JOURNAL OF KUFA–PHYSICS
www.uokufa.edu.iq/journals/index.php/jkp | ISSN: 2077–5830

Preparation and Characterization of the Carbon Quantum Dots

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ARTICLE INF.:

Article history:
Received: 22 MAY, 2019
Accepted: 03 OCT, 2019
Available Online: 25 DEC, 2019

Keywords:

Carbon
quantum dot
optical properties
emission spectra

ABSTRACT

The carbon quantum dots (CQDs) were prepared by using an easy and economic one – pot method. The starting materials are the ascorbic acid as a carbon source and copper acetate as a catalyst to accelerate the reaction. The structural and optical properties of the CQDs are studied by UV-VIS spectrophotometer and photoluminescence (PL) measurements, transmission electron microscope (TEM), X-ray diffraction (XRD) and Fourier transform-infrared spectroscopy (FTIR). The excitation wavelength and the pH-dependent of PL properties was investigated also. The results show that the CQDs have strong absorption peak in the UV-region. The PL is the excitation wavelength dependent. The PL of CQDs decreases upon lowering the pH value of the solutions and the PL peaks shifted to the shorter wavelength. The average size of the CQDs is 4 nm from the TEM measurements.

DOI: http://dx.doi.org/10.31257/2018/JKP/2019/110207

تحضير ومميزات النقاط الكمية الكربونية

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الكلمات المفتاحية:

كاربون
نقطة كمية
خصائص بصرية
أطياف الانبعاث

الـــخُـــلاصـــة

تم تحضير النقاط الكمية الكربونية (CQDs) باستخدام طريقة بسيطة سهلة واقتصادية. باستخدام المواد الأولية حمض الأسكوربيك (مصدر للكربون) وخلات النحاس (عامل مساعد في تسريع التفاعل). تمت دراسة الخواص التركيبية والبصرية لـ CQDs بواسطة مطياف الأشعة فوق البنفسجية (UV-VIS) وجهاز قياس انبعاث الضوء (PL) ، المجهر الإلكتروني النافذ (TEM) ، حيود الأشعة السينية (XRD) والتحليل الطيفي للأشعة تحت الحمراء (FTIR). وتم دراسة تأثير انبعاث الضوء PL حسب الطول الموجي للإثارة وتأثير تغيير قيم pH على انبعاث الضوء PL. تظهر النتائج أن CQDs لديها ذروة امتصاص قوية في منطقة الأشعة فوق البنفسجية. يعتمد PL على طول موجة الإثارة. تزداد قيم PL لمحلول CQDs عند انخفاض قيمة pH وإزاحة قمم PL إلى الطول الموجي الأقصر. متوسط حجم CQDs هو (4 nm) حسب قياسات TEM.

1. INTRODUCTION

In recent years, the scientific and industrial committee show a great interest in the carbon nanomaterials due to their unique properties and applications, such that, photocatalysis, optoelectronic devices[1], sensors, security, and bioimaging, etc. [2]. One of the most important of these materials is carbon quantum dots (CQDs or C-dots) [3]. The CQDs are spherical particles mostly with size (2-10nm) [4, 5]. It's discovered by chance during the purification of carbon nanotubes in the electrophoresis method in 2004 [6]. It structure consists of a nanocrystalline core of the graphitic SP2-hybridized, with functional groups on the surface. These functional groups are vary according to the raw materials which are used in the synthetic procedures [7].The CQDs have attracted much the attention from researchers due to: First of all, being of their eco-friendly, high biocompatible, chemically stable, low toxicity and highly soluble in water [8-9]. Secondly, the CQDs are characterized by the electronic and optical properties such as electron acceptor or donor, high photoluminescence, that have made it an important material in applications ,electronic, optical and sensing devices, bioimage, delivery of drug[10-14].Finally, the CQDs can be prepared using fast, low-cost method, and by from like natural raw materials or organic waste [15-16]. Indeed, this properties made CQDs are a good alternative to conventional semiconductors (CdS, CdSe, ZnS, etc.), which are toxic and hazardous to the environment and because they contain heavy elements [17, 18]. Several methods have been proposed to prepare the CQDs where they can be modified during or after the reaction. In general, synthetic CQDs are divided into two main groups [19]: Top-down methods including, laser ablation [20], Chemical oxidation [21], electrochemical Synthesis [22]. Bottom-up including hydrothermal synthesis [23], Soft template [24], microwave irradiation method [25]. In both methods, there are four problems facing the CQDs synthesis: (i) Carbonation during carbonization. (ii) To obtain uniform sizes, standardization is important in optical applications and is done after the preparation.(iii)The surface properties, which effect on the solubility and photoluminescence properties.[١٩,٢٦]

In this paper, chemically prepared CQDs have been used as a soluble solution. The effect of the excitation wavelength and pH values on the PL is studied also. The optical and structural properties have been studied by using, FTIR, XRD, UV-VIS-NIR and TEM techniques.

2. EXPERIMENTAL

2.1. Materials

Ascorbic acid (A.A.)($C_6H_8O_8$) was purchased from (HIMEDIA) (India). $(CH_3COO)_2Cu.H_2O$, HCl and NaOH from Laboratory Reagent (India). Water used throughout all experiments is distilled twice. All other chemicals are purchased from local market and use without any further purification.

2.2. Synthesis of CQDs

The chemical method is used to prepare the CQDs. The A.A. is used as a source of carbon and the copper acetate as a catalyst to accelerate the reaction. The A.A. (2.4792 g) is dissolved in (236.86 ml) and Copper acetate (0.2786 g) is dissolved in (13.14 ml) distilled water, separately. Then, two solutions are mixed together and magnetically stirred for 10 min at RT. The solution was then placed in a glass flask and its temperature raised up to 90 ° C, the reaction is conducted under continuously stirring for 5h. A dark brown solution was obtained with a red deposit at the bottom of the beaker. The solution is left to cool naturally at room temperature. The final product is a yellow-gold solution indicates the formation of CQDs. The centrifuge (8000 rpm) was then used for 10 minutes to separate the impurities and unreacted materials. Then, we use a rotary

evaporator to separate the solid material from the solvent and obtain a dark brown the CQDs powder.

2.3. Characterization techniques

The XRD pattern were acquired on by using (XRD- 6000 powder) with Cu K_α radiation at 40 KV generation voltage and 20 mA emission current. Fourier transformed infrared spectrum (FTIR) is recorded by Vertex 70 BRUKER device. The FTIR measurement was done by maxing a small amount of the CQDs powder with KBr, were grounded together and then pressed into discs. In order to determination size and morphology of CQDs, transmission electron microscope (TEM) type SUPRA 55 VP Carl Zeiss AG – Germany, were used to taken images. Photoluminescence spectra (PL) were recorded by a RF-5301PC (SHIMADZU) fluorescence spectrophotometer. The absorption spectra were carried out using a UV-VIS-NIR 1800 (SHIMADZU), double beam spectrophotometer.

3. RESULTS AND DISCUSSION

3.1. FT-IR

Fig.1 displays the FT-IR transmittance spectrum of the CQDs. The peaks are tabulated in Table 1. The main peaks are: The band of O-H stretching vibration at 3392.79 cm^{-1}, and 3410.15 cm^{-1}, C-H at 2899.01 cm^{-1} and 2978.09 cm^{-1},C=O at 1558.48 cm^{-1} and 1631.78 cm^{-1}, C-O-C at 1398.39 cm^{-1}, C=C at 1558.48 cm^{-1} and 1631.78 cm^{-1}. This result indicates that the CQDs are composed of a core and surrounded by effective surface groups such as hydroxyl, carboxyl, and alkyl [27]. The origin of the active groups is from the raw materials used in the preparation procedure. These active groups formed by the dehydration of groups exist in the raw materials [28].

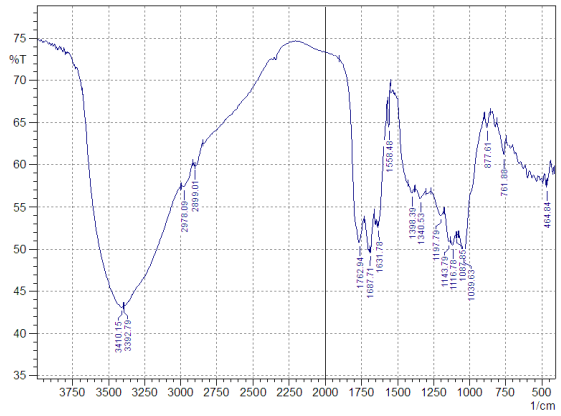


Fig. 1 FT-IR spectrum of the CQDs

Table 1. Active groups

Peak(cm^{-1})	Active groups
3410.15	O-H
2978.09	C-H(stretch)
1762.94	C=O
1631.78	C=C
1398.39	C-O-C
1197.799	C-O(stretch)
877.61	C-H(bend)
761.88	C-O(bend)

3.2 The particles size

The TEM images Fig. 2 (A), show that the CQDs are nearly spherical in the shape and have a narrow size distribution .The average size of the CQDs are about 4 nm. The histogram shown in the Fig.2B, indicates the CQDs have very low dispersivity.

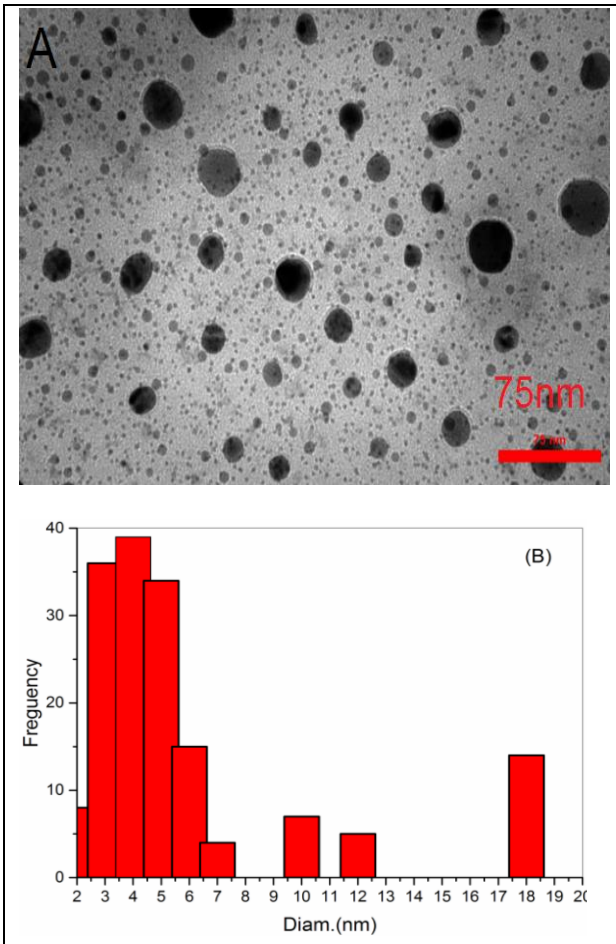


Fig.2: (A) TEM of the as prepared sample. (B)Histogram to the particles size

3.3 X-Ray diffraction (XRD)

The XRD pattern (Fig. 3) displays a broad peak at, ($2\theta = 20^{\circ}$) .The interlayer spacing is equal to (0.45 nm) is calculated from the Bragg's equation, which is greater than the spacing of the bulk part, the graphite (0.35 nm).The XRD pattern reflects a relatively low crystallization structure [27]. Here, the low crystallization of the CQDs is because of the larger surface area to the size. Which is leading to the proliferation of oxygen – rich surface functional groups on the surface of the CQDs. As confirmed from the FT-IR spectrum analysis (Fig. 1).

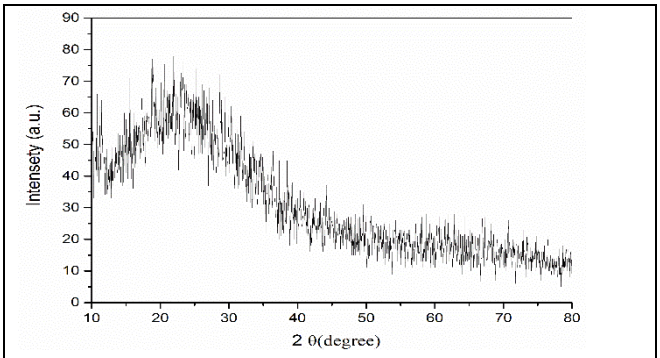


Fig. 3 X-Ray diffraction pattern of a CQDs Sample

4. Optical properties of the CQDs

4.1. UV-VIS spectra

Fig 4, shows the optical absorbance of the CQDs aqueous solution, it is a yellow color under visible light .There are two distinguished peaks (i.e., absorption edges), one at (294nm) and anther at (367.72nm). The peak at (294nm) is attributed to the existence of a dense π-electron system [29] and it is attributed to the (π-π *) transition, from the core CQDs (SP^2 C=C)[29]. The second peak (367.72 nm) is attributed to the (n- π *) transition from surface group (C=O) [30], and extends to the tail in the visible region. The absence of absorption in the long wavelength region indicates that there are no other carbon materials resulting from partial carbonation [32]. The optical band gap prepared around (3.37ev) for the CQDs dissolved at the water. The band gap is calculated by using the following formula [33]:

$$E_g = \frac{1240}{\lambda} \qquad (1)$$

Where (λ) is the optical absorption edge.

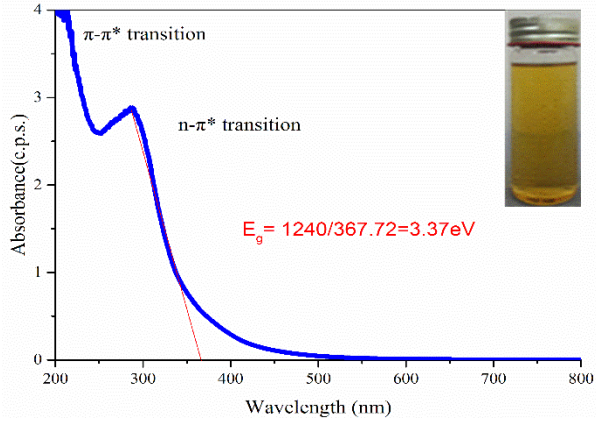


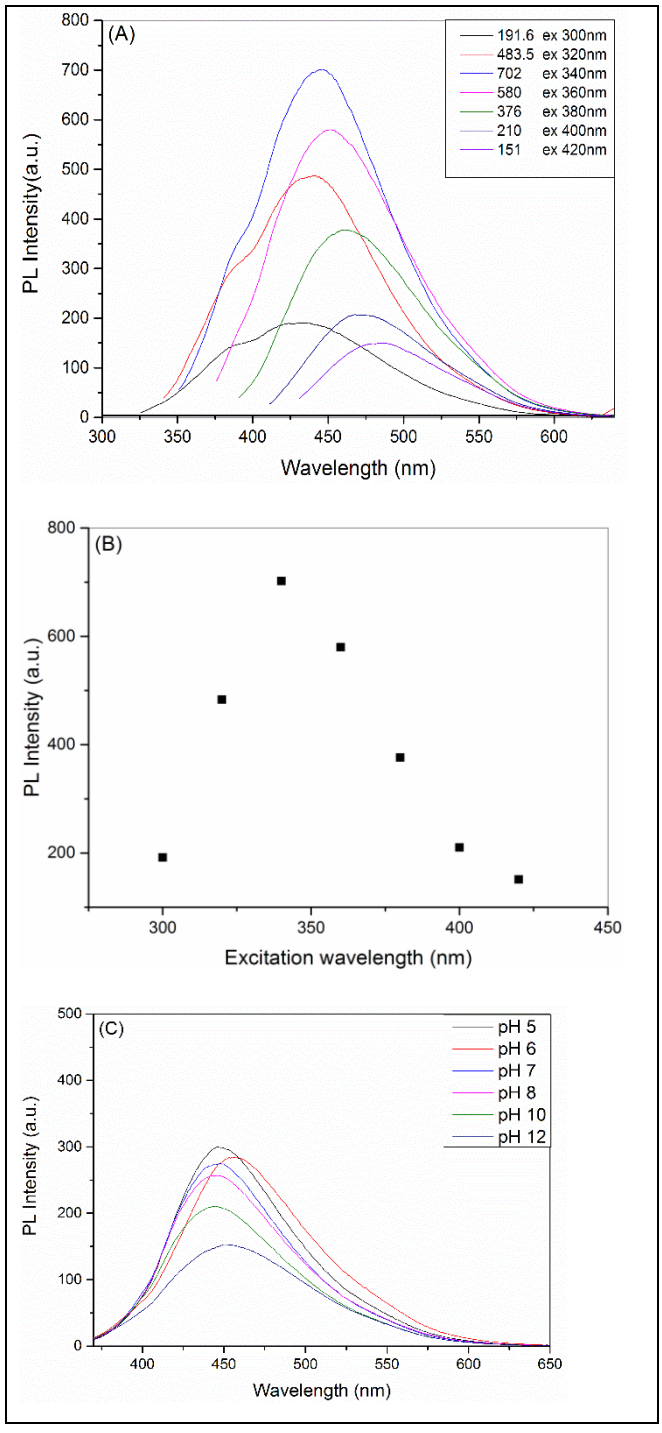
Fig.4 UV- VIS absorption spectrum.

4.2. PL analysis

Fig.5A shows the PL spectra of the CQDs at the concentration (20%). Which show clearly their excitation wavelength dependent. The higher intensity of the peak emission at wavelength (445nm) and lowest is at (485nm). The PL intensity increased progressively with the excitation wavelength and then decreases as shown in Fig.5B. And can we observed there are a red shifts (~40 nm) between the emission at the maximum (445nm at λ_{ex} 340nm) and the emission at the minimum (485nm λ_{ex} 420 nm) also.

The mechanism of the PL emission arises from the internal band gap resulting from the association of SP^2carbon core and effective oxygen –rich functional groups on the surface of CQDs [31].Surface groups (carboxyl, hydroxyl, and alkyl) contribute to large deformation and create different energy gaps between (HOMO-LUMO) [33]. The new energy gap leads to the different PL emission lines and red shift to large wavelength [26, 34].

Fig.5C, shows that the effect of the pH on the, PL properties at different the pH values and at a constant wavelength excitation 365nm. The pH are adjusting by added the solution (0.1N NaOH, 0.1N HCl)). It was observed that, when the pH values increasing leads to the decreasing in the PL emission intensity as shown in Fig5 D. This behavior because of the polarity of CQDs surface decreases at high pH values. These results are agreement with other results [18].



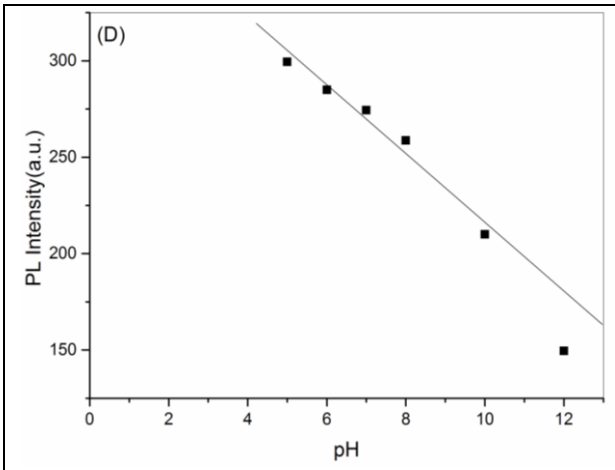


Fig. 5 (A) PL spectra of CQDs excited by λ_{ex} (300 -420 nm), (B) Shows the change in emission intensity with wavelength of excitation,(C) Effect of the pH on PL (λ_{ex}= 365 nm), and (D) Show decreases PL with increasing pH.

5. CONCLUSION

In summary, we have prepared the CQDs in a one-pot green method using an A.A. in the aqueous solution at the low temperatures. They have very narrow size dispersivity. The CQDs has a high water dispersion and have a strong absorbing in the UV region. The PL in the visible region and it depends on the excitation wavelength and on the pH values of the solution. Finally, the all interesting features mentioned above of the CQDs, cited that this materials can be used in many application in different fields, such medical and optoelectronics.

6. REFERENCES

[1] M. P. Ramuz, M. Vosgueritchian, P. Wei, C. Wang, Y. Gao, Y. Wu, Y. Chen and Z. Bao, ACS Nano, 6(2012)10384.

[2] S. C. Ray, N. R. Jana, Carbon Nanomaterials for Biological and medical Applications,(2017),(Chapter4),Elsevier Inc.

[3] D. Chowdhury, N. Gogoi and G. Majumdar, RSC Adv. Commun., 2(2012)12156.

[4] P. C. Hsu, Z. Y. Shih, C. H. Lee and H. T. Chang, Green Chem.,14(2012)917.

[5] Y. Zhou, A. Desserre, S. K. Sharma, S. Li, M. H. Marksberry, C. Chusuei, P. L. Blackwelder and R. M. Leblanc,Chemphyschem,18(2017)2.

[6] J. Deng, Q. Lu, N. Mi, H. Li, M. Liu, M. Xu, L. Tan, Q. Xie, Y. Zhang and S. Yao,Chem. Eur. J. ,20(2014)4993.

[7] P. Mirtchev , E. J. Henderson, N. Soheilnia , C.M. Yip and G.A. Ozin, J. Mater. Chem., 22(2012)1265.

[8] P. Anilkumar , X. Wang ,L. Cao, S. Sahu , J. H. Liu, P. Wang, K. Karch , K. N. Tackett, A. Parnzan and Y. P. Sun, Nanoscale,3(2011)2023.

[9] H. Li, X. He , Y. Liu, H. Huang, S. Lian , S. T. Lee and Z. Kang, Carbon,49(2011)605.

[10] X. Wang , L. Cao , F. Lu , M. J. Meziani , H. Li , G. Qi , B. Zhou , B. A. Harruff , F. Kermarrec and Y. P. Sun , RSC Chem. Commun. , 66(2009) 3774.

[11] S. Paulo , G. Stoica , W. Cambarau , E. M. Ferrero , E. Polomares, Synth. Metals, 222(2016)17.

[12] Y. Guo, L. Zhang, F. Cao, Y. Leng , Scient. Repor. , 6(2016) 35795.

[13] S. L. Dsouza , B. Deshmukh , K. A. Rawat , J. R. Bhamare , N. Lenka and S. K. Kailasa , RSC Adv. , 6(2016)1.

[14] S. Sahu, B. Behera, T. K. Maiti and S. Mohapatra, Chem. Commun., 48(2012)1.

[15] J. R. Bhamore, S. Jha, R. K. Singhal, S. K. Kailasa, j., Fluoresc. , 27(2016) 1.

[16] Y. Hu , J. Yang , J. Tian , L. Jia, J. S. Yu , J. Carbon ,77(2014)775-782.

[17] J. B. Essner, C. H. Laber , S.Ravula , L. P. Parada and G. A. Baker, Green Chem.,18(2016)1.

[18] S. Han, H. Zhang, Y. Xie, L. Liu, C. Shan,X. Li, W. Liu and Y.Tang, Appl. Surf. Scien. , 238(2015)1.

[19] Y. Wang and A. Hu, RSC, J. Mater. Chem. C, 2 (2014)6921.

[20] H. Gorcalves , P. A. S. Jorge , J. R. A. Fernandes , J. C. G. E. da Silva , Sensors and Actu. B: Chem., 145(2010)702.

[21] Z. A. Qiao, Y. Wang, Y. Gao, H. Li, T. Dai, Y. Liu and Q. Huo, RSC Chem. Commun., 46(2010)8812.

[22] H. Ming , Z. Ma , Y. Liu , K. Pan , H. Yu , F. Wang and Z. Kang , Dalton Trans. ,41(2012)9526.

[23] L. Zhou, B. He and J. Huang, RSC Chem. Commun. , 49(2013)1.

[24] W. Kwon, G. Lee, S. Do, T. Joo and S. W. Rhee, J. Small, 10(2013)1.

[25] V. Milosavljevic , A. Muick , P. Kopel, V. Adam , R. Kizek, J. Metallomics and Nanotech. , 3(2014)16.

[26] Y. Chen, M. Zheng, Y. Xiao, H. Dong, H. Zhang, J. Zhuang, H. Hu, B. Lei and Y. Liu,Adv. Mater., 28(2016) 312-318.

[27] B. De and N. Karak, RSC Adv., 3(2013)3.

[28] Y. Ding, F. Zhang, J. Xu, Y. Miao, Y. Yang, X. Liu and B. Xu, RSC Adv., 7(2017)28754.

[29] L. Bao, C. Liu, Z. L. Zhang and D. W. Pang, Adv. Mater. , 27(2015)3.

[30] S. Y. Lim , W. Shen and Z. Gao, Chem. SOC Rev. ,44(2014)4.

[31] A. Mewada, S. Randey, M. Thakur, D. Jadhav and M.Sharon, J. Mater. Chem. B, 2(2014) 700.

[32] R. Vadivel , S. K. Thygarajan , K. Raji , R. Suresh , R. Sekar and P. Ramamurthy , ACS Sustainable. Chem. Eng., 4 (2016)11.

[33] M. Sun, X. Ma, X. Chen, Y. Sun, X. Cui, and Y. Lin, RSC Advances,4(2014) 1121-1126 .

[34] R. Bandi, B. R. Gangapuram, R. Dadigala, R. Eslavath, S. S. Singh and V. Guttena, RSC Adv., 6(2016) 3.