.; Wang, P.; Shiral, K.A.F.; Sun, Y.P. Characteristic Excitation Wavelength Dependence of Fluorescence Emissions in Carbon "Quantum" Dots. J. Phys. Chem. C **2017**, 121, 28180–28186.

40. Shi, Y.; Li, C.; Liu, Z.; Zhu, J.; Yang, J.; Hu, X. Facile synthesis of fluorescent carbon dots for determination of curcumin based on fluorescence resonance energy transfer. RSC Adv. **2015**, *5*, 64790–64796.

41. Muhammad, M.; Baig, F.; Chen, Y.C. Bright carbon dots as fluorescence sensing agents for bacteria and curcumin. J. Colloid Interface Sci. **2017**, 501, 341–349.

42. Wu, X.; Song, Y.; Yan, X.; Zhu, C.; Ma, Y.; Du, D.; Lin, Y. Carbon quantum dots as fluorescence resonance energy transfer sensors for organophosphate pesticides determination. Biosens. Bioelectron. **2017**, 94, 292–297.

43. Sciortino, A.; Marino, E.; Dam, B.V.; Schall, P.; Cannas, M.; Messina, F. Solvatochromism Unravels the Emission Mechanism of Carbon Nanodots. J. Phys. Chem. Lett. **2016**, 7, 3419–3423.

44. Zhu, S.; Song, Y.; Zhao, X.; Shao, J.; Zhang, J.; Yang, B. The photoluminescence mechanism in carbon dots (graphene quantum dots, carbon

nanodots, and polymer dots): Current state and future perspective. Nano Res. **2015**, 8, 355–381.

45. Essner, J.B.; Baker, G.A. The emerging roles of carbon dots in solar photovoltaics: A critical review. Environ. Sci. Nano 2017, 4, 1216–1263.
46. Malfatti, L.; Innocenzi, P. Sol-Gel Chemistry for Carbon Dots. Chem. Rec. 2018, 18, 1192–1202.

47. Lim, S.Y.; Shen, W.; Gao, Z. Carbon quantum dots and their applications. Chem. Soc. Rev. **2015**, 44, 362–381.

48. Wang, Y.; Zhu, Y.; Yu, S.; Jiang, C. Fluorescent carbon dots: Rational synthesis, tunable optical properties and analytical applications. RSC Adv. **2017**, 7, 40973–40989.

49. Wang, R.; Lu, K.Q.; Tang, Z.R.; Xu, Y.J. Recent progress in carbon quantum dots: Synthesis, properties and applications in photo catalysis. J. Mater. Chem. A **2017**, 5, 3717–3734.

50. Wu, Z.L.; Liu, Z.X.; Yuan, Y.H. Carbon dots: Materials, synthesis, properties and approaches to long-wavelength and multicolor emission. J. Mater. Chem. B **2017**, 5, 3794–38009.