A Simple Hydrothermal Synthesis of Luminescent Carbon Quantum Dots from Different Molecular Precursors

A dissertation

Submitted for the partial fulfilment for the

Degree of

Master of Science in Chemistry

Submitted by

Ms. Sonali Paikaray   **&**   **Ms. Priyanka Moharana**

Roll no: 411CY2027   **Roll no: 411CY2024**

Under the supervision of

Dr. Sasmita Mohapatra

Department of chemistry
National Institute of Technology (NIT)
Rourkela, Odisha, India.
Pin: 769008

Acknowledgement

Dr. Sasmita Mohapatra
Assistant Professor,
Department of Chemist
National Institute of Technology
Rourkela
Odisha-769008

CERTIFICATE

This is to certify that the dissertation entitled, **"A Simple Hydrothermal Synthesis of Luminescent Carbon Quantum Dots from Different Molecular Precursors"** submitted by Ms. SonaliPaikaray& Ms. Priyanka Moharana for the award of Master of Science in Chemistry during the period of August 2011- May2013 in the Department of Chemistry, National Institute of Technology, Rourkela, is a record of authentic work carried out by them under my supervision. To the best of my knowledge, the matter embodied in this dissertation has not been previously submitted for any degree in this/any other institute.

Date: **Dr. Sasmita Mohapatra**

Content

ABSTRACT

In this work,highly photoluminescent C-dots have been synthesised from different precursors such as sucrose, ascorbic acid, citric acid and their combinations under similar conditions to that of recently reported synthesis of C-dots from orange juice.The synthesized carbon nanoparticles have been characterized by XRD, FTIR, UV, and fluorescence measurements. The fluorescence quantum yields of carbon dots synthesized from different precursors have been compared to verify the suitability of C-dots for different applications. We have also thoroughly investigated the effect of excitation wavelength, pH, and electrolyte concentration on luminescent properties.

Keywords: Fluorescent, C-dot, Quantum Yield, Hydrothermal Synthesis

1. Introduction

Photoluminescent materials have drawn increasing attention due to their promising and diverse applications ranging from optoelectronics to biomedical fields, such as cellular imaging, biosensing,and drug delivery.[1-4] The most widely used fluorescent materials are organic dyes and/or CdSe/ZnS quantum dots (QDs). However the photobleaching, quenching of dye molecules, toxicity of QDs limit their applications in biomedical field.[5,6]Most recently, fluorescent carbon dots (C-dots) a new class of carbon-based nanomaterials serve as a suitable alternative of these traditional fluorescent materials due to their excellent luminescence properties, including large two-photon excitation cross-sections, lack of blinking, high water solubility, low cytotoxicity, and excellent biocompatibility.[7-12]

During the past few years, much progress has been achieved inthe synthesis, properties and applications of C-dots, as recently reviewed by Baker et al. and Li et al.[13,14]Several top down approaches such as laser ablation,[8] electrochemical synthesis,[12]arc discharge[15]have been proposed to produce fluorescent C-dots.These methods however involve a non- selective exfoliation process, and therefore may require toxic reagents and special equipment. On the other hand, bottom up approaches like carbonization of glucose, sucrose, glycol, ascorbic acid, citric acids etc. have achieved significant attention for the production of fluorescent C-dots.[16-20] However most of these synthesis methods need several steps and strong acids and post treatment with surface passivating agents[8] are essential in order to improve their water solubility and luminescence property. Urgently one-step, facile approach with economicchemistry is required to produce self-passivatedphotoluminescent C-dots.Among them, syntheses of amino-functionalized fluorescent carbon nanoparticles by hydrothermal carbonization of chitosan at high temperature,[21]microwave assisted hydrothermal carbonization of sucrose,[22] and carbonization of glucose in reverse micelle[23]are few scanty examples for the fabrication of fluorescent carbon nanoparticles without any surface passivation. Inparticular, it is possible to control the size, shape, and physicalproperties of the carbon nanoparticles by careful selection ofcarbon source and surface modifier.[24]Howeversubstantial production of C-dots with tailored composition, structure, morphology andsize by a simple and cheap method is still challenging.

2. Review on various Synthetic methods

Synthetic approaches for C-dots can generally be classified into two main groups: top-down and bottom-up methods. Top-down approaches, where larger carbon structures are broken off to smaller c-dots include arc discharge, electrochemical oxidation and laser ablation technique. Bottom-up methods include combustion/thermal/hydrothermal, supported synthesis, microwave/ultrasonic, solution chemistry methods during which C-dots are formed from molecular precursors.

2.1. Top-down approaches
2.1.1 Arc-discharge Methods

Ironically, C-dots were discovered by Xu et al. while purifying single-walled carbon nanotubes (SWCNTs) derived from arc-discharge soot.[15]They fractionated these carbonaceous materials into a number of components which showed size-dependent fluorescent properties. They oxidized thearc soot with 3.3 M HNO_3 to introduce carboxyl functionalgroups,which improve the hydrophilicity of the material, and then the sediment was extracted with NaOH solution(pH 8.4) to produce a stable black suspension. The suspension was separated by gel electrophoresis into SWCNTs, shorttubular carbons, and fluorescentC-dots. The absence of characteristic C-H out of plane bending modes of polyaromatichydrocarbons (PAHs) in FTIR spectrum indicated that the origin of thePL was not derived from PAH sources.

2.1.2 Electrochemical Oxidation

For the first time Zhou et al. demonstrated the electrochemical synthesis of C-dots.[2]They grew multiwall carbonnanotubes (MWCNTs) formed from scrolled graphenelayerson carbon paper by chemical vapour deposition. They used these nanotubes as the working electrode in an electrochemical cellconsisting of a Pt wire counter electrode and a $Ag/AgClO_4$reference electrode with degassed acetonitrile solution containing 0.1Mtetrabutylammonium perchlorate ($TBA^+ClO_4^-$)as the electrolyte.The C-dots produced were spherical and exhibited λex -dependent PL. No C-dots were formedeither when carbon paper without any MWCNTs was used. Chi and co-worker also synthesisedC-dots from electrochemical oxidation of graphite rod with a Pt mesh counter electrode, and Ag/AgClreferenceelectrode assembly in phosphate buffer solution (pH 7.0).[25]
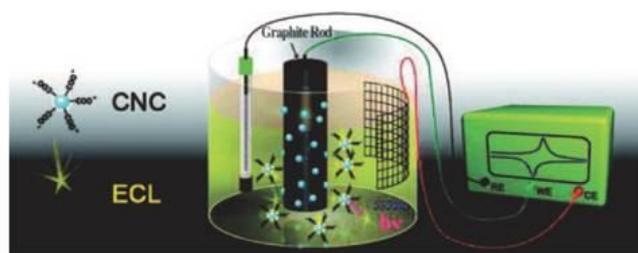
Fig.1. Electrochemical production of C-dots from a graphite rod.[25]

2.1.3 Laser-Ablation Methods

Sun et al. Produced C-dots using Laser ablation technique, by hot-pressing a mixture of graphite powder and cement, followed by stepwise baking, curing, and annealing under an argon flow at $900^{o}C$ and 75 kPa.[8] For better fluorescence they passivated the surface of C-dots using different polymeric agents such as diamine-terminated poly(ethylene glycol),[8] poly(propionyl-ethylenimine-co-ethylenimine).[9] Then highly fluorescent pure C-dots were separated by dialysis against water, followed by a centrifugation step.[26] A slightly modified technique using ^{13}C powder and more rigorous control was introduced to produce C-dots with high quantum yield of 20%.[10] Hu et al. introduced a single-step procedure where a pulsed Nd:YAG laser was used to irradiate graphite or carbon black dispersed in diamine hydrate, diethanolamine, or PEG_{200N} for 2 h, which serve as surface passivating agent (Fig. 2).[27]
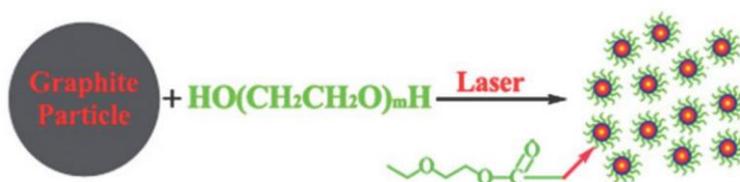
Fig.2. One step synthesis of C-dots in PEG_{200N} solvent.[27]

2.2 Bottom-up Approaches

2.2.1 Combustion/Thermal/Hydrothermal Methods

An elegantly simple source of C-dots is the soot derived from the combustion of unscented candles or natural gas burners.[3,28] Mao et al. produced water soluble multicolour fluorescent c-dots (< 2 nm) from the combustion soot of candles through oxidative acid treatment, which introduced OH and COOH groups to the C-dot surfaces.[3] They purified the particles by using polyacrylamide gel electrophoresis(PAGE) fraction.

Surface passivated C-dots were produced using one-step thermal decomposition of low-temperature-melting molecular precursors.[4]Careful selection of the carbon source and surface modifier resulted better control over the geometry and physical properties of the C-dots. Highly blue luminescent C-dots with PL QY of 31.6–40.6% were prepared by a one-step pyrolytic route from ethylenediamine–tetraacetic acid salts. Also chemical oxidation of carbohydrates (glycerol, glycol, glucose, sucrose, citric acid, etc.) was another important approach to obtain C-dots.[24,29] However, most of these synthesis methods need several steps and strong acid, and further treatment with other compounds to improve the water solubility and PL properties.Wu et al. exploited a high-yield synthesis of hydrophilic C-dots by controlled carbonization of sucrose.[30]They effectively separated green luminescent C-dots and non-luminous C-dots, which on functionalization with PEG emitted blue fluorescence. Other groups also exploited hydrothermal technique for produce C-dots with high quantum yield taking different molecular precursor such as glucose, fructose sucrose, and ascorbicacid etc.[18,31,32]

Recently,in our laboratory, large scale synthesis of highly photoluminescent C-dots was achieved by hydrothermal treatment of cheap and readily available orange juice.[33]Due to high photostability and low toxicity these C-dots are demonstrated as excellent probes in cellular imaging. Zhu et al. also produced bifunctional florescent C-dots by hydrothermal treatment of soya milk, which exhibited good electrocatalytic activity towards oxygen reduction.[34]
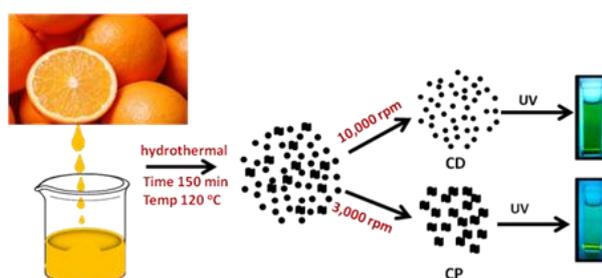
Fig.3. Illustration of formation of CDs from hydrothermal treatment of orange juice.[33]

2.2.2 Microwave/Ultrasonic Synthesis

Yang et al. reported a microwave pyrolysis approach to synthesize C-dots with electrochemiluminescence properties by combining PEG_{200} and a saccharide (for example, glucose, fructose) in water to form a transparent solution, followed by heating in a 500 W microwave oven for 2–10 min.[35] Size and PL properties of these C-dots are related to the

duration of the microwave heating. Kang et al. synthesised C-dots, those exhibited colourful PL covering the entire visible-to-NIR spectral range from glucose or active carbon by using an ultrasonic treatment method.[17] Same group also synthesised water-soluble fluorescent C-dots from active carbon by a one-step hydrogen peroxide-assisted ultrasonic treatment.[36] These C-dots exhibited up-conversion fluorescent properties and emitted bright and colorful photoluminescence covering the entire visible-to-near infrared spectral range. Recently phocatalytic active fluorescent N-doped C-dots (NCDs) was synthesised via one-pot ultrasonic synthesis, which was used in the photodegradation of methyl orange under visible light.[37]
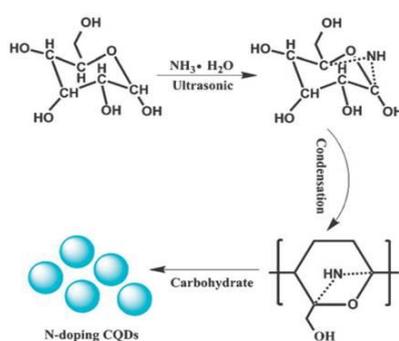

Fig.4.Schematic presentation for the formation process of the NCDs.[37]

2.2.3 Supported Synthetic Methods

Supported synthetic method has been adopted for the synthesis of mono-disperse C-dots, where the supportserves to localize the growth of C-dots, by blocking nanoparticle agglomeration during high-temperature treatment. Li et al. used surfactant-modified silica spheres as supports for C-dot growth, the silica spheres were then removed by etching with 2M NaOH solution.[38] The surface passivation and oxidation with 3M HNO_3 was done to produce hydrophilic photoluminescent C-dots. Giannelisand co-workers used an appropriately ion-exchanged NaY zeolite as support for the synthesis of C-dots.[39]

Hydrophilic C-dots was synthesised by Zhu et al. using mesoporous silica (MS) spheres as nanoreactors.[40]MS spheres were impregnated with a mixed solution of complex salts and citric acid, which on subsequent calcination and removal of supports generated monodisperse, hydrophilic C-dots.
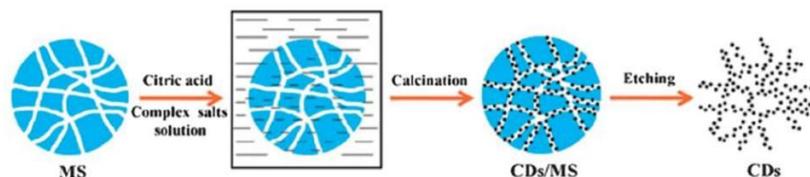
Fig.5. Synthesis of photoluminescentC-dots.[40]

3. Objective of the present work

A variety of carbon precursors used for the synthesis of C-dots can influence the size shape and thus photoluminescent properties of C-dots. Therefore we aim to compare the photoluminescent properties of C-dots synthesised from different precursors. For this, we have used the individual constituents of orange juice, such as sucrose, ascorbic acid and citric acid and their combinations as carbon precursors under similar conditions to that of reported synthesis from orange juice.[33]The synthesized carbon nanoparticles have been characterized by XRD, FTIR, UV, and fluorescence measurements. The fluorescence quantum yields of carbon dots synthesized from different precursors have been compared. We have also thoroughly investigated the effect of excitation wavelength, pH, and electrolyte concentration on luminescent properties.

4. Experimental

4.1.1. Materials and Methods

Sucrose, ascorbic acid, citric acid and ethanol were procured from Merck India and all chemicals were used as supplied without further purification. Millipore water (18.2 MΩ cm) was used throughout the experiment

C-dots were synthesized by hydrothermal treatment of different precursor such as sucrose, citric acid, ascorbic acid separately and also their mixture. In a typical procedure, 5 wt% of carbon precursor was dissolved in water (30 ml) and ethanol (20 ml) mixture, and then the mixture was transferred into an 80 ml Teflon-lined stainless-steel autoclave and was heated at constant temperature of 120 $^\circ$C for 150 min (1 $^\circ$C/min). After the reaction, the autoclave was cooled down naturally. The resulted solution was lyophilised to get the fluorescent C-dots.

4.1.2. Characterization

Particle size and zeta potential of C-dots were measured after suitable dilution of its solution at 25.0 ± 0.5 $^\circ$C, by laser light scattering using a particle size analyzer (Nano ZS 90,

Malvern). The crystalline phase was investigated by an Expert Pro Phillips X-ray diffractometer. The Fourier transform infrared spectroscopy (FTIR) spectra were measured by a Thermo Nicolet Nexux FTIR model 870 spectrometer with the KBr pellet technique ranging from 400 to 4000 cm $^{-1}$. Fluorescence spectroscopy was performed with a Horiba Fluoromax 4 spectrophotometer at different excitation energies ranging from 320 to 450 nm. UV-vis absorption spectra were obtained using a Shimadzu 220V (E) UV-vis spectrophotometer.

4.1.3. Quantum yield Calculation

The quantum yield (Φ) of the C-dots was calculated using quinine sulfate as reference.[33] For calculation of quantum yield, five concentrations of each compound were made, all of which had absorbance less than 0.1 nm at 340 nm. Quinine sulfate (literature Φ = 0.54) was dissolved in 0.1 M H_2SO_4 (refractive index (η) of 1.33) while the C-dots were dissolved in water (η = 1.33). Their fluorescence spectra were recorded at same excitation of 340 nm. Then by comparing the integrated photoluminescence intensities (excited at 340 nm) and the absorbency values (at 340 nm) of the C-dots with the references quinine sulfate quantum yield of the carbon sample was determined.

The quantum yield was calculated using the below equation

$$\Phi_x = \Phi_{ST} \ (m_x \ / \ m_{ST}) \ (\eta^2_x \ / \eta^2_{ST})$$

Where Φ is the quantum yield, m is slope, η is the refractive index of the solvent, ST is the standard and X is the sample.

5. Results and Discussion

In our experiment, a facile and one-step hydrothermal synthetic route was employed for the fabrication of fluorescent C-dots. The C-dots were prepared from different carbon precursor: sucrose (S), citric acid (C), ascorbic acid (A), sucrose-citric acid (SC), sucrose-ascorbic acid (SA) and they all exhibit strong photoluminescence in visible region.

5.1. C-Dot formation Mechanism

The mechanism for synthesis of carbon dots from sucrose/ascorbic acid/citric acid involves their carbonization. In fact, in the hydrothermal carbonisation of sucrose for the formation of final material structure is complicated and a clear scheme has not yet been

reported. The plausible mechanism for the formation of carbons dots may be illustrated as follows.

Fig.6.
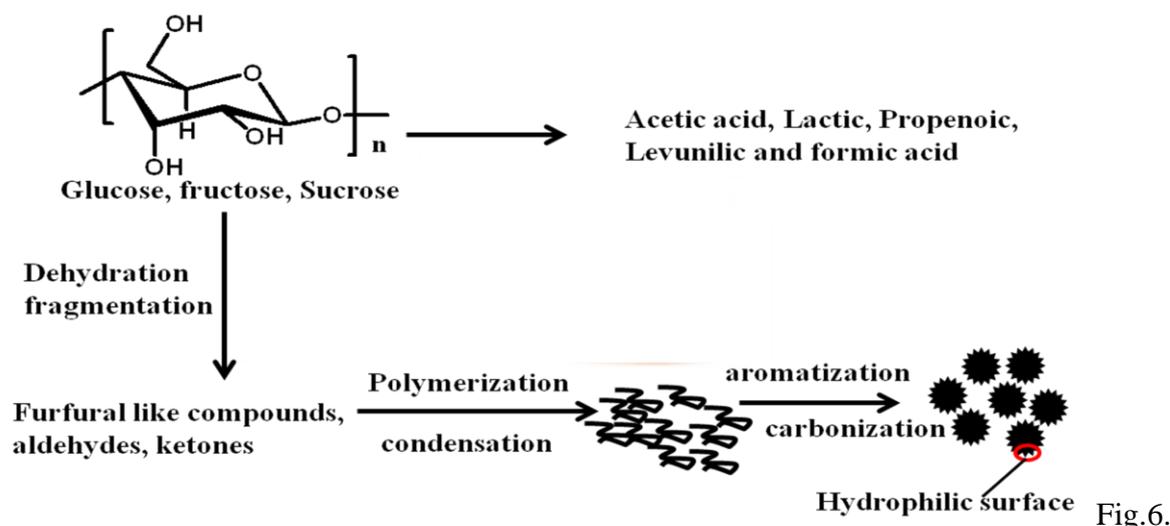
Schematic presentation of formation mechanism of carbon dots

Sucrose when hydrothermally treated undergoes hydrolysis to form glucose and fructose. Glucose subsequently isomerises to form fructose.[41] The dehydration and decomposition of fructose/glucose gives rise to different soluble products such as furfural compounds (for ex: 5-hydroxymethyl furfural, furfural, 5-methyl furfural etc), several organic acids such as acetic, lactic, propionic, livulinic and formic acids, aldehydes and phenols. It is worth mentioning that the hydronium ion formed from these acids act as a catalyst in subsequent decomposition reaction stages. The polymerisation and condensation of these products gives rise to soluble polymers. Aromatization and formation of aromatic clustures take place via aldol condensation, cycloaddition and a hydroxymethyl mediated furan resin condensation. When concentration of aromatic clusters reaches a critical supersaturation point a burst nucleation takes place and carbon dots are formed.

5.2. Characterization

An XRD pattern and FTIR spectrum were used to characterize the C-dots. The XRD profiles of C-dots from ascorbic acid (A) shows the [002] peak centred at 19.0 degree which has been shifted to 19.6 degree in case of SA (Fig. 6a). The corresponding interlayer spacing in graphite (0.34 nm) becomes larger in SA (0.45 nm) which shifts to further larger end in A (0.46 nm). The increase in d value indicates increase in amorphous nature attributed to the introduction of more oxygen containing groups.FTIR spectrum of the synthesised C-dots shows the presence of C=C, C-O, COOH bonds which clearly indicates that the C-dots are

functionalized with hydroxyl, epoxy, carbonyl, and carboxylic acid groups (Fig. 6b). The presence of these functional groups imparts excellent solubility in water without further chemical modification. Also the presence of surface –COOH group is also evidenced of zeta potential measurement. Measurement of zeta potential against pH shows that at low pH zeta potential is positive which shifts to negative at higher pH which indicates the presence of – COOH groups on the surface (Fig. 6c).
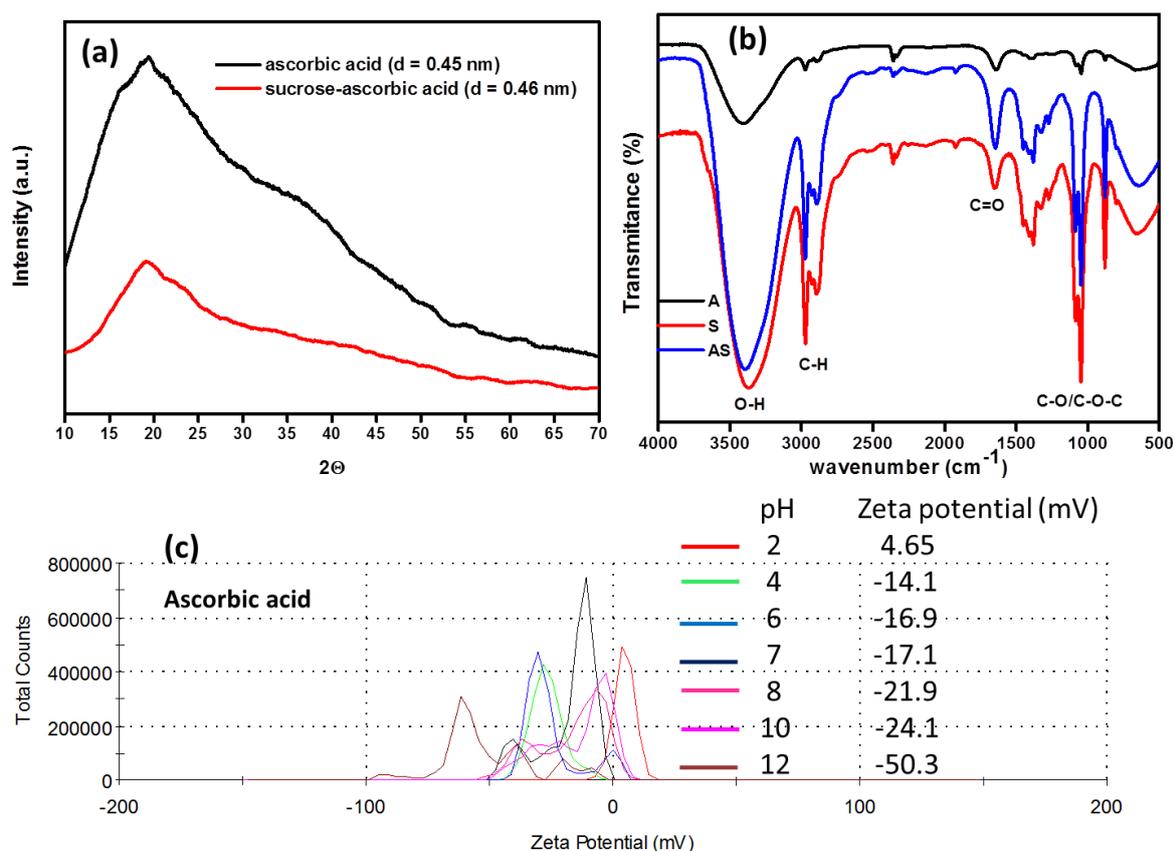

Fig.7. XRD patterns of A and SA (a), FTIR spectra of A, Sand AS (b), Zetapotential of A with pH (c)

The as synthesised C-dots without any surface modification could easily disperse in millipore water with an average diameter in between 16 nm to 40 nm. Among the different C-dots the hydrodynamic diameter increases in the order SA < S < SC < A < C, which is in agreement with red shift of emission spectra of the sample from AS to C. This change in optical property with increase in particle size is consistent with the reported result.[42]
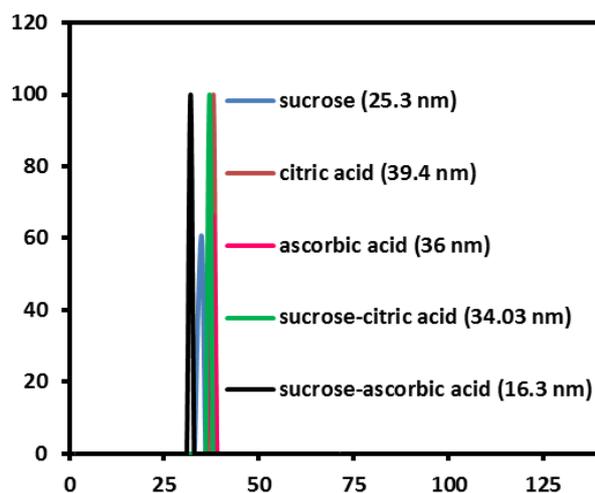
Fig.8. Hydrodynamic size of S, A, C, SA and SC

The UV-Vis spectra for synthesised C-dots were shown in Fig. 3, which demonstrated that the peak forAS, CS and A was centered at 263, 283 and 280 nm respectively. However the nature ofthe absorbance peaks for S and C were different in nature, they show two absorption maxima for each at 211 nm and 288 nm for S, and 210 nm and 256 nm for C. Appearance of two absorption maxima can be attributed the non-uniform size distribution of C-dots. The good size distribution as indicated by uv absorbance maxima can be achieved in case of sugar-acid mixture, which might be due to catalytic action of acid on sugar. Here it is important to note that due to presence of weak acids like citric acid and ascorbic acid the dehydration and decomposition reaction of sucrose proceeds in a controlled manner. The absorption in C-dots is typically ascribed to the presence of aromatic π orbitals present on C-dots.

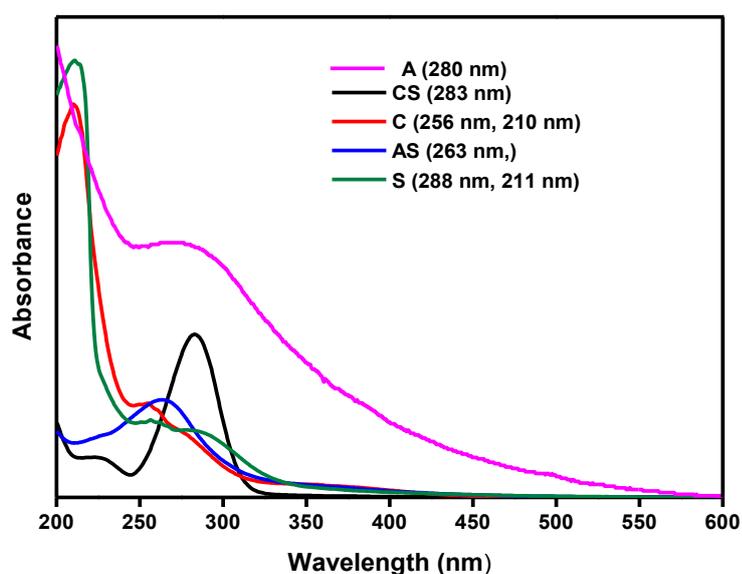Fig.9. UV absorbance of S, A, C, SA and SC

At a fixed λex=330 nm, C-dots from different source show emission peak at 416, 421, 427, 432 and 438 nm for SA, S, SC, A and C respectively. This difference in position of eission peak is attributed to the variation in size, as recently reported by Penget. al.[43]This result is also in consistence with hydrodynamic diameter. Furthermore, the unique phenomemon of excitation dependent photoluminescence was observed in case of all synthesised C-dots consistency with the PL property of CQDs reported by other groups (Fig. 3b). Apart from reasons like excitons of carbon,[2] emissive traps,[44] aromatic conjugate structures[45] and free zig-zag sites,[46] the excitation dependent PL behavior could arise because of presence of "surface states".[22]
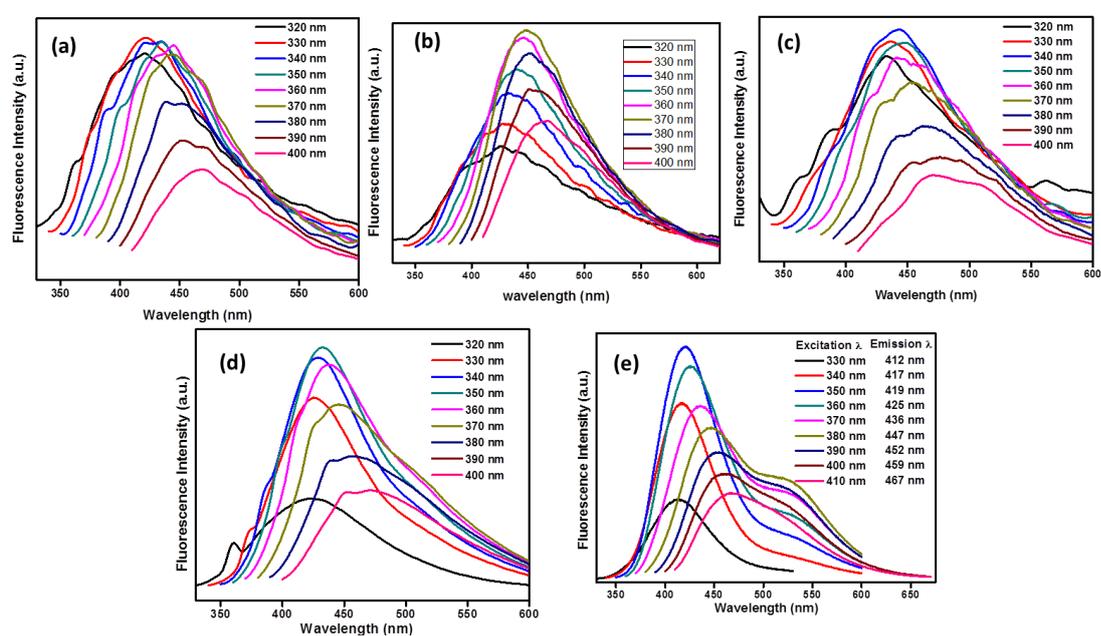
Fig.10. Emission spectra of S (a), A (b), C (c), SC (d), and SA (e) recorded for progressively longer excitation wavelength of 10 nm increments

Another interesting phenomenon here is the pH dependent PL behaviour, which is shown by our all synthesised C-dots. The photoluminescent intensity of all C-dots gradually decrease from acidic to basic medium, the trend is however not smooth. In case of SA and SC the photoluminescent intensity is nearly constant in the neutral range (pH = 6-8). Due to consistent PL within biological pH range, these C-dots may be suitable for biological imaging.
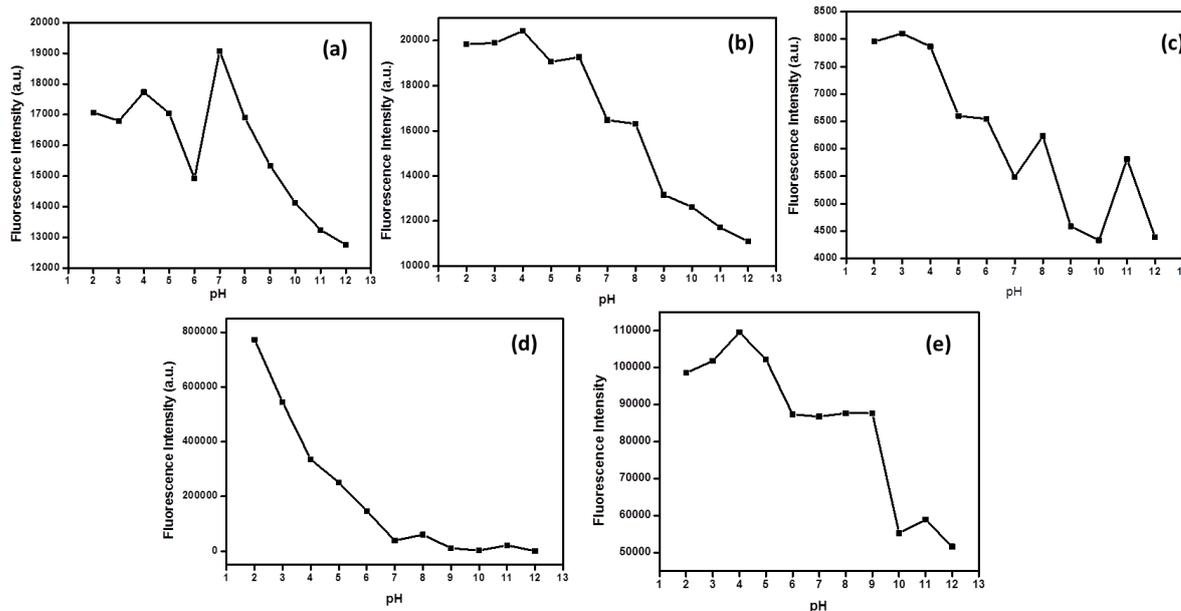
Fig.11. Effect of pH on fluorescence intensity of S (a), A (b), C (c), SC (d), and SA (e) C-dots

Also the effect of ionic strength on PL intensity of synthesise C-dots are studied using various amount of NaCl. It was observed that for SA the ionic strength has no effect on PL intensity, also the Pl intensity is almost constant for S, A and C samples. However in case of SA sample the PL intensity gradually decreases with increasing ionic strength from 0 M to 1.25 M, which remain constant for further increase to 2M.
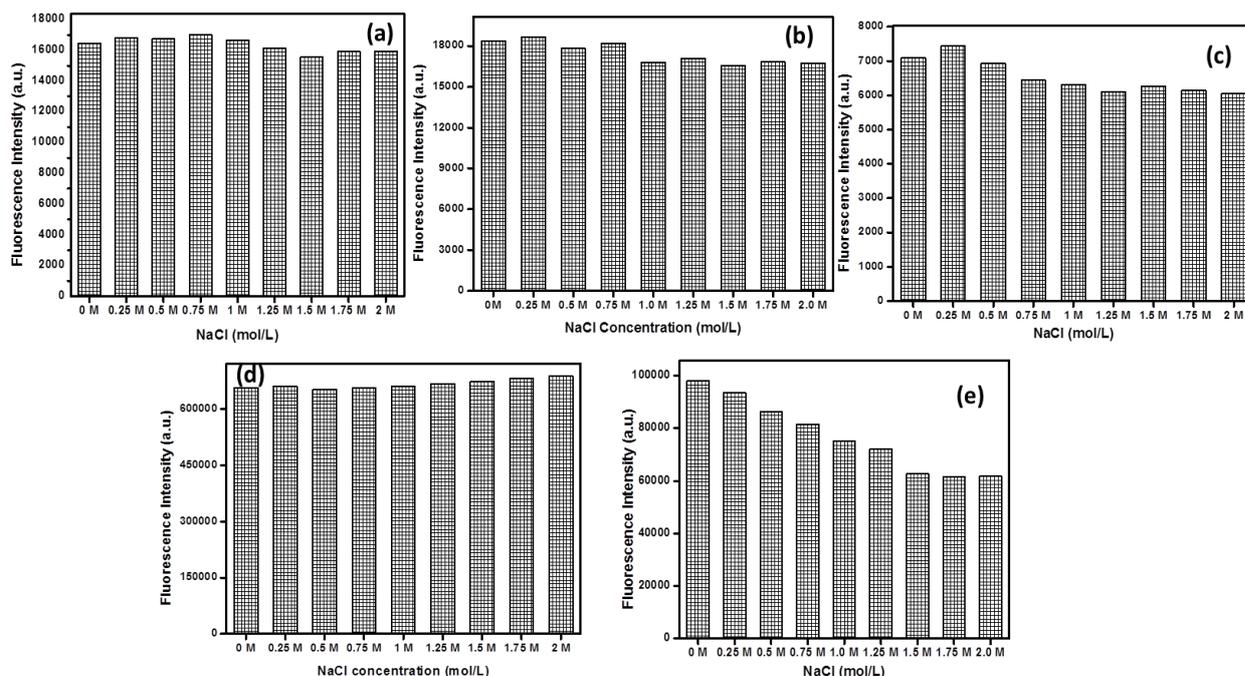
Fig.12. Effect of ionic strength on the fluorescence intensity of S (a), A (b), C (c), SC (d), and SA (e) C-dots (ionic strengths were controlled by various concentrations of NaCl)

The PL quantum yields of the synthesised C-dots were calculated using quinine sulphate as standard. The PL quantum yield of the sample S was as high as 13.5%, which is much higher than other samples. Table 1 presents PL quantum yields of C-dots synthesized from different precursors.

Plot legend and fit parameters:
$m_{QS} = 7.91229 \times 10^{8}$, $R^2 (QS) = 0.999$, $\Phi_S = 13.5\%$
$m_S = 1.98267 \times 10^{8}$, $R^2 (S) = 0.996$, $\Phi_C = 6.9\%$
$m_C = 1.0104 \times 10^{8}$, $R^2 (C) = 0.971$, $\Phi_A = 9.2\%$
$m_A = 1.34819 \times 10^{8}$, $R^2 (A) = 0.994$, $\Phi_{AS} = 9.72\%$
$m_{AS} = 1.42706 \times 10^{8}$, $R^2 (AS) = 0.9897$, $\Phi_{CS} = 7.23\%$
$m_{CS} = 1.05958 \times 10^{8}$, $R^2 (CS) = 0.9694$
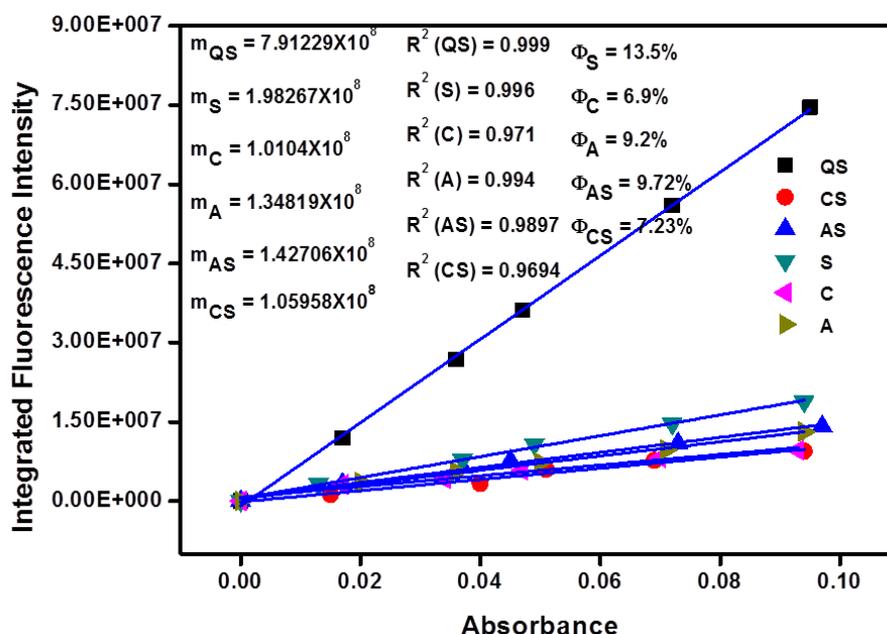
Fig.13. Fluorescence and Absorbance of S, A, C, SA, SC and Quinine Sulfate (QS)

Table-1: Comparison of HD size, λ_{em}, PL quantum yield (Φ)of C-dots synthesised from different precursors

Sample ID	composition	Hydrodynamic Size	λemission at λex $_=$ 330 nm	Quantum Yield (Φ)
S	Sucrose	25.3 nm	421 nm	13.5 %
A	Ascorbic acid	36.0 nm	432 nm	9.2 %
C	Citric acid	39.4 nm	438 nm	6.9 %
SA	Sucrose-Ascorbic acid	16.3 nm	416 nm	9.7 %
SC	Sucrose-Citric acid	34.03 nm	427 nm	7.3 %

6. Conclusion

A simple economic synthesis for the preparation of highly photoluminescent C-dots from different carbon precursor has been developed. The size distribution of the synthesised C-dots was controlled by the addition of ascorbic and citric acid to sugar. By this approach we were able to fabricate individual carbon quantum dots with different quantum yield, where sucrose shows the highest value. The effect of pH and ionic strength on synthesised C-dots has been investigated. Due to consistent PL within biological pH range for SA and SC sample, they may be suitable for biological imaging.

References

1. S. J. Yu, M. W. Kang, H. C. Chang, K. M. Chen and Y. C. Yu, *J. Am. Chem. Soc.*, 2005, **27**, 17604.

2. J. Zhou, C. Booker, R. Li, X. Zhou, T. Sham, X. Sun and Z. Ding, *J. Am. Chem. Soc.,* 2007, **129**, 744.

3. H. P. Liu, T. Ye and C. D. Mao, *Angew. Chem., Int. Ed.,* 2007, **46**, 6473.

4. A. B.Bourlinos,A.Stassinopoulos, D.Anglos,R.Zboril,M.Karakassides, E. P. Giannelis, *Small*, 2008, **4**, 455.

5. A. P. Alivisatos, *Science,* 1996, **271**, 933.

6. Y. W. Lin, W. L. Tseng, H. T. Chang, *Adv. Mater.,* 2006, **18**, 1381.

7. A. Safavi, F. Sedaghati, H. Shahbaazi, E. Farjami, *RSC Adv.,* 2012, **2**, 7367.

8. Y. P. Sun, B. Zhou, Y. Lin, W. Wang, K. A. S. Fernando, P. Pathak, M. J. Meziani, B. A. Harruff, X. Wang, H. F. Wang, P. J. G. Luo, H. Yang, M. E. Kose, B. L. Chen, L. M. Veca, S. Y. Xie, *J. Am. Chem. Soc,.* 2006, **128**, 7756.

9. L. Cao, X. Wang, M. J. Meziani, F. S. Lu, H. F. Wang, P. J. G. Luo, Y. Lin, B. A. Harruff, L. M. Veca, D. Murray, S. Y. Xie, Y. P. Sun, *J. Am. Chem. Soc.,* 2007, **129**, 11318.

10. S. T. Yang, X. Wang, H. Wang, F. Lu, P. G. Luo, L. Cao, M. J. Meziani, J. H. Liu, Y. Liu, M. Chen, Y. Huang, Y. P. Sun, *J. Phys. Chem. C,* 2009,**113**, 18110.

11. S. T. Yang, L. Cao, P. G. Luo, F. S. Lu, X. Wang, H. F. Wang, M. J. Meziani, Y. F. Liu, G. Qi, Y. P. Sun, *J. Am. Chem. Soc.,* 2009, **131**, 11308.

12. Q. L. Zhao, Z. L. Zhang, B. H. Huang, J. Peng, M. Zhang, D. W. Pang, *Chem. Commun.,* 2008, 5116.

13. S. N. Baker, G. A. Baker, *Angew. Chem. Int. Ed.,* 2010, **49**, 6726.

14. H. Li, Z. Kang, Y. Liu, S. T. Lee, *J. Mater. Chem.*, 2012 (DOI: 10.1039/c2jm34690g).

15. X. Y.Xu, R. Ray, Y. L. Gu, H. J. Ploehn, L. Gearheart, K. Raker, W. A. Scrivens, *J. Am. Chem. Soc.,* 2004, **126**, 12736.

16. F. Wang, Z. Xie, H. Zhang, C. Liu, Y. Zhang, *Adv. Funct. Mater.,* 2011, **21**, 1027.

17. H. T. Li, X. D. He, Y. Liu, H. Huang, S. Y. Lian, S. T. Lee, Z. H. Kang, *Carbon*, 2011, **49**, 605.

18. B. Zhang, C. Liu, Y.un Liu, *Eur. J. Inorg. Chem.,* 2010, 4411.

19. A. B. Bourlinos, A. Stassinopoulos, D. Anglos, R. Zboril, M. Karakassides, E. P. Giannelis, *Small*, 2008, **4**, 455.

20. D. Y. Pan, J. C. Zhang, Z. Li, C. Wu, X. M. Yan M. H. Wu, *Chem. Commun.*, 2010, **46**, 3681.

21. Y. Yang, J. Cui, M. Zheng, C. Hu, S. Tan, Y. Xiao, Q. Yang, Y. Liu,*Chem. Commun.,* 2012, **48**, 380.

22. L. Tang, R.Ji, X.Cao, J.Lin, H. Jiang, X. Li, K.S.Teng,C. M. Luk, S. Zeng, J. Hao, S. P. Lau, *ACS Nano*, 2012, **6**, 5102.

23. W. Kwon, S. W. Rhee, *Chem. Commun.,* 2012, **48**, 5256.

24. F. Wang, M. Kreiter, B. He, S. Pang, C. Liu, *Chem. Commun.,* 2010, **46**, 3309.

25. L. Y. Zheng, Y. W. Chi, Y. Q. Dong, J. P. Lin, B. B. Wang, *J. Am. Chem. Soc.,* 2009, **131**, 4564.

26. Y. P. Sun, X. Wang, F. S. Lu, L. Cao, M. J. Meziani, P. J. G. Luo, L. R. Gu, L. M. Veca, *J. Phys. Chem. C,*2008, **112**, 18295.

27. S. L. Hu, K. Y. Niu, J. Sun, J. Yang, N. Q. Zhao, X. W. Du, *J. Mater. Chem.* 2009, **19**, 484.

28. S. C. Ray, A. Saha, N. R. Jana, R. Sarkar, *J. Phys. Chem. C*, 2009,**113**, 18546.

29. M. J. Krysmann, A. Kelarakis, P. Dallas, E. P. Giannelis, *J. Am. Chem. Soc.,* 2012,**134**, 747.

30. J. C. Zhang, W. Q. Shen, D. Y. Pan, Z. W. Zhang, Y. G. Fang, M. H. Wu, *New J. Chem.,* 2010, **34**, 591.

31. X. He, H. Li, Y Liu, H. Huang, Z. Kang, S. T. Lee, *Colloids Surf. B,* 2011, **87**, 326..

32. Z. C. Yang, X. Li, J. Wang, *Carbon*, 2011, **49**, 5207.

33. S. Sahu, B. Behera, T. K. Maiti, S. Mohapatra, *Chem. Commun.,* 2012, **48**, 8835.

34. C. Zhu, J. Zhai, S. Dong, *Chem. Commun.,*2012, **48**, 9367.

35. H. Zhu, X. L.Wang, Y. L.Li, Z. J. Wang, F.Yang, X. R. Yang, *Chem.Commun.,* 2009, 5118.

36. H. T. Li, X. D. He, Y. Liu, H. Yu, Z. H. Kang, S. T. Lee, *Mater.Res. Bull.,* 2011, **46**, 147.

37. Z. Ma, H. Ming, H. Huang, Y. Liu, Z. Kang, *New J. Chem.,* 2012, **36**, 861.

38. R. L. Liu, D. Q. Wu, S. H. Liu, K. Koynov, W. Knoll, Q. Li, *Angew. Chem. Int. Ed.,* 2009, **48**, 4598.

39. A. B. Bourlinos, A.Stassinopoulos, D. Anglos, R. Zboril,V.Georgakilas, E. P. Giannelis, *Chem. Mater.,* 2008, **20**, 4539.

40. J. Zong, Y. H. Zhu, X. L. Yang, J. H. Shen, C. Z. Li, *Chem. Commun.,* 2011, **47**, 764.

41. M. Sevilla, A.B. Fuertes, *Carbon*, 2009,**47**, 2281–2289

42. W. Kwon and S-W Rhee, *Chem. Commun.* 2012, 48, 5256.

43. J. Peng,W. Gao, B. K. Gupta, Z. Liu, R. Romero-Aburto, L. Ge, Li Song, L. B. Alemany, X. Zhan, G. Gao, S. A. Vithayathil, B. A. Kaipparettu, A. A. Marti, T. Hayashi, J. Zhu and Pulickel M. Ajayan, *Nano Lett.* 2012, **12**, 844.

44. V. N. Mochalin and Y. Gogotsi. J. Am. Chem. Soc., 2009, 131, 4594.

45. S. Zhu, J. Zhang, C. Qiao, S. Tang, Y. Li, W. Yuan, B. Li, L. Tian, F. Liu, R. Hu, H. Gao, H. Wei, H. Zhang, H. Sun and B. Yang, *Chem. Commun.* 2011, **48**, 6858.

46. D. Y. Pan, J. C. Zhang, Z. Li and M. H. Wu, *Adv. Mater.,* 2010, **22**, 734.