

# Synthesis and Application of Carbon Quantum Dots for Organic Reactions

DISSERTATION

Submitted in Partial Fulfillment of the Degree of M. Sc

(Organic Chemistry)

By

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To

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April 2020

# STATEMENT

I hereby declare that the matter presented in this dissertation entitled, “**Synthesis and Application of Carbon Quantum Dots for Organic Reactions**” is based on the results of investigations carried out by me in the School of Chemical Sciences, Goa University under the supervision of **Dr. Sandesh T. Bugde** and the same has not been submitted elsewhere for the award of a degree of diploma.

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# CERTIFICATE

This is to certify that the dissertation entitled, “**Synthesis and Application of Carbon Quantum Dot for Organic Reactions**”

Herein I confirm that the work carried out by **Miss. Siddhi Krishnanath Salgaonkar** under my supervision in partial fulfilment of the requirements for the award of the degree of Master of Science in Chemistry at the School of Chemical Sciences, Goa University.

**Dr. Sandesh T. Bugde**

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# CERTIFICATE FROM HEAD

This is to certify that the dissertation entitled, “**Synthesis of porphyrin and its photocatalytic activity**”

Herein I confirm that work carried out by **Miss. Siddhi Krishnanath Salgaonkar** under the supervision of **Dr. Sandesh T. Bugde** for the award of the degree of Master of Science in Chemistry at the School of Chemical Sciences, Goa University.

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# ACKNOWLEDGEMENT

I take this opportunity to express my gratitude to my project guide **Dr. Sandesh T. Bugde**, for his guidance in completing my project work and for his valuable suggestions which has improved the quality of my work and experimental skills.

I would like to express my sincere gratitude to Prof. V. S. Nadkarni, the Dean of School of Chemical Sciences for allowing me to carry out the dissertation work and for their useful suggestions.

I am also thankful to my teachers Prof. S. G. Tilve, Ms. Siddhali Rajadhakshya, Prof. Sheshnath Bhosle, as well as the Research Scholars and non-teaching staff at the School of Chemical Sciences, Goa University for their constant support and help.

I would like to thank Research Scholar Mr. Pritesh Khobrekar for his support and giving his knowledge throughout the project.

I would like to thank my friends for encouraging and supporting me throughout this project.

Last, but not the least, I thank my parents for their support and encouragement without whom I would not be able to pursue my studies and complete my dissertation work.

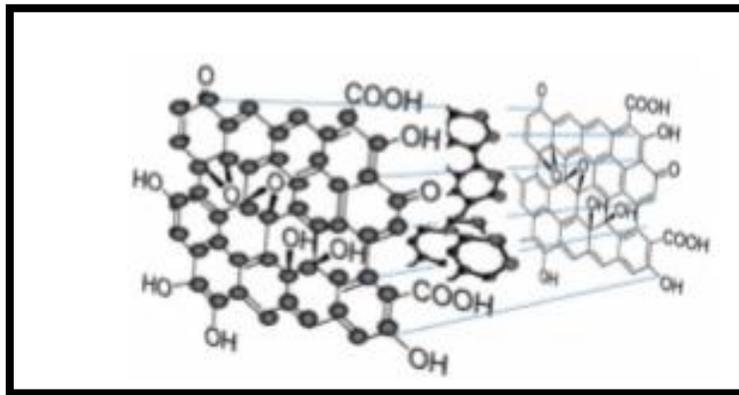
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# 1. INTRODUCTION

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Carbon quantum dots (CQDs) or carbon nanodots (CD's) discovered in the mid-2000s,<sup>1,2</sup> are one of the emerging class of nanomaterials made from carbon sources .The term carbon dots (CDs) has been used to describe a new class of carbon-based nanomaterials which are typically discrete, quasi-spherical nanoparticles, with sizes usually less than 10 nm in diameter (although bigger sizes have recently been reported),<sup>3</sup> typically composed by carbon, oxygen, nitrogen and hydrogen (fig 1).<sup>2</sup> CDs are the latest addition to the carbon family, which were accidentally discovered by Xu *et al.*<sup>1</sup> during gel electrophoresis purification of single-walled CNTs produced by the arc-discharge method.



**Fig 1:** Probable chemical structure of CQD.<sup>13</sup>

The most important criteria of CQD is a bright fluorescence, tunable across the visible range, which has changed the traditional pattern 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, non-toxicity, high sensitivity to the external environment, stable photoluminescence, cell membrane permeability,<sup>4</sup> tunable surface functionalities<sup>4</sup> 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.<sup>2,13</sup>

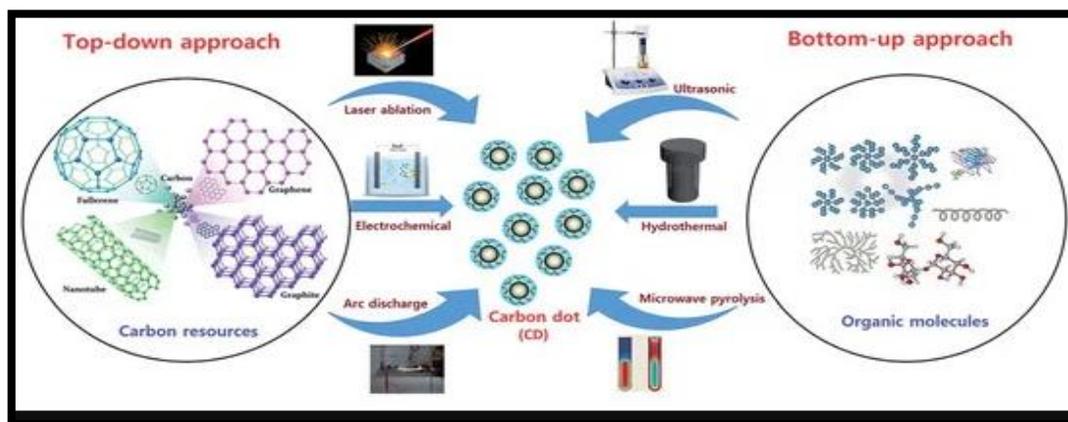
Fluorescence-based sensing is gaining popularity due to its virtues of excellent sensitivity, fast response, simple fabrication procedure or straightforward sensing, and low development cost.<sup>5</sup> This sensing method involves various types of fluorescent materials, such as organic dyes, fluorescent proteins, metal–organic frameworks, and quantum dots (QDs), which are often associated with low photostability, blinking effects, and may also pose toxicity concerns.<sup>5</sup> From the practical point of view, the optical properties of CDs are somehow comparable, and often competitive, to fluorescent semiconductor quantum dots (QDs)<sup>2</sup> For instance, group II–VI semiconductor QDs such as cadmium sulfide and cadmium telluride, which have been previously employed for biological sensing purposes, can be viewed as a legitimate toxicity concern as these QDs may potentially degrade and release toxic cadmium ions intracellularly. This has led to the exploration of new materials with negligible toxicity and excellent physical and optical properties.<sup>5</sup> Luminescent CDs are superior in terms of aqueous solubility, high resistance to photobleaching, low toxicity and good biocompatibility [2] and hence have been hailed as potential non-toxic replacements to traditional semiconductor quantum dots (QDs). Particularly in the areas of live imaging and drug delivery.<sup>3</sup>In addition, CQD's 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.<sup>2,13</sup>

However, CDs have a low quantum yield (QY), which limits their applications. Their band gap and electronic density could be effectively modulated using chemical doping with heteroatoms, which would enhance the QY of CDs and are critically required in biological imaging.<sup>4</sup> Heteroatom doping suppresses non radiative electron hole pair recombination and leads to high QY of CQDs.<sup>6</sup>

## **1.1 Synthesis of CQDs**

Generally, the synthetic procedures for CDs can be divided into two main groups, namely top-down and bottom-up methods. Top-down synthesis routes involve breaking or cutting bulk carbon precursors into nanosized particles.<sup>3</sup> Electrochemistry, chemical oxidation, arc discharge and laser ablation approaches are the common top-down methods employed to prepare CDs. Conversely bottom-up methodologies rely on the use of a molecular precursor which can be treated in such a way as to seed the formation of a CD.<sup>13</sup>Typical starting materials include amino

acids, citric acid, biomass and carbohydrates, which can be reacted using include direct pyrolysis, microwave-assisted pyrolysis, reverse-micelle approaches, chemical or hydrothermal oxidation, microwave, acid mediated reflux, ultrasonic irradiation or silica nanoparticle templated synthesis.<sup>3-5,9</sup>



**Fig 2.** Representation of the possible synthesis methods to prepare carbon dots. Reproduced with permission from.<sup>7,2</sup>

One important benefit of top-down synthesis routes is that the obtained CDs typically have simple and well-defined structures (e.g., graphitic nanosphere) that leave no room for structural ambiguity.<sup>8,2</sup> In contrast, bottom-up methods can be much harder to control: various side products (e.g., small fluorescent molecules) can be formed along with CDs, hence the need for a careful purification after synthesis. However, bottom-up synthesis methods bear their own advantages. On one hand, they are particularly simple and surface passivation can be usually achieved in “one pot” without the need of post-synthesis chemical processing. In fact, the surface of as-synthesized CDs via the most popular bottom-up procedures, spontaneously achieves the appropriate structure needed for an intense fluorescence. In addition, while the structure of CDs obtained by top-down synthesis typically resembles the structure of the precursors (e.g., graphitic CDs from laser ablation or chemical oxidation of graphite<sup>1,2,8</sup>, bottom-up routes are more versatile and yield a much larger variety of CD structures, especially with combined with doping strategies.<sup>9,13</sup>

However these methods, except hydrothermal and direct pyrolysis requires sophisticated instruments, strong acid treatment and have uncontrolled reaction conditions. The hydrothermal method is widely used due to its simple and efficient process with mild reaction conditions.<sup>6</sup>

## **1.2 Applications of CQD's**

These relatively new nanomaterials have found many applications in the fields of photo- and electrocatalysis, chemical sensing, biosensing, bioimaging and nanomedicine<sup>3,9</sup>. The fluorescent properties of CQDs has been utilized as a sensor or fluorescent probe for the detection of various metal ions such as  $\text{Cu}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Fe}^{3+}$  and for the detection of small organic molecules such as ascorbic acid, citric acid etc. CQDs have also been used as a promising material in drug delivery and in enzyme detection.<sup>6</sup> CQDs have been used for variety of photoredox reactions involving different C-C, C-X bond formation reactions.<sup>10,13</sup>

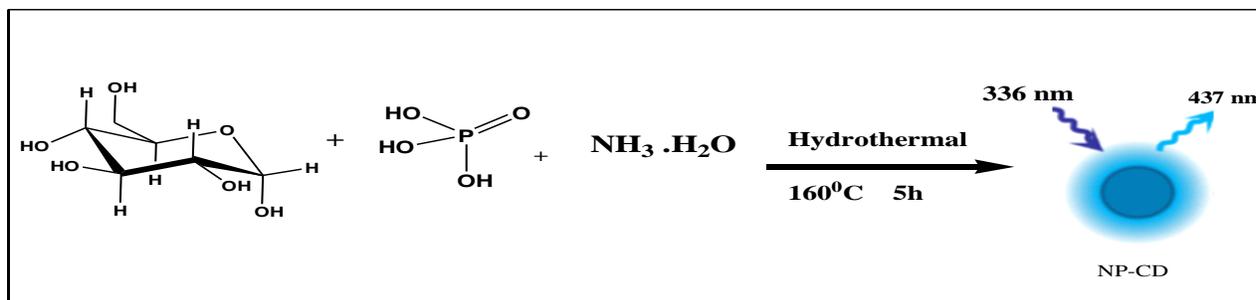
In our study we are using PEG and potato (carbohydrates) as the carbon source (precursor). PEG is a water soluble polymer; it is the most popular surface passivating material and has been found to be effective in improving the solubility and biocompatibility of nano particles. Moreover, PEG can be used for various biomedical applications due to its non-toxicity, non-immunogenicity and application reactivity to other biomolecules.<sup>10</sup> Carbohydrates are one of the most diverse and important class of biomolecules in nature and offer well-defined chiral scaffolds primed for modification at the anomeric position and alcohol functionalities. Therefore, the use of carbohydrates as a starting material for synthesizing CDs is extremely attractive not only due to their abundance, availability and heterogeneity, but also due to their high water solubility, low-carbonisation temperatures, low cost and typically inherently lack toxicity.<sup>3</sup>

# 2. LITERATURE REVIEW

## 2.1. SYNTHESIS OF CARBON QUANTUM DOTS (CQD's)

### 1] Synthesis of the N,P-CDs.<sup>4</sup>

In 2016, Bingfang Shi *et al.*<sup>4</sup> reported a hydrothermal approach for synthesis of nitrogen and phosphorus codoped carbon dots (N,P-CDs) that use glucose as carbon source, and ammonia, phosphoric acid as dopant, respectively (Scheme 1). The prepared N,P-CDs exhibited sufficient water solubility, excellent fluorescence properties; they also resist light illumination and extreme pH. and it shows a sensitive response to  $\text{Fe}^{3+}$  in the concentration range of 5–100 nM with the detection limit of 1.8 nM. Significantly, the as-prepared N,P-CDs possessed negligible cytotoxicity and excellent biocompatibility. Thus these prepared N,P-CDs was further applied for detection of  $\text{Fe}^{3+}$  in human serum and intracellular  $\text{Fe}^{3+}$  imaging.



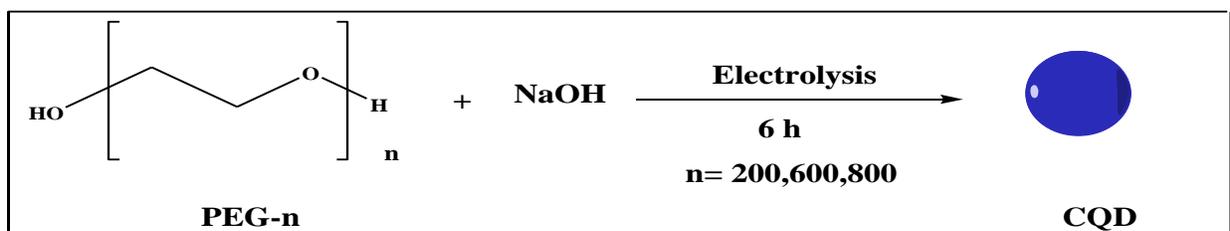
Scheme: 1

### 2) Synthesis of CQD's from PEG using thermal decomposition method.<sup>10</sup>

In 2014, M. Chen *et al.* reported a single step thermal decomposition route without further modification steps. The only reagent was polyglycol (PEG, PPG or PTMG) acting as both the carbon source and the passive agent. The produced CND,s showed fluorescence and good stability. It was observed that when reaction was carried in protection of N<sub>2</sub> it took more time for formation of CND's. Also it was observed that use of starting material with higher oxygen to carbon ratio (C/O) lead to more facile formation of CQD's.

### 3) Synthesis of CQD's from PEG using electrolysis method.<sup>14</sup>

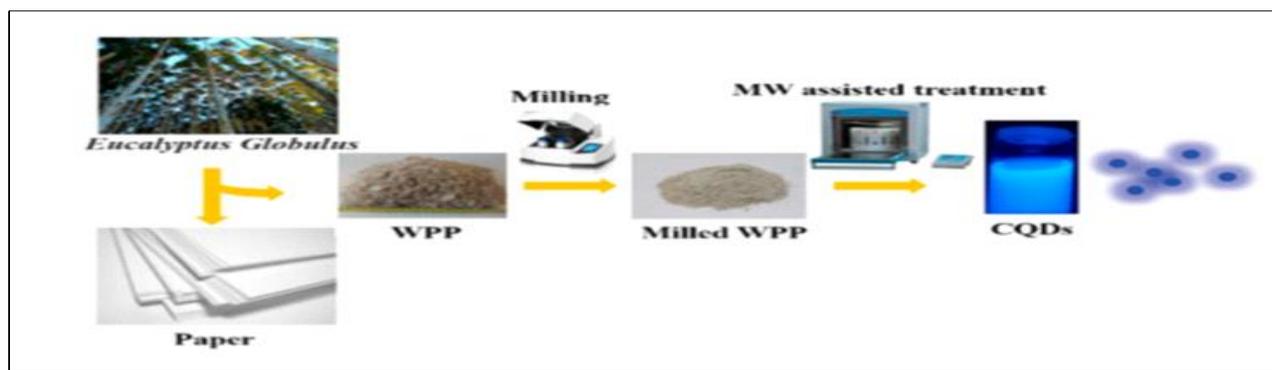
In 2014, Hao Li *et al.* developed a low cost electrolysis method for synthesis of high-intensity fluorescent CQD's with PEG as the carbon source (scheme 2). Different types of PEG (PEG 200, PEG 600 and PEG 800) were employed to achieve high intensity fluorescence, among which CQD's using PEG as the carbon source exhibited the highest fluorescence.



Scheme: 2

### 4] Synthesis of carbon quantum dots from wood.<sup>11</sup>

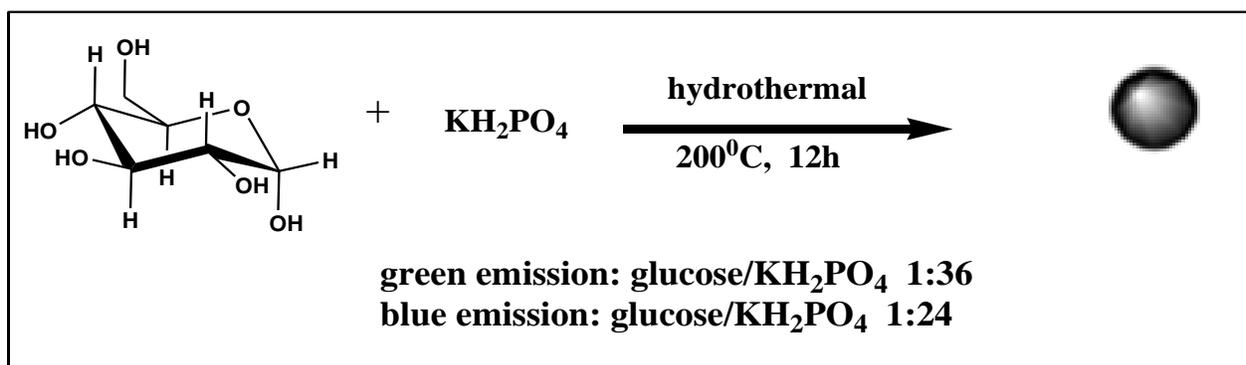
In 2018, Rodríguez-Padrón *et al.* reported a Microwave-assisted (top-down) preparation of carbon quantum dots from lignocellulosic residues using a solid acid catalyst (scheme 3). A well dispersed nanoparticles with spherical regularity, corresponding to the CQDs where obtained. The average diameter of the obtained nanoparticles was 17.5 nm. Remarkably, no nanoparticles could be observed when the WPP was treated in the absence of the solid acid catalyst, indicating its crucial role in the microwave assisted step to obtain CQDs.



Scheme: 3

### 5] Synthesis of C-dots from glucose using $\text{KH}_2\text{PO}_4$ as a dehydrating agent.<sup>12</sup>

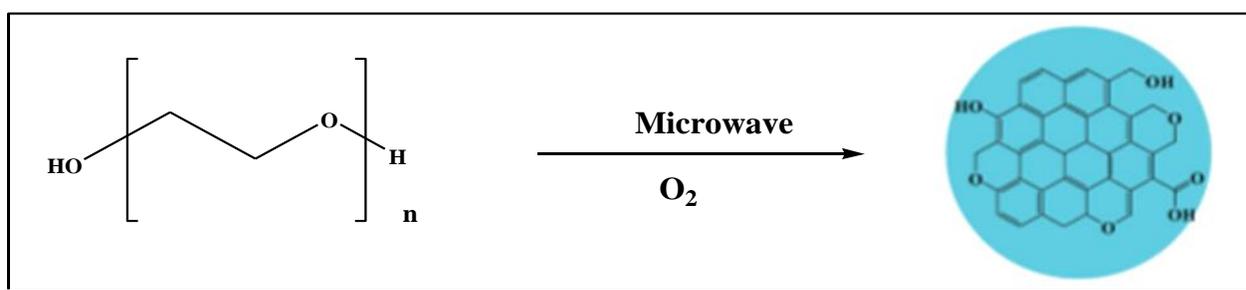
In 2011, Yang *et al.* developed a method to synthesize intrinsically fluorescent carbon dots by hydrothermal treatment of glucose in the presence of monopotassium phosphate (scheme 4). The  $\text{KH}_2\text{PO}_4$  plays an important role in controlling the size of the C-dots thus produced. The fluorescence emission of the C-dots thus produced is tunable by adjusting the concentration of  $\text{KH}_2\text{PO}_4$ .<sup>12</sup> In the absence of  $\text{KH}_2\text{PO}_4$ , irregular black carbon aggregates were obtained.<sup>3</sup> The CQD's obtained are promising candidates for fluorescent cellular imaging.



Scheme:4

### 6) Synthesis of CQD's from PEG using microwave assisted technique.<sup>15</sup>

In 2017, Zhao *et al.* reported a microwave assisted synthesis of CQD's from polyethylene glycol. Microwave irradiation, (scheme 5) by interacting with the matter in a solution, can elevate the temperature of the solution up to  $1000^\circ\text{C}$  within only one minute, and use of such irradiation is thus energy efficient. In his study he reported that Oxygen can be used to accelerate the synthesis of CQD's from PEG and remarkably influenced the properties of the CQD's using PEG as a single component precursor without subsequent passivation.

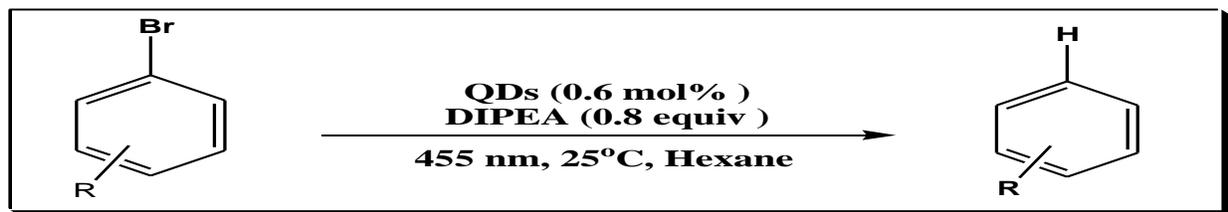


Scheme: 5

## 2.2. APPLICATION OF QD IN ORGANIC REACTIONS.

### 1) Applications of Quantum Dots in Visible-Light Photoredox Reduction of Aryl Halides.<sup>16</sup>

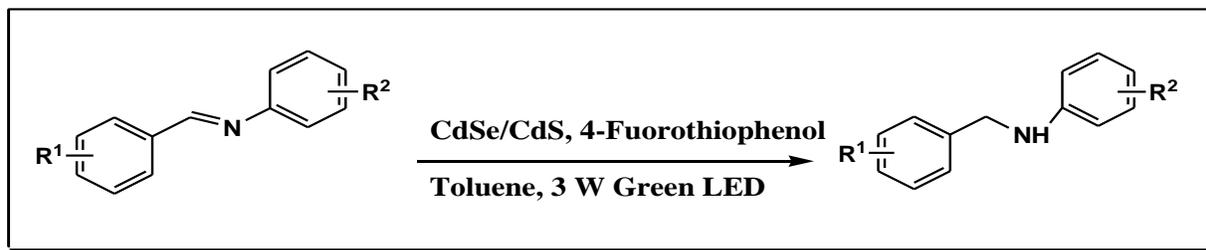
In 2017, Pal *et al.*<sup>16</sup> used these QDs for photoredox reductive generation of aryl radicals from aryl halides (scheme 6). He found that even as low as 0.6 mol % catalyst concentration provides evidence for extremely efficient photoredox catalytic generation of aryl or heteroaryl radicals from (hetero)aryl halides under visible-light photoirradiation. The limitation of the synthesized QDs was that the reaction does not take place for aryl halides with neutral or electron-donating groups that possess higher reduction potentials than the available reduction potential of the QDs.



Scheme: 6

### 2) CdSe/CdS core/shell QDs as photocatalysts for transfer hydrogenation reaction.<sup>17</sup>

Xi *et al.* in 2018,<sup>17</sup> in his work used, nearly defect-free CdSe/CdS core/shell QDs as photocatalysts for transfer hydrogenation reaction of imines with thiophenol as hydrogen source for a wide scope of amines (scheme 7). CdSe/CdS core/shell QDs were more stable and efficient as photocatalysts than the plain-core CdSeQDs in the series of reactions that he studied. Thus this makes the former QDs a suitable photocatalysts for a wide range of reactions. Most of the reactions proceeded with more than 80% yield whether the substituent was electron-rich or electron deficient on either of the phenyl rings.



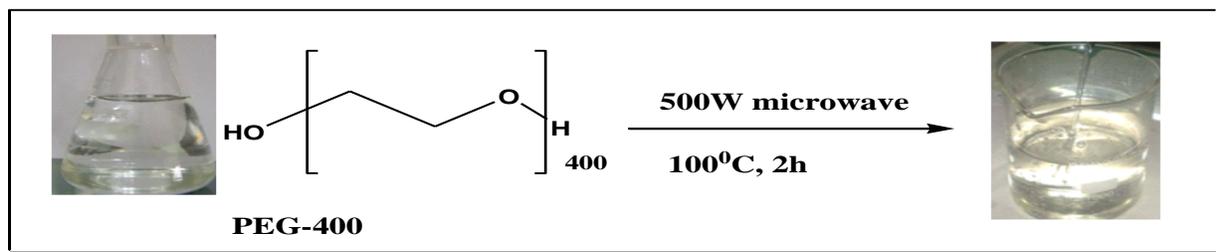
Scheme: 7

# 3. RESULTS AND DISCUSSION

## 3.1. SYNTHESIS

We synthesized CQDs using various bottom up methods such as, microwave assisted pyrolysis, direct pyrolysis (domestic microwave), hydrothermal and thermal decomposition. We used PEG-400 and potato as the carbon sources and the passivation agent which made this synthesis cost-efficient, environment friendly, and fascinating when compared with other CQDs preparation.

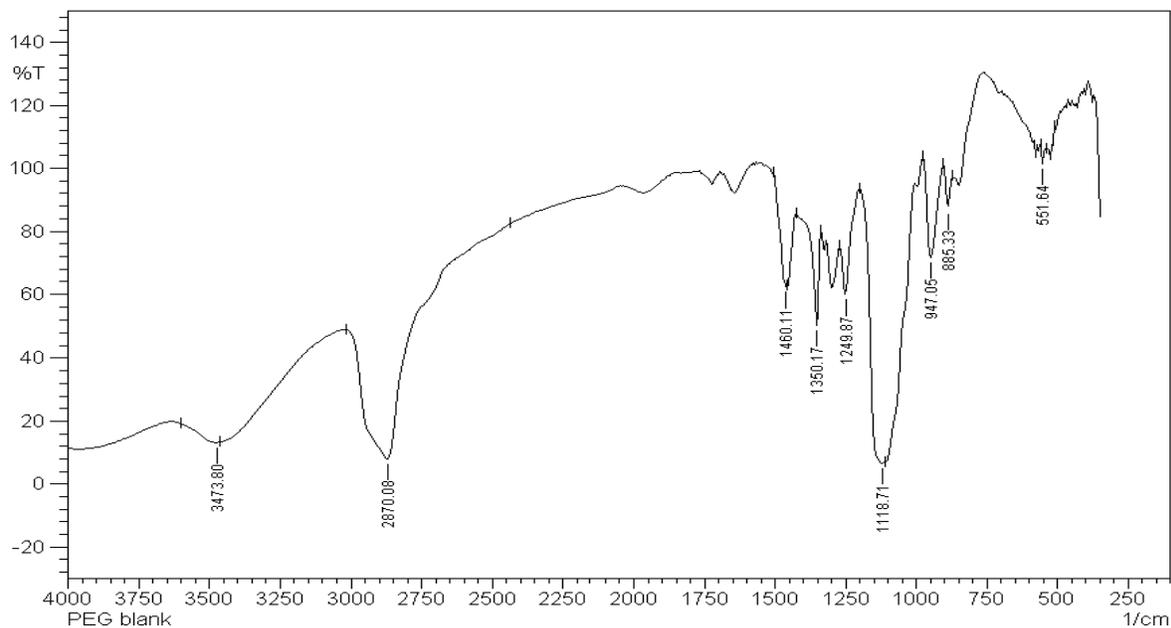
The microwave assisted technique with PEG-400 as carbon source in the absence of gases like oxygen, nitrogen; etc (scheme 8) did not result in formation of CQDs. Thus from experimental work and literature review we can infer that presence of gases during this process is necessary.



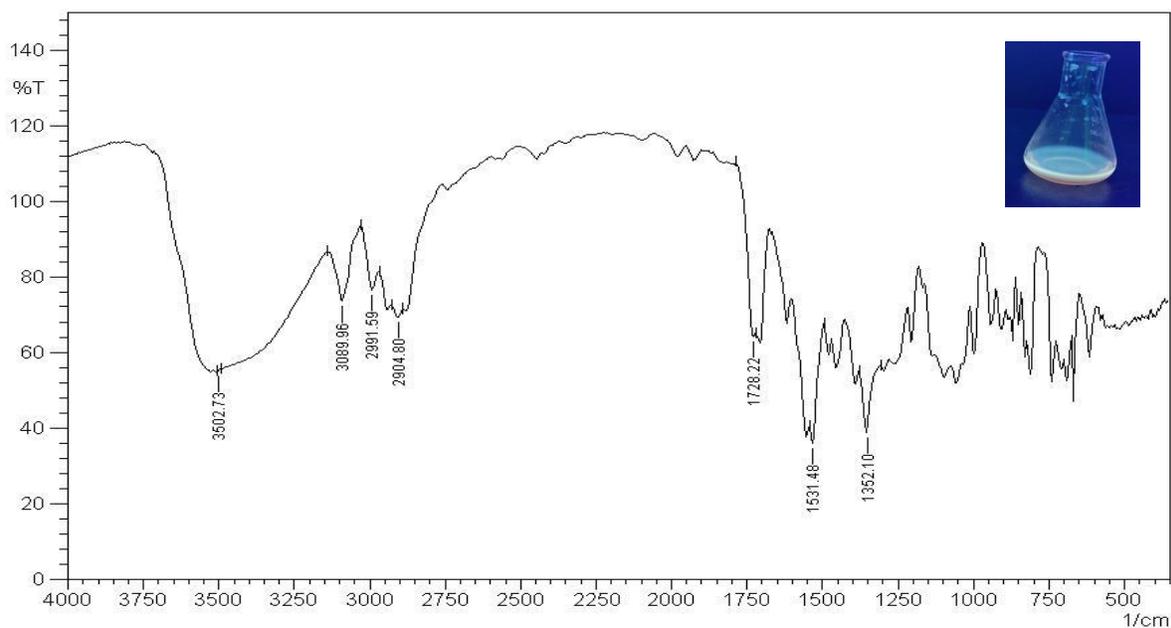
**Scheme: 8**

We then synthesized CQDs by thermal decomposition route, wherein we heated the solution at high temperature (i.e. 160°C) for particular time interval. A faint yellow color to dark yellow color solution was obtained containing CQDs after heating for different time interval. When these solutions were exposed to UV light, only one solution i.e. the one which was heated for 6hrs emitted yellow orange fluorescence (fig4). Thus indicating that a sufficient heat was required for formation of CQDs. further FTIR spectrum of CQDs was recorded as shown in fig 4. Which showed new peaks at 3000-2850cm<sup>-1</sup> (-CH stretch), 1728.22cm<sup>-1</sup> (-C=O), and

1531.48 $\text{cm}^{-1}$  ( $\text{-C=C-}$ ), which is absent in IR spectra of PEG-400 (Fig 3.), also the  $\text{-OH}$  peak obtained is strong and broad as compared to that seen in IR spectra of PEG-400, thus indicating formation of CQDs.

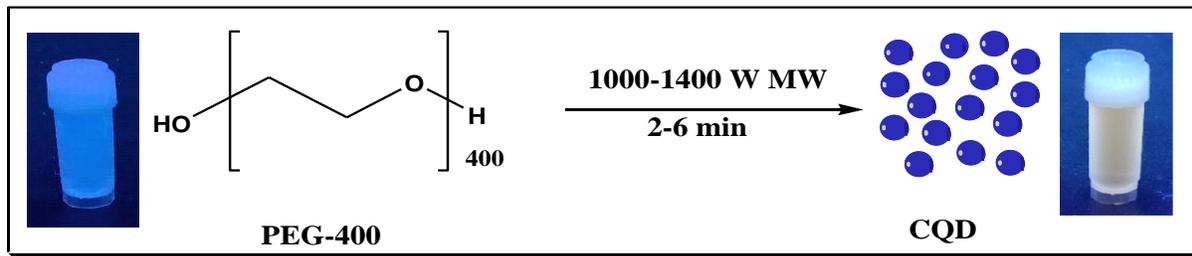


**Fig 3.** IR spectra of PEG-400 (blank)

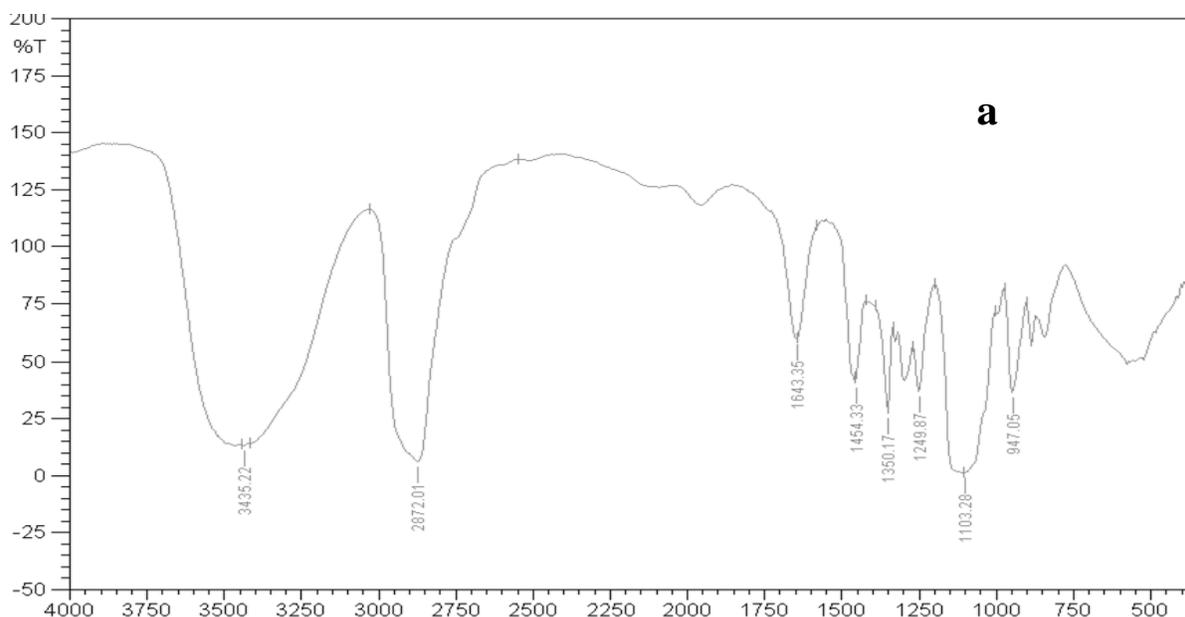


**Fig 4:** IR spectra of synthesized CQD's (thermal decomposition). Picture inside is CQDs showing fluorescence.

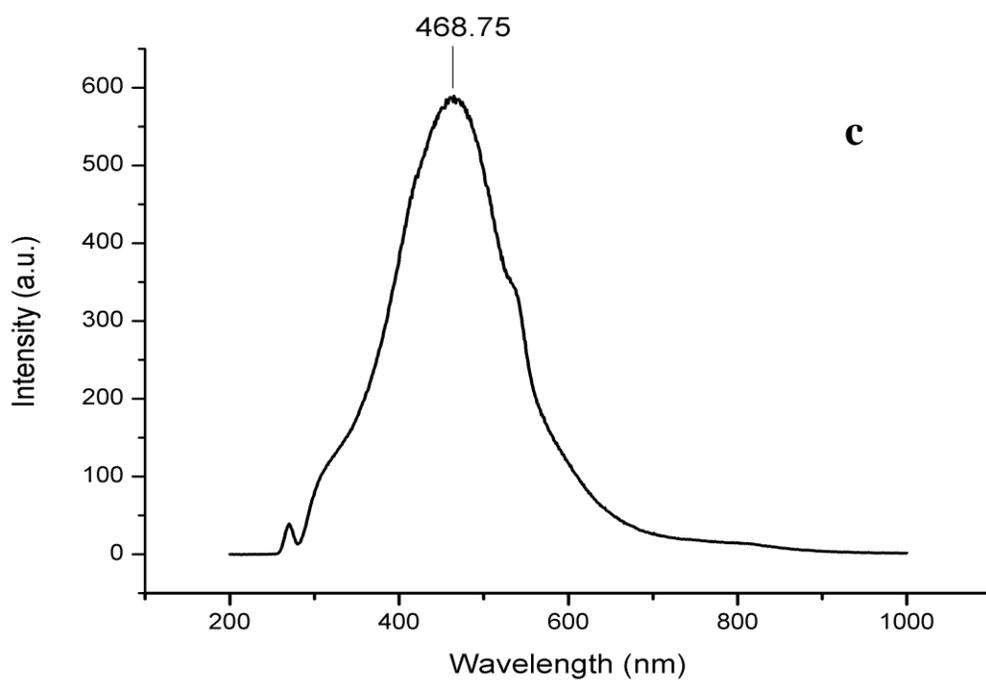
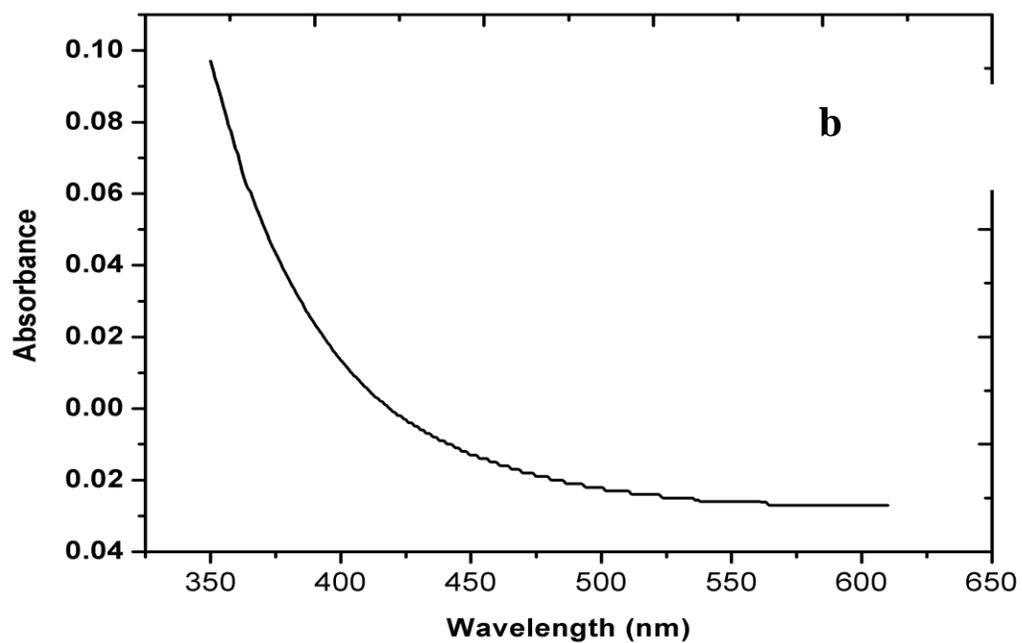
We were successful in synthesizing CQDs from PEG-400 by direct pyrolysis (i.e. heating in domestic microwave) scheme 9. A brown color solution containing CQDs was obtained which emitted fluorescence under UV light.



To further confirm the formation of CQDs FTIR spectroscopy was performed as depicted in fig.3 and fig. 5a of PEG-400 and CQDs obtained from PEG-400 respectively. The new band in fig 5a at 1643 (C=C Stretching) and a strong broad band at 3435.22 cm<sup>-1</sup> (-OH) indicates formation of CQD's which is absent in fig3. Photophysical properties of synthesized CQDs were studied using UV-vis absorption spectra (fig 5b) and photoluminescence decay spectra in water with excitation at 270 nm (fig 5c). CQD's typically show optical absorption in the UV region with a tail extending to the visible region. When we performed the same procedure with potato as carbon source instead of PEG-400 we did observe the fluorescence when exposed to UV lamp but isolation of these CQDs is complicated.

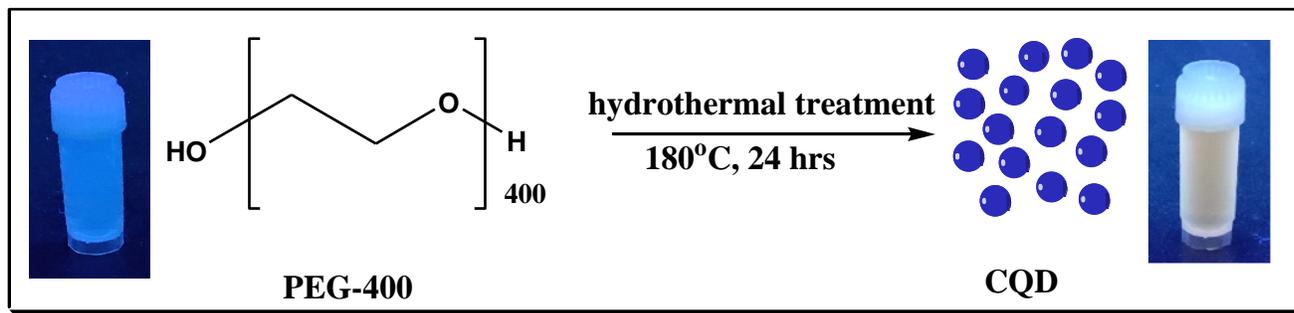


**Fig 5: a)** IR spectra of synthesized CQD's (direct pyrolysis)

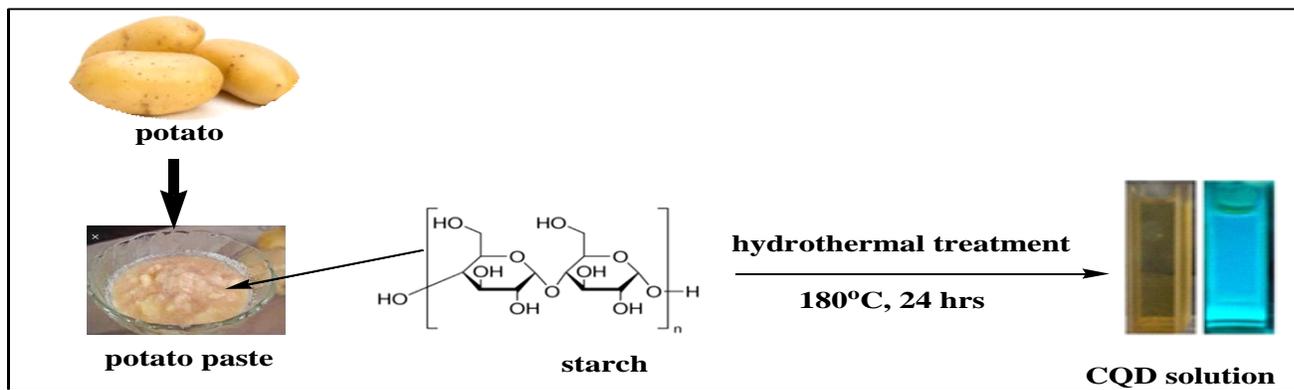


**Fig 5:** (b) UV-vis absorption spectrum of as-prepared CQDs at 260-320 nm and (c) PL emission spectra of CQDs with excitation at 270 nm

We were also successful in synthesizing CQDs using hydrothermal method from PEG - 400 and potato as a carbon sources (scheme 10 and scheme 11 respectively).



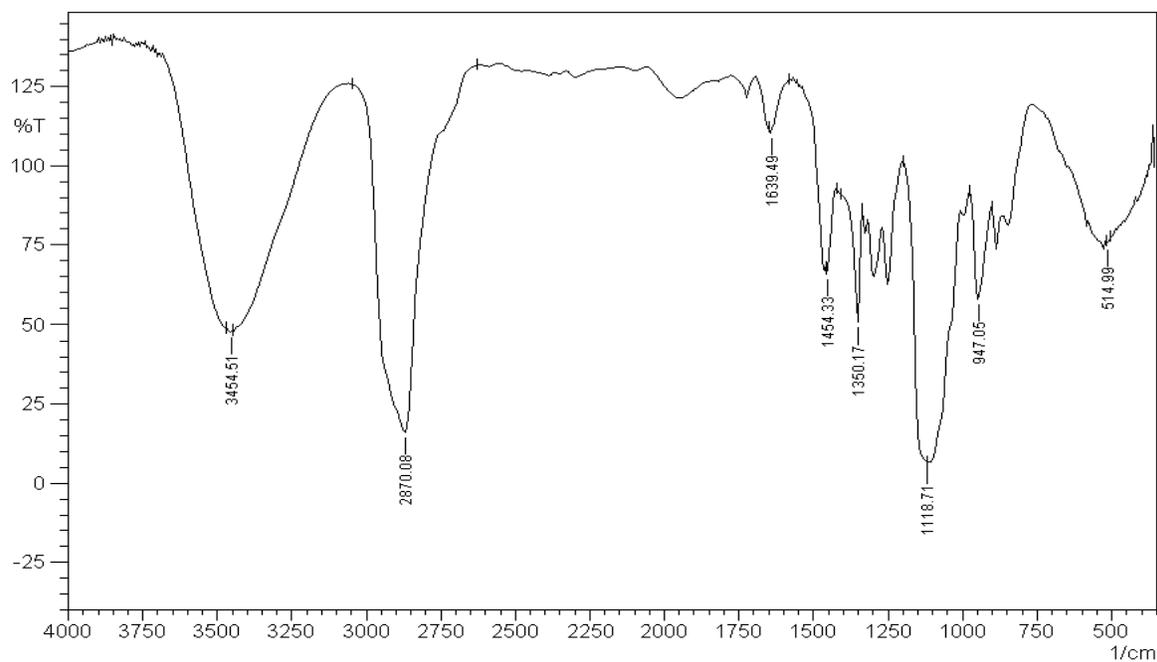
**Scheme 10**



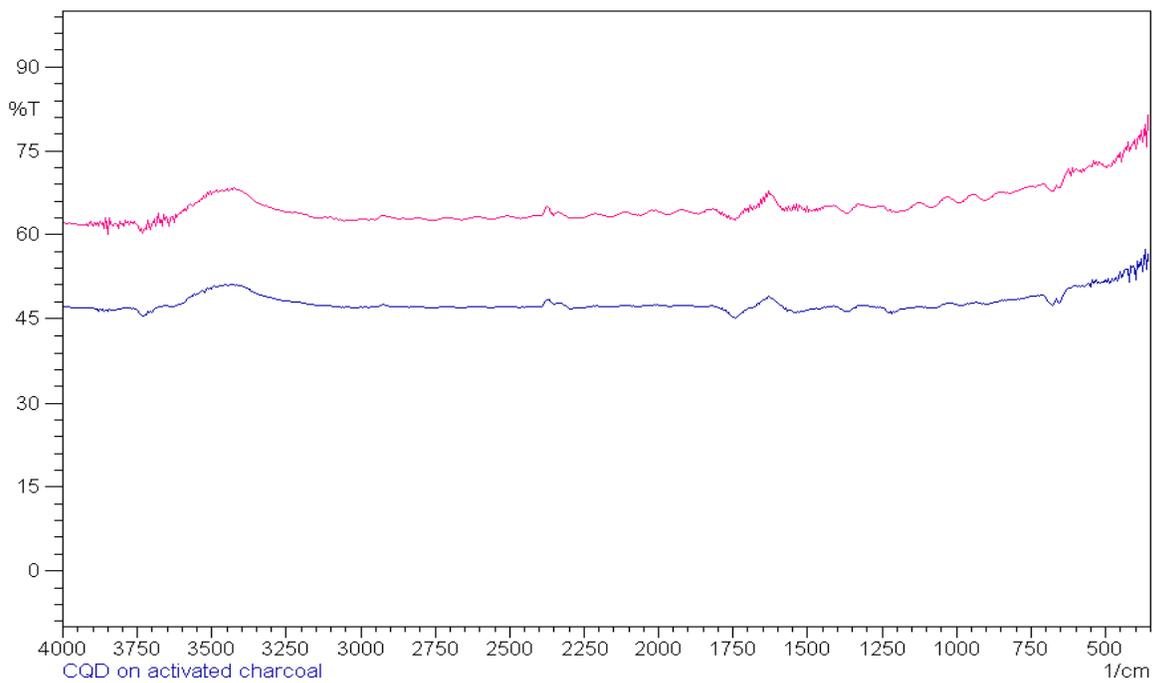
**Scheme 11**

A faint yellow color solution containing CQDs were obtained which when irradiated with UV lamp (365nm) emitted orange fluorescence in CQDs from PEG 400 and blue fluorescence in case of CQDs from potato. We further studied CQDs prepared from PEG-400 using FTIR spectroscopy (fig .6). A band at 1639.49 (C=C stretching) and a strong broad band at 3454.1cm<sup>-1</sup> (-OH) was observed which was absent in PEG-400 IR spectra (fig 3). This confirms formation of CQDs.

We were unable to synthesize CQDs adsorbed on activated charcoal as depicted in fig.7.



**Fig 6:** IR spectra of synthesized CQD's (hydrothermal)



**Fig 7:** IR spectra of CQDs adsorbed on activated charcoal (blue) and IR spectra of plain activated charcoal (red).

### **3.2. APPLICATIONS**

We synthesized CQDs using various methods as discussed above. We then studied the use of these CQDs in organic reactions.

#### **Applications of Quantum Dots as Visible-Light Photoredox catalyst for nitro aldol reaction.**

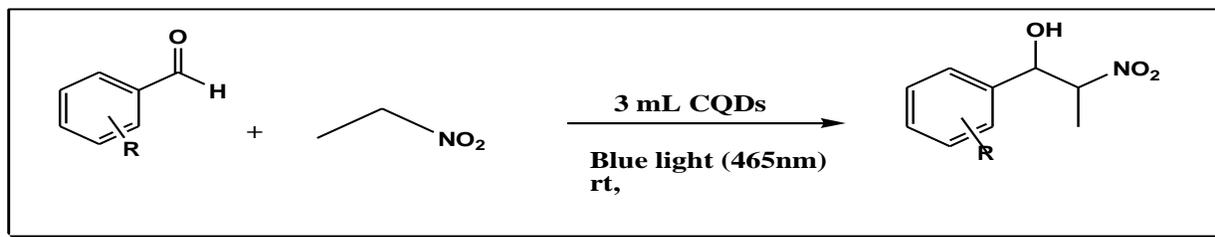
We used nitro aldol reaction as a model reaction to study the application of CQDs as photoredox catalyst using commercially available and inexpensive nitroethane and m-nitrobenzaldehyde as the substrates (model substrate, see Table 1 and Fig.8). After 2 hrs the product was obtained in 87% yield. Control experiments (table.1) confirmed that the presence of CQDs and blue-light (465nm) photoirradiation are important for the photoredox catalytic reactions to occur.

**Table 1: Control reaction for synthesis of 2-nitro-1-(3-nitrophenyl)propan-1-ol (henry reaction ) using CQDs.**

<b><u>Sr.No.</u></b>	<b><u>Condition</u></b>	<b><u>Catalyst</u></b>	<b><u>Solvent</u></b>	<b><u>Time</u></b>	<b><u>% Yield</u></b>
1.	Day Light	CQD's	--	6 hours	69.31
2.	Blue Light	CQD's	--	2 hours	87.26
3.	Day Light	PEG-400	--	1 day	--
4.	Blue Light	PEG-400	--	4 hours	49
5.	Blue Light	--	Acetonitrile	5 days	Traces <sup>a</sup>

a. The yield was too low to be detected by column chromatography. b. the CQDs used was 3ml.

We explored the scope of the reaction with other aryl aldehydes under the optimized reaction conditions. This method is suitable only for aryl Aldehydes possessing electron withdrawing groups (see table 2 entry 1 and Fig. 8). The photoredox catalysis does not proceed for aryl Aldehydes with neutral or electron-donating groups (table 2 entry 2 & 3).



**Table 2:**

Sr. No	Substrate	Product	Time	% yields
1.			2 hrs	87%
2.			6 hrs	a
.3.			6 hrs	a

a. till 6 hrs no product was obtained, further reaction could not be monitored.

The product obtained (table 2 entry 1) was studied using FTIR spectroscopy (fig 8a). A strong two band at  $1531.48\text{cm}^{-1}$  attribute to  $\text{NO}_2$  stretching. Strong band around the range of  $3000\text{-}2850\text{cm}^{-1}$  and a sharp peak at  $1352\text{cm}^{-1}$  are ascribed to the stretching and banding frequencies of C-H. The broad peak at  $3507.73\text{cm}^{-1}$  indicates the stretching vibration of O-H. To further confirm the chemical structure of the product  $^1\text{H}$  NMR spectroscopy (fig 8b) were carried out as shown in fig.9. a singlet at 8.2025 ppm (for aromatic protons with EWG in close proximity), a doublet at 8.150 ppm (for aromatic protons in close proximity with EWG), a doublet at 7.672 ppm (for aromatic protons), a triplet at 7.554 ppm (for aromatic protons), a doublet at 5.124 ppm (for benzylic protons), a multiplet at 5.226 ppm (for aliphatic protons with EWG in environment), a singlet at 3.269 ppm (for alcoholic proton) and a doublet at 1.356 ppm (for aliphatic sp protons). The functional groups of aldol product was determined by  $^1\text{H}$  NMR spectroscopy which are in good agreement with FTIR results

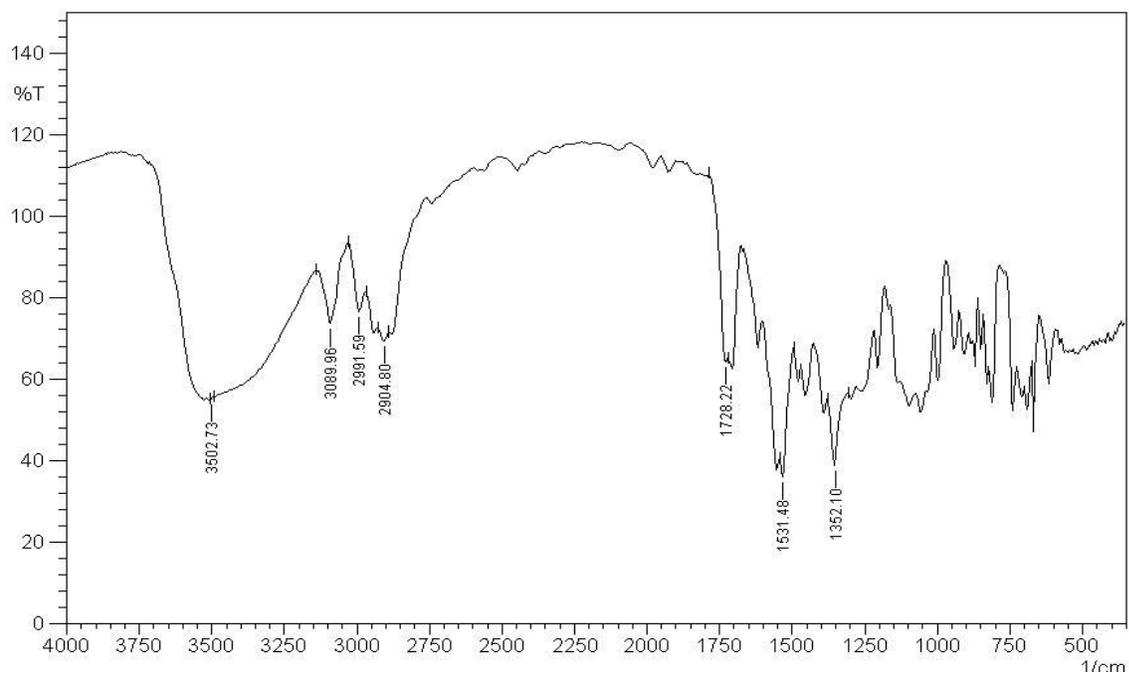


Fig 8: (a) IR spectra

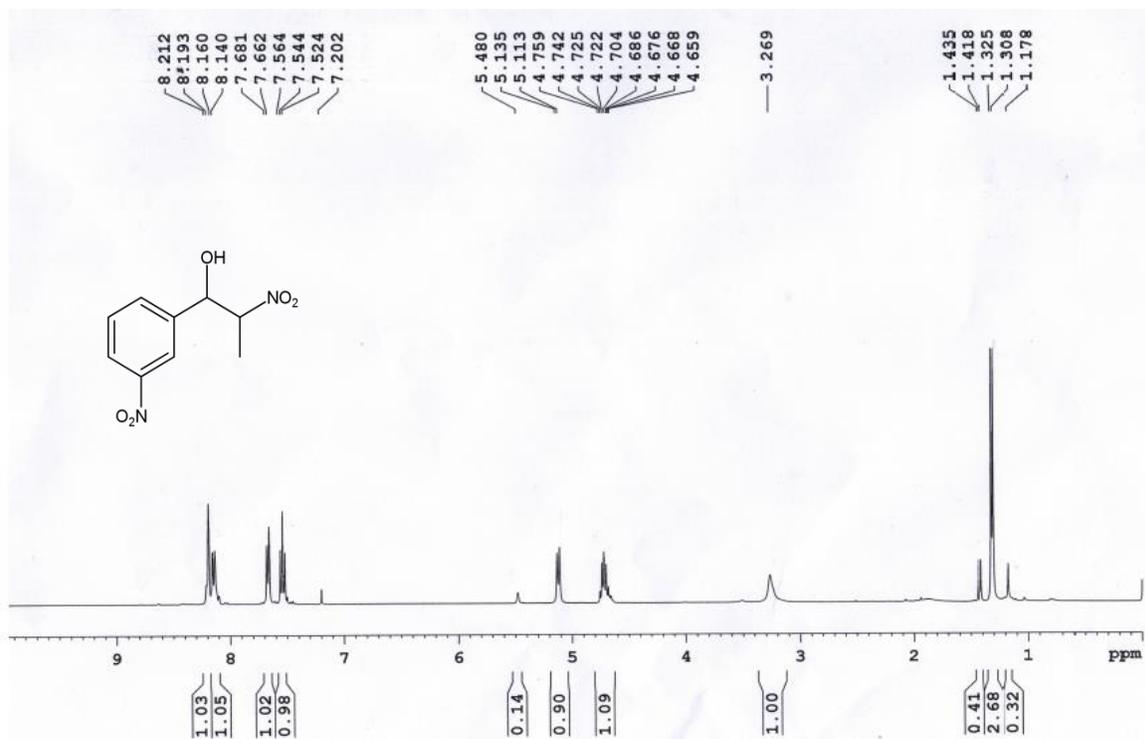
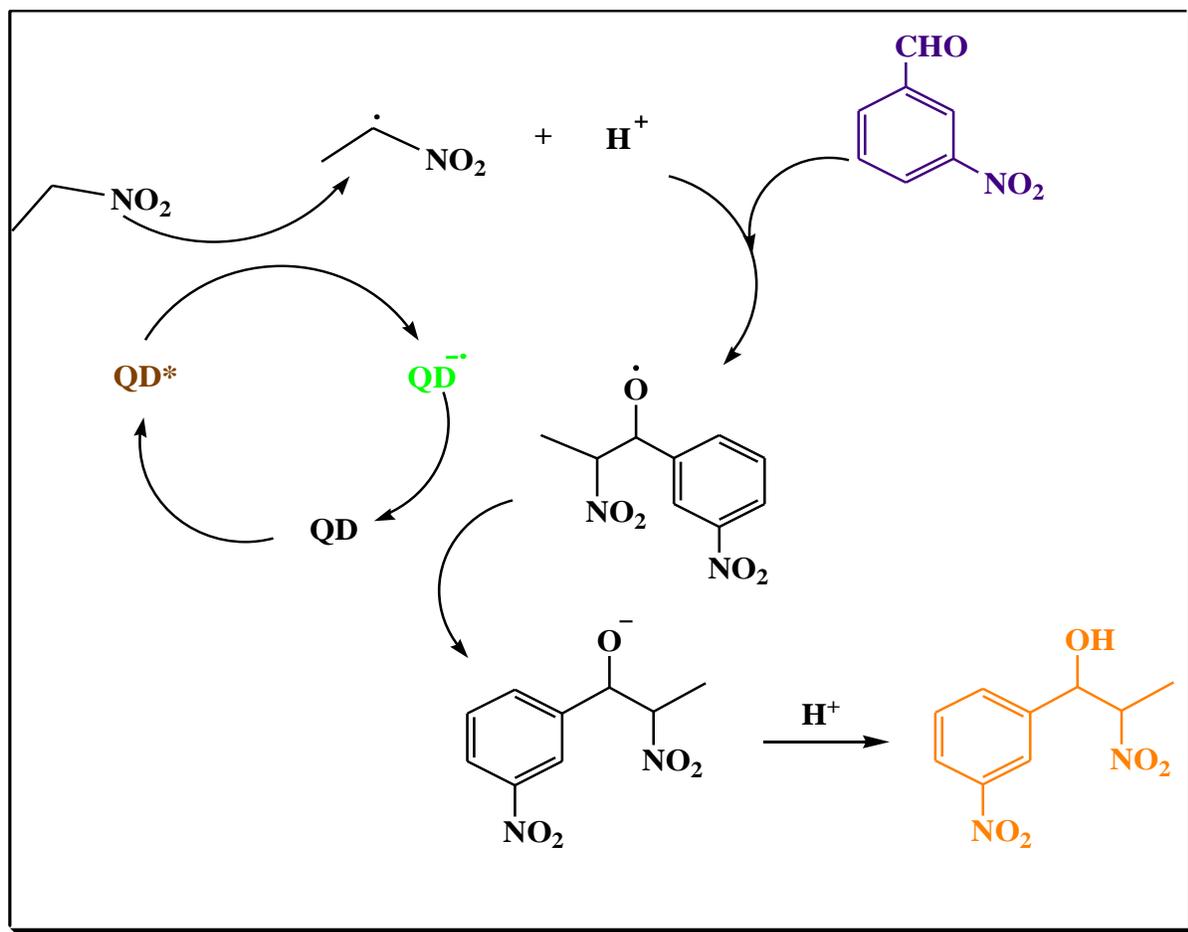


Fig 8: (b) <sup>1</sup>H NMR spectra of nitro aldol product

### 3.3. MECHANISM

Owing to the knowledge of use of carbon quantum dots for the synthesis of nitro aldol product (henry reaction) we proposed a Mechanism of the photoredox catalytic cycle depicted in Figure 9. Upon visible-light photoexcitation, CQDs catalyzes the reaction via single electron transfer mechanism. To yield the desired product.



**Fig. 9:** Probable mechanism of CQDs as photoredox catalyst.

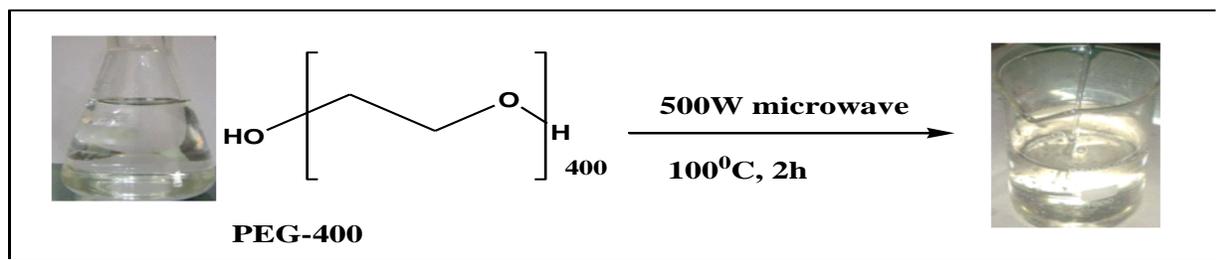
CQDs gets excited and initiates the radical cleavage of nitroethane into stable secondary nitroethane radical and unstable proton radical. Proton radical ( $\text{H}^\cdot$ ) being highly unstable gives its electron to the QD thus forming radical anion of QDs ( $\text{QDs}^{\cdot-}$ ) and  $\text{H}^+$ . Nitroethane radical couples with the m-nitrobenzaldehyde and forms nitro aldol radical. The QDs radical anion transfers an electron to the nitro aldol radical, giving the corresponding anion, which takes a hydrogen atom, likely from the radical cation of nitroethane, to form the nitro aldol product.

# 4. EXPERIMENTAL WORK

## 4.1. SYNTHESIS OF CARBON QUANTUM DOTS.

### 1) Preparation of CQD's by microwave-assisted technique with PEG 400 as carbon source.

PEG of molecular weight 400 Da (PEG 400) was used as both a carbon source and solvent. For synthesizing CQD's 10 ml of PEG 400 was taken into a 50ml Teflon container; and was placed in a 500W microwave reactor to 100°C with a stirring speed of 500rpm by using a magnetic agitator, for 2hrs (scheme 8). The reaction was carried out in absence of gases like O<sub>2</sub>, CO<sub>2</sub>, N<sub>2</sub>, etc. finally the solution was checked for color change, and fluorescence.



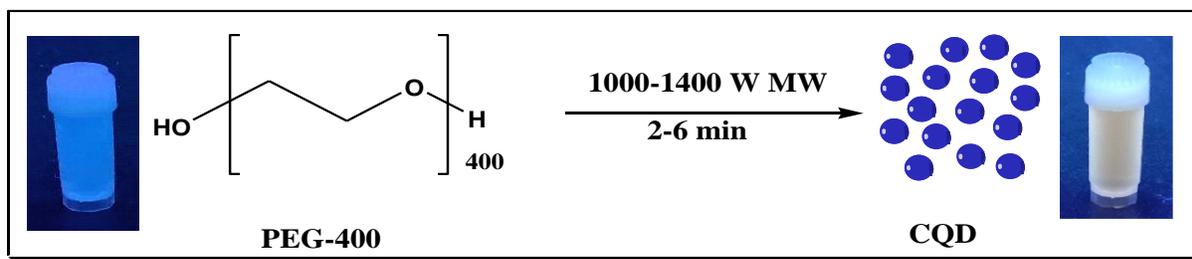
Scheme: 8

### 2) Preparation of CQD's by thermal decomposition with PEG 400 as carbon source.

For preparation of CQD's 15-20 ml of PEG 400 was taken into a 100 ml round bottom flask. This reaction flask was placed in a preheated oil bath at 160°C for different time period (0.5 h, 2 h and 6 h). The reaction time showed a distinct effect on the growth of CQD's. Upon heating the viscous colorless liquid turned into a low viscosity fluid and the color changed to pale yellow and finally became dark brown. The flask was cooled to room temperature and was further characterized using FTIR spectroscopy as shown in Fig. 4 the bands observed are at 3502.73cm<sup>-1</sup> (-OH), 3000-2850cm<sup>-1</sup> (-CH stretch), 1728.22cm<sup>-1</sup> (-C=O), 1531.48cm<sup>-1</sup> (-C=C), 1454cm<sup>-1</sup> (-CH band), and 1110.31cm<sup>-1</sup> (-C-O stretch). When exposed to UV light of 365 nm, the solution exhibited orange-red emission.

### 3) Preparation of CQD's by direct pyrolysis method with PEG 400 as carbon source.

For preparation of CQD's 10 ml of PEG 400 was taken in a 50 ml conical flask. This reaction flask was placed in a microwave oven (1000-1400 W; Domestic oven) for different time period (2 min, 4 min, 6 min, 8 min, 10min and 12 min), and was checked for fluorescence under UV light(365 nm). The reaction time showed a distinct effect on the growth of CQD's. Upon heating the viscous colorless liquid turned into a low viscosity fluid and the color changed to pale yellow and finally became dark brown. During the heating process the flask must not kept for continues heating in the oven i.e. after every 2 min the flask was removed, cooled and then placed (since the glass flask due to overheating might break). Similarly the glass flask was cooled to room temperature for further characterized using FTIR spectroscopy as shown in Fig.5a the bands observed are at  $3435.22\text{cm}^{-1}$  (-OH),  $2872.01\text{cm}^{-1}$  (-CH stretch),  $1643.35\text{cm}^{-1}$  (-C=O),  $1454.33\text{cm}^{-1}$  (-CH band), and  $1103.28\text{cm}^{-1}$  (-C-O stretch). When exposed to UV light of 365 nm, the solution exhibited orange-red emission, as shown in Scheme 9. The CQDs were further studied using UV-vis (fig. 5b) and PL (fig. 5c) spectroscopy.



Scheme: 9

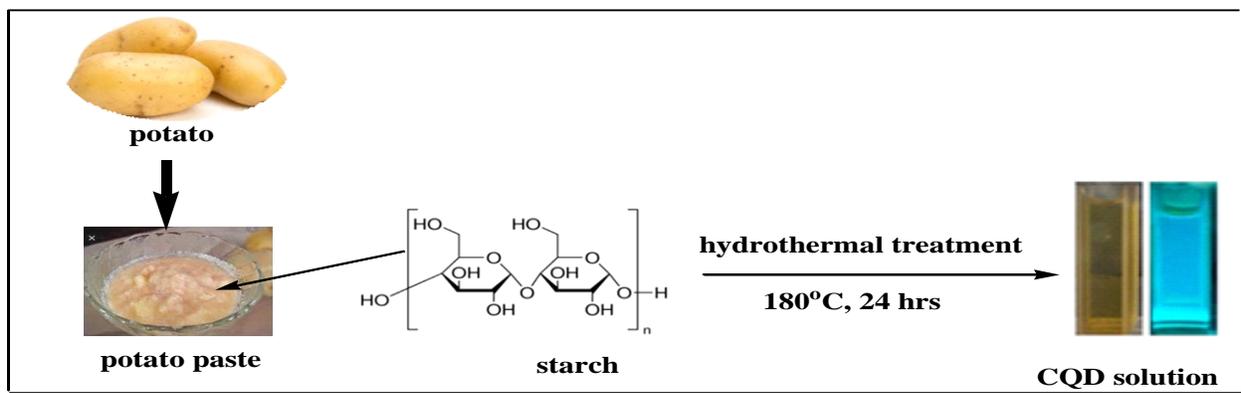
### 4) Preparation of CQD's by direct pyrolysis method with potato as carbon source.

Potato was used as carbon source and water as solvent since CQD's are water soluble. For preparation of CQD's 2 potatoes was peeled and grinded into thick puree without adding water. 5 ml of puree and 5 ml of water was mixed and this mixture was taken in a 50 MI flask. This reaction flask was placed in a microwave oven (1000-1400 W; Domestic oven) for different time period (2 min, 4 min, 6 min, 8 min, 10min and 12 min), and was checked for fluorescence



## 6) Preparation of CQD's by direct hydrothermal method with potato as carbon source.

A hydrothermal method was used to prepare the CQDs. Briefly, 5 ml potato paste was mixed with 5 ml distilled water, after which the mixture was transferred into a 50 ml Teflon-lined stainless steel autoclave. The mixture was then heated at 180 °C for 24 h under vigorous stirring. After being cooled to room temperature naturally, the resulting dark brown mixture was centrifuged for 1 hr 1000 rpm, so that the non-fluorescent substance gets deposited and fluorescent CQDs are well separated. This prepared CQDs were then extracted using ethyl acetate. The dark yellow organic layer was separated and excess solvent was distilled using a rotary evaporator. When exposed to UV light of 365 nm, the solution exhibited blue emission, as shown in Scheme 11. The prepared CQDs were subjected for further study, and stored at 4 °C for further use.



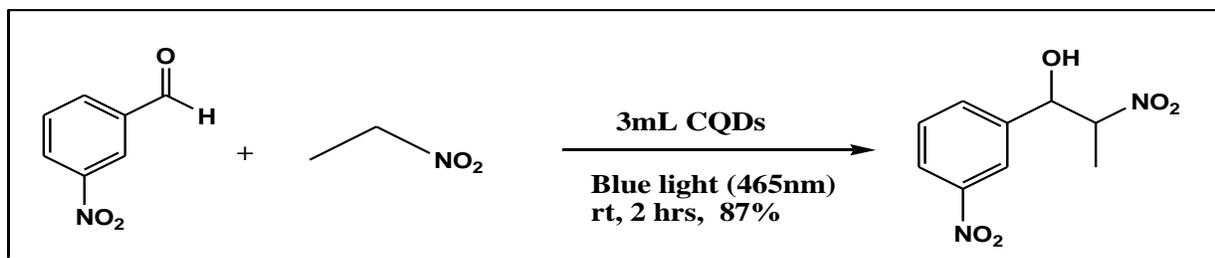
Scheme: 11

## 4.2. APPLICATION OF CQDs.

### 4.2.1. Application of CQDs in nitro al.dol reaction (Henry reaction).

#### a) Synthesis of 2-nitro-1-(3-nitrophenyl)propan-1-ol

1 g of m-nitrobenzaldehyde (0.0066M) and 0.95mL of nitroethane (0.013M) was taken in a 50 mL round bottom flask. To this 3mL of synthesized CQDs was added and the mixture was reflux in blue Light environment with stirring on magnetic stirrer for 2 hours (scheme 12). The same reaction was performed under different conditions and different time intervals as depicted in table 1. The reaction was monitored using TLC. After the completion of reaction the mixture was poured in 10mL distilled water as the CQDs are water soluble and the organic layer containing excess of reactants was discarded. The aqueous layer containing CQDs was transferred into separating funnel and extracted using ethyl acetate. The dark yellow organic layer was separated and Excess solvent was distilled using a rotary evaporator. The crude compound was purified using column chromatography.

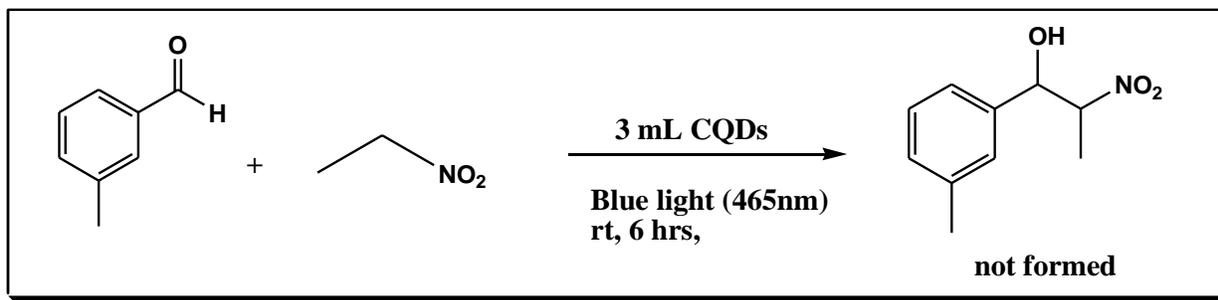


**Scheme: 12**

Further FTIR spectroscopy studies were carried out to investigate the formation of product as shown in fig.8a following peaks were observed  $1531.48\text{cm}^{-1}$ (-NO<sub>2</sub>),  $3000\text{-}2850\text{cm}^{-1}$ (stretching-CH),  $1352\text{cm}^{-1}$ (Bending -CH) and  $3507.73\text{cm}^{-1}$ (-OH). To further confirm the chemical structure of the product <sup>1</sup>H NMR spectroscopy were carried out as shown in fig.8b the peaks obtained were 8.2025 ppm (1H, singlet), 8.150 ppm (1H, doublet), 7.672 ppm (1H, doublet), 7.554 ppm (1H, triplet), 5.124 ppm (1H, doublet), 5.226 ppm (1H, multiplet), 3.269 ppm (1H, singlet) and 1.356 ppm (3H, doublet).

### b) Synthesis of 2-nitro-1-m-tolylpropan-1-ol

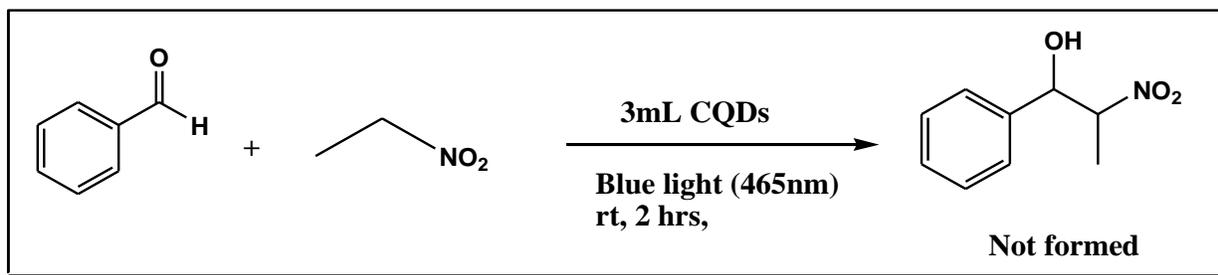
0.89mL of anisaldehyde (0.0073M) and 1.1mL of nitroethane (0.015M) was taken in a 50 mL round bottom flask. To this 3mL of synthesized CQDs was added and the mixture was reflux in blue Light environment with stirring on magnetic stirrer for 6 hours (scheme 13). The reaction was monitored using TLC.



Scheme: 13

### c) Synthesis of 2-nitro-1-phenylpropan-1-ol.

0.96 mL of benzaldehyde (0.009M) and 1.42mL of nitroethane (0.018M) was taken in a 50 mL round bottom flask. To this 3mL of synthesized CQDs was added and the mixture was reflux in blue Light environment with stirring on magnetic stirrer for 6 hours (scheme 14). The reaction was monitored using TLC.



Scheme: 14

# 5. CONCLUSION

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In conclusion, three different methods (bottom up) were successfully utilized to prepare CQDs efficiently. CQDs were also prepared from new source (potato). Synthesized CQDs were characterized by its fluorescence and other spectroscopic techniques. A facile one step Microwave method is applied to synthesize CQD's using PEG-400. Efficacies of synthesized CQDs were utilized in nitroaldol reaction. The obtained CQD's under Blue light ( $\lambda_{\text{max}}=465\text{nm}$ ) act as a brilliant catalyst for Nitro-Aldol reaction giving 87% yield in 2 hours. CQDs were also screened for various other aldehydes and nitromethane but did not give any yield.

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