

**In the name of God**

**Carbon quantum dots and their applications**

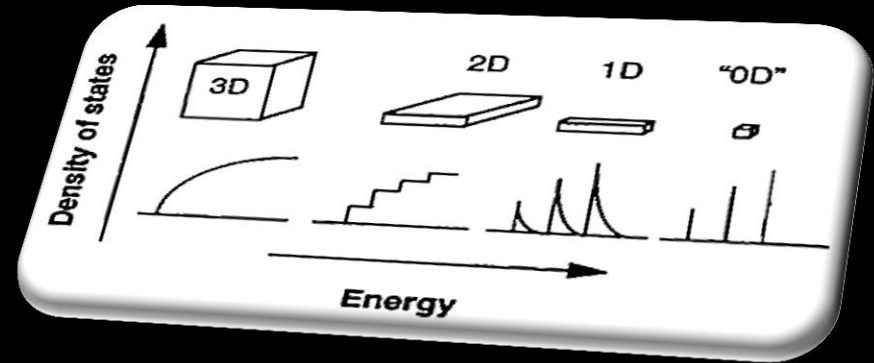
*Marzieh pashaei*



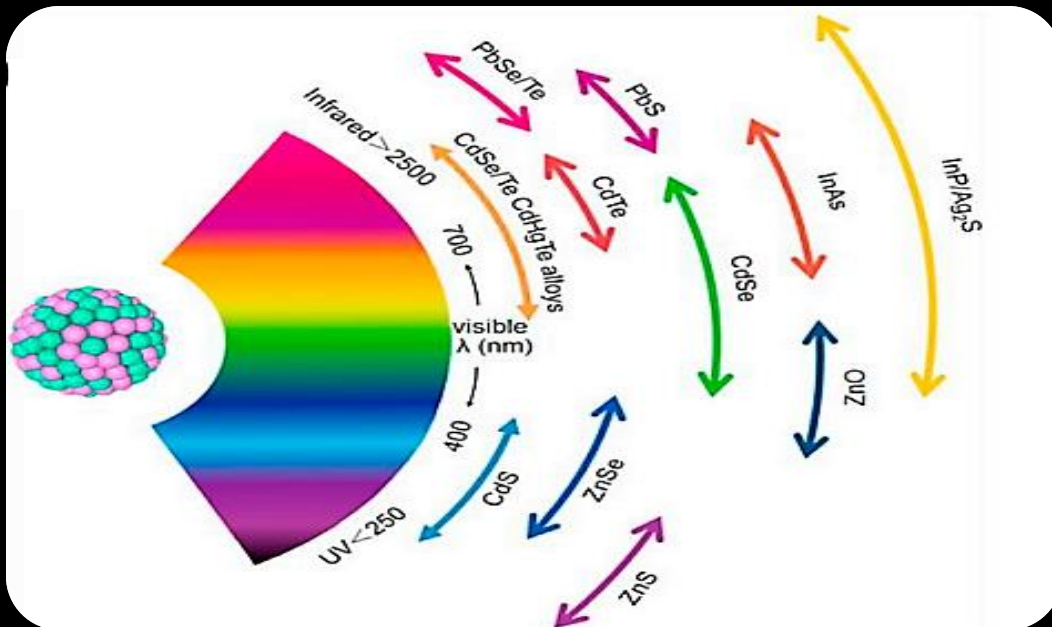
# 1. Introduction

The nanomaterials can be categorized into:

- 1) zero-dimensional or quantum dots (QDs)
- 2) one-dimensional ones, e.g., nanowires
- 3) two-dimensional ones, e.g., thin films



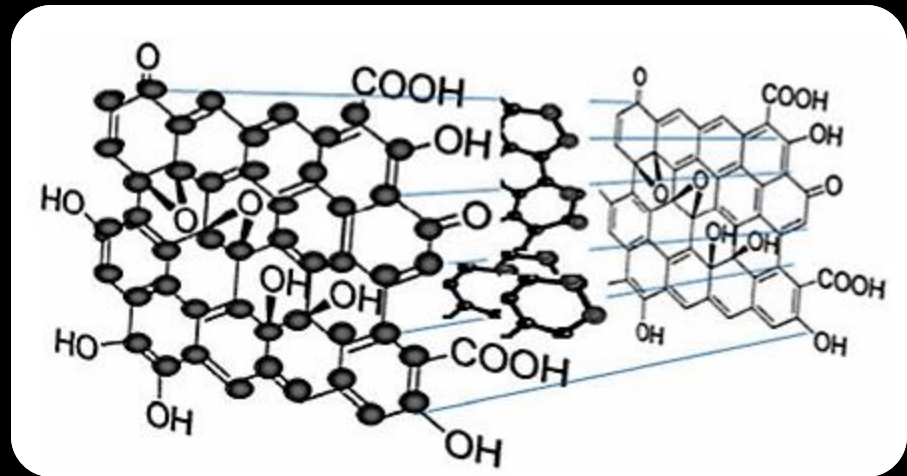
**in any material, the substantial variation of fundamental electrical and optical properties strongly depends on their size because the quantum confinement of both the electron and hole in all three dimensions leads to an increase in the effective bandgap of the material**



**QDs such as CuInSe , PbS and Ag2S , possessing higher near-infrared (NIR) emission properties, have also attracted attention in the field of bioimaging**

Illustration representing the emission wavelength of colloidal QDs.  
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**CQDs are typically quasi-spherical nanoparticles comprising amorphous to nanocrystalline cores with predominantly graphitic or turbostratic carbon (sp<sup>2</sup> carbon) or graphene and graphene oxide sheets fused by diamond-like sp<sup>3</sup> hybridised carbon insertions**

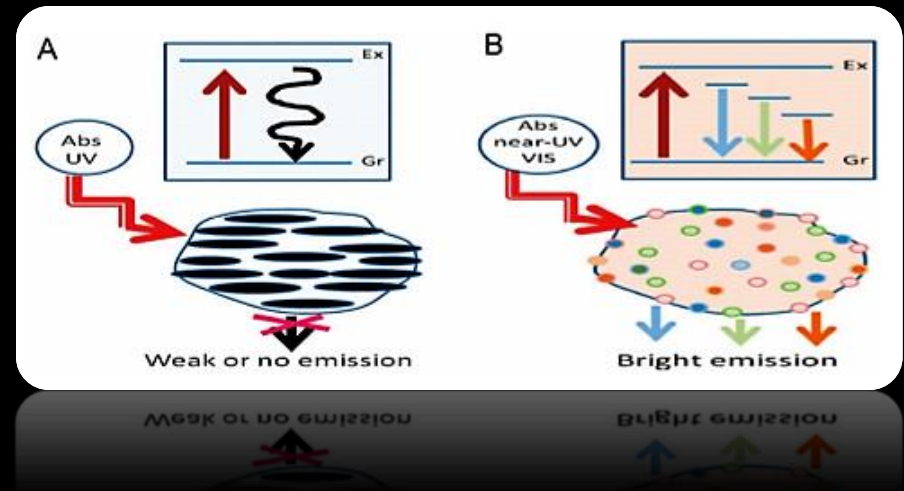


Chemical structure of CQDs

- ❖ Among the electronic and physicochemical characteristics of CQDs, their optical properties and their fluorescence emissions in particular have attracted increasing interest in recent years.
- ❖ semiconductor quantum dots have been extensively investigated for their strong and tunable fluorescence emission properties, which enable their applications in biosensing and bioimaging.
- ❖ semiconductor quantum dots possess certain limitations such as high toxicity due to the use of heavy metals in their production.
- ❖ This prompted the creation of CQDs to replace semiconductor quantum dots due to their low toxicity, biocompatibility, low cost and chemical inertness in addition to having similar fluorescence properties

## 2. Fluorescence properties of CQDs

(A) CQDs with strong absorption in the UV region and weak emissions and (B) CQDs with weak absorption in the near UV-vis region but strong multicolour emissions in the visible region



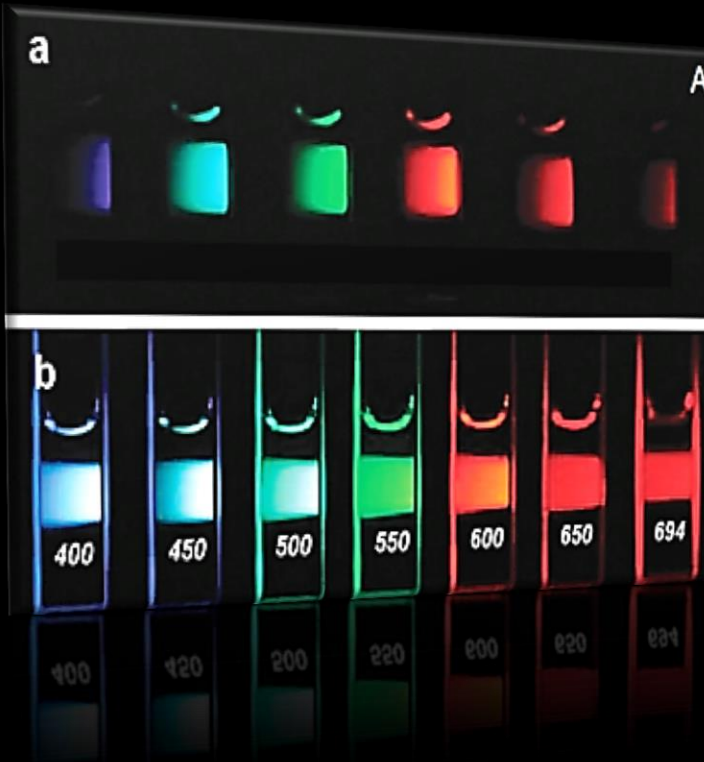
### 2.1 Fluorescence emissions from bandgap transitions of conjugated P-domains

- ❖ These p-domains are isolated by creating sp<sup>2</sup> hybridised islands rich in p-electrons through the reduction of graphene oxides obtained by using Hummers method of oxidising and exfoliating graphite flakes.
- ❖ Such electronic transitions display strong absorption in the ultraviolet (UV) region, but weak or no fluorescence emissions

### 2.2 Fluorescence emissions of surface defect-derived origins

- ❖ The second class of the fluorescence mechanism arises from surface-related defective sites – generally any sites that have nonperfect SP<sup>2</sup> domains will result in surface energy traps.
- ❖ These surface defects behave like aromatic molecules that are individually incorporated into solid hosts, exhibiting multicolour emissions due to the existence of multiple surface defects with different excitation and emission properties

## **2.3 Tunable fluorescence emissions of CQDs**



- ❑ *The tunable emissions of the surface-passivated CQDs could be a result of varied fluorescence characteristics of particles of different sizes of the CQDs and the distribution of different emissive sites on the surface of the CQDs.*
- ❑ *In addition to the excitation wavelength-dependent emission, several reports have indicated that the fluorescence emissions of CQDs are pH-dependent*

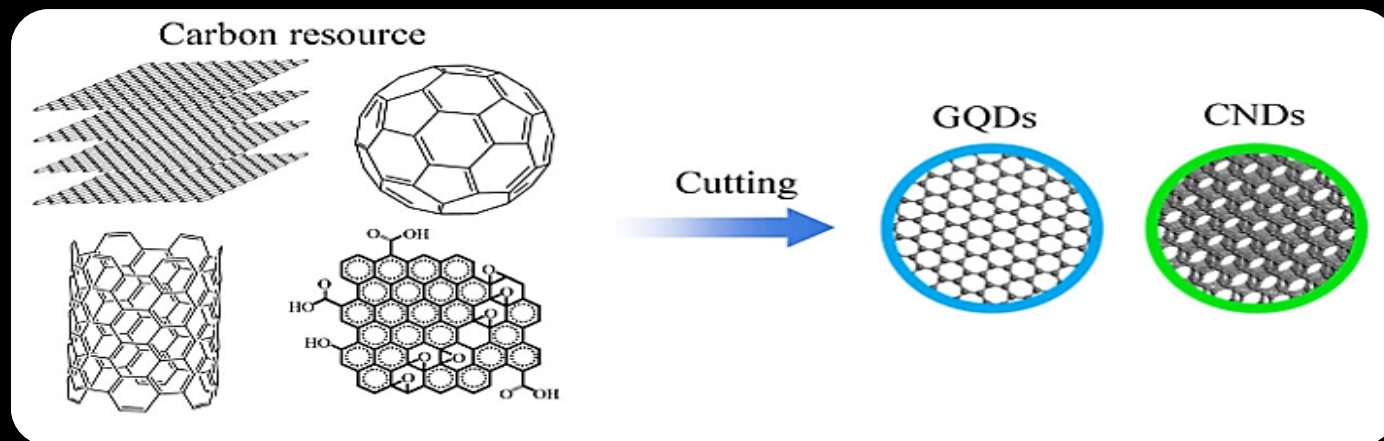
## **2.4 Up-conversion fluorescence**

Up-conversion fluorescence emission is an optical phenomenon wherein the fluorescence emission wavelength is shorter than the used excitation wavelength, which is particularly attractive for in vivo bioimaging since bioimaging at longer wavelengths especially in the NIR region is usually preferred owing to the improved photon tissue penetration and reduced background auto-fluorescence.

### 3. Synthesis of CQDs

#### 3.1 Top-down synthetic route

The former involves breaking down larger carbon structures, such as nanodiamonds, graphite, carbon nanotubes, carbon soot, activated carbon and graphite oxide by methods like arc discharge, laser ablation and electrochemical oxidation



The most common cutting method uses a concentrated oxidizing acid (HNO<sub>3</sub> or an H<sub>2</sub>SO<sub>4</sub>/HNO<sub>3</sub> mixture).

In this process, the bulk carbon materials are cut into small pieces and the surfaces of the pieces are modified by oxygen-based groups. The resulting small carbon product is known as GQDs, CQDs, or CNDs.

- Electrochemistry
- hydrothermal/solvothermal/special oxidation
- metal-graphite intercalation
- discharge
- laser ablation
- nanolithography by reactive ion etching (RIE)

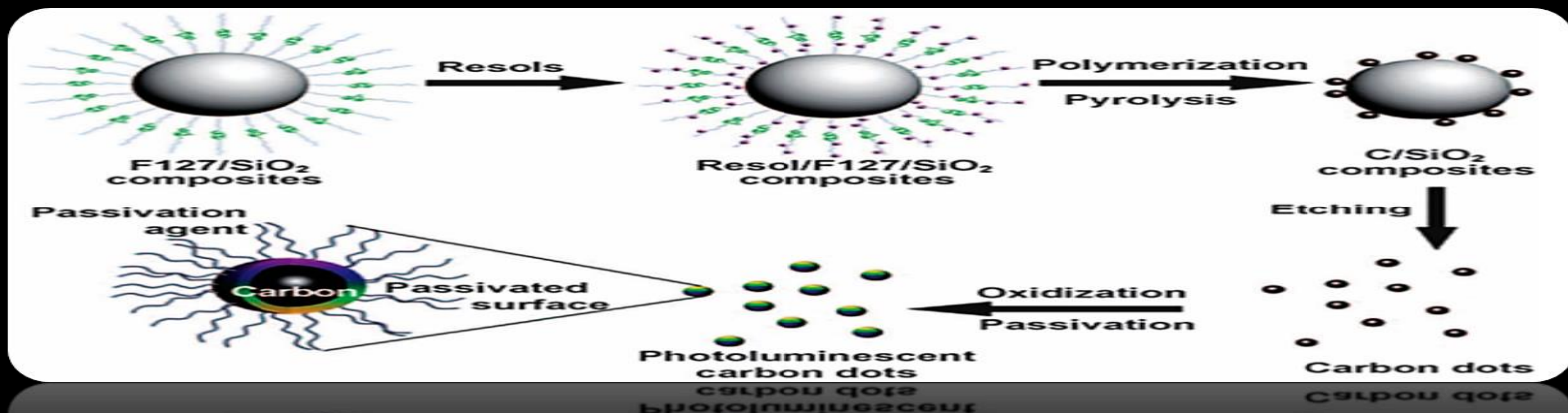


### 3.2 Bottom-up synthetic route

the “bottom-up” approaches synthesise CQDs from molecular precursors such as citrate, carbohydrates and polymer–silica nanocomposites through combustion/ thermal treatments, and supported synthetic and microwave synthetic routes



- hydrothermal
- microwave
- combustion methods
- pyrolysis in concentrated acid
- carbonization in a microreactor
- enhanced hydrothermal (microwave-hydrothermal and plasma-hydrothermal ) methods

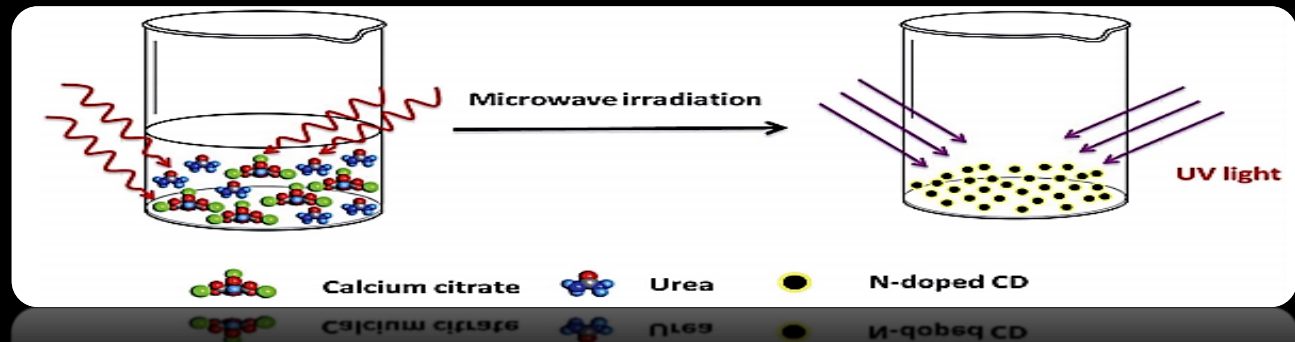


Supported-synthesis of CQDs using modified silica spheres as carriers and resols as carbon precursors

## hydrothermal method

- I. 40 mg of glucose and 1090 mg of  $\text{KH}_2\text{PO}_4$  with the molar ratio of glucose/ $\text{KH}_2\text{PO}_4$  of 1/36 were dissolved in 40 mL of deionized (DI) water.
- II. The solution was then placed in a Teflon-lined autoclave chamber and  $\text{N}_2$  was blown into it for 1 hour to remove  $\text{O}_2$  dissolved in the solution.
- III. the chamber was sealed and put into an oven. Upon completion of hydrothermal reaction in the oven at 200  $^{\circ}\text{C}$  for 12 hours, the reaction product was centrifuged at 9000 rpm for 15 minutes to remove the black precipitates.
- IV. The yellow supernatant was collected and freeze dried. The powder thus obtained was re-dispersed in ethanol to form a yellow suspension through vortexing and the dispersion was allowed to stand for 2 hours to allow the free salt to precipitate from ethanol.
- V. The yellow ethanol solution was then filtered through a PTFE syringe filter with pore size of 1.0  $\mu\text{m}$  and ethanol was gently evaporated off through rotary evaporation.

## Microwave method



- i. Calcium citrate (3 g, 5.3 mmol) and urea (3 g, 50.0 mmol) were placed in 10 mL deionized water and stirred to form a suspension.
- ii. After heating the heterogeneous solution in a domestic microwave oven (800 W) for 5 min, the suspension solution changed from a turbid liquid to a yellow clustered solid, indicating the formation of N-doped CDs.
- iii. The solid was then heated at 60 $^{\circ}\text{C}$  for 1 h. The turbid liquid of the crude N-doped CDs was centrifuged at 8270g for 30 min to remove the unreacted calcium citrate.
- iv. The obtained solution was concentrated and then transferred to a silica gel column.
- v. Next, the solution was eluted with mixtures of methanol and dichloromethane at ratios varying from 1 : 2 to 1 : 1 (v/v) to obtain bright yellowish-green fluorescent N-doped CDs.



# Microwave-Assisted Synthesis of Poly(L-lysine)-Based Polymer/Carbon Quantum Dot Nanomaterials for Biomedical Purposes

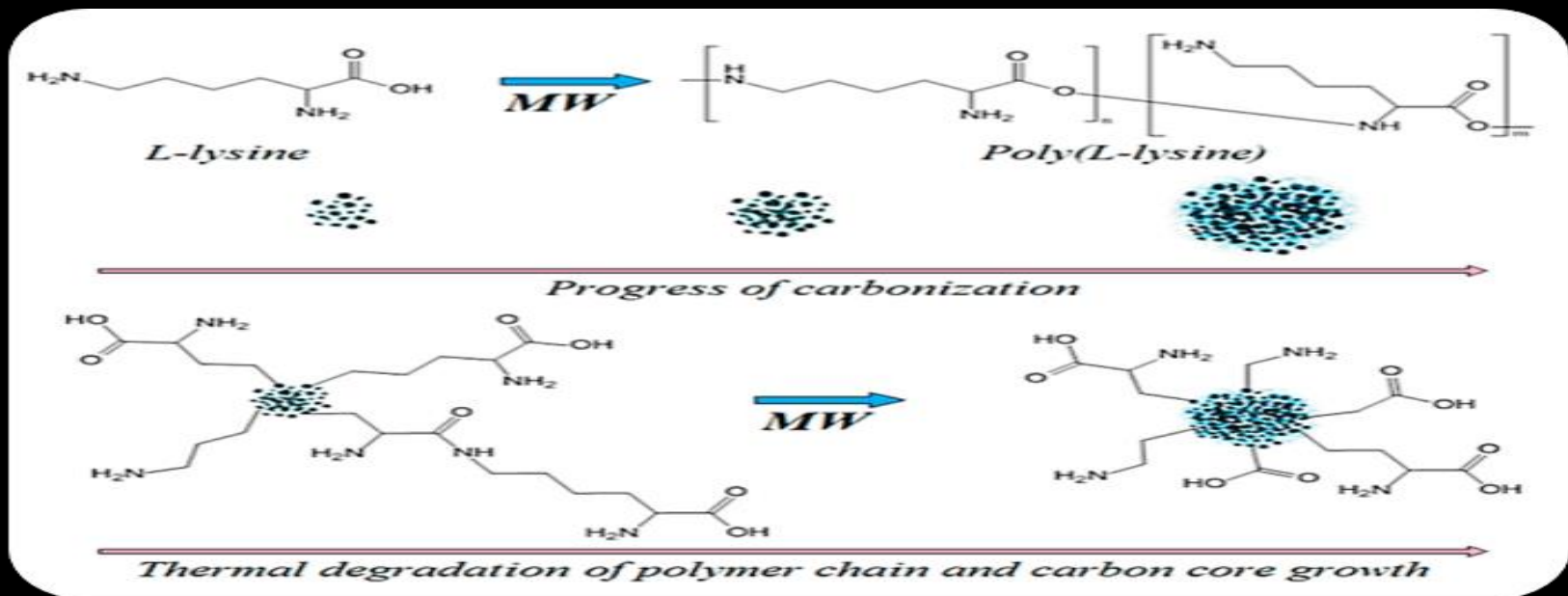
## -Poly(L-lysine)-Based CQDs Preparation

- 5 g of L-lysine and 15 mL of propylene carbonate were added into the reaction vessel reaction vessel was placed into a Prolabo Synthewave 402 microwave (MW) reactor
- During the polycondensation process, lysine was successfully dissolved in propylene carbonate. The ready product was cooled down

Table 1. Synthesis parameters of poly(lysine)/carbon quantum dot obtainment under MW radiation.

Entry	Poly(L-Lysine) in Propylene Carbonate, g	Amount of 35% H <sub>2</sub> SO <sub>4</sub> , mL	Reaction Time, min	MW Power, W
CQDs-1	0.40	0.20	1	300
CQDs-2	0.40	0.20	2	300
CQDs-3	0.40	0.20	3	300
CQDs-4	0.40	0.20	4	300
CQDs-5	0.40	0.20	5	300
CQDs-6	0.40	0.40	1	300
CQDs-7	0.40	0.40	2	300
CQDs-8	0.40	0.40	3	300
CQDs-9	0.40	0.40	4	300
CQDs-10	0.40	0.40	5	300

CQDs-10	0.40	0.40	2	300
CQDs-2	0.40	0.40	4	300
CQDs-8	0.40	0.40	3	300
CQDs-5	0.40	0.40	5	300

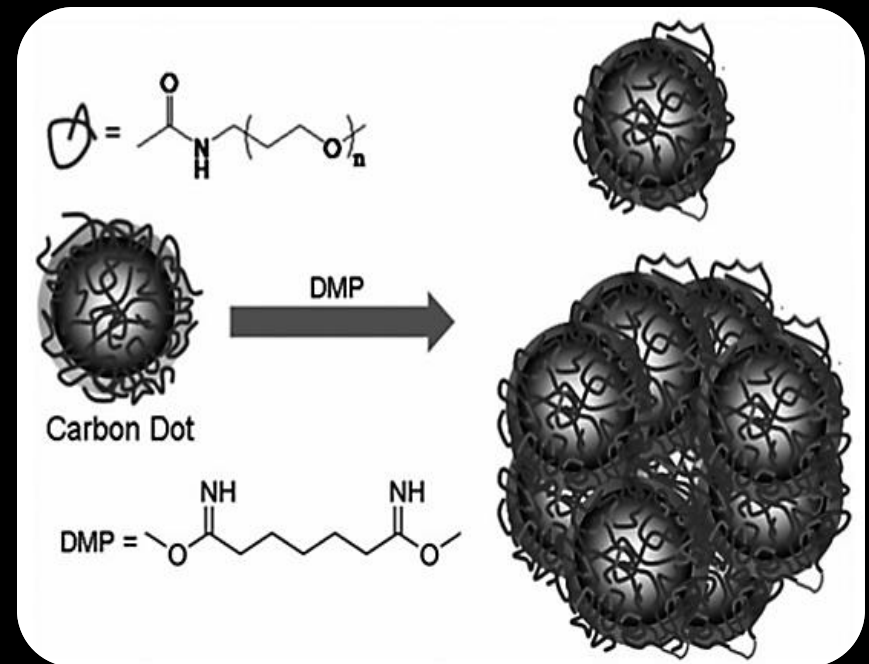


- After carbonization process, the aquatic solution of the product was diluted using distilled water followed by placing in an ultrasonic bath for 10 min (set temperature  $-50^{\circ}\text{C}$ ).
- the solution was purified from macro particles using standard filter paper.
- the solution was treated with sodium hydroxide (2 M) to achieve  $\text{pH} = 7$  and separated from microparticles by membrane filters with the pore diameter of  $0.2 \mu\text{m}$ .
- pre-purified solutions were separated from micro and nano leftovers of the low and high molecular weight non-carbonized poly(lysine) fragments using dialysis tubes

### 3.3 Surface passivation and functionalization

- ❖ Surfaces of CQDs possess high sensitivity to contaminants in their environment, such that their properties are easily affected by tiny levels of contaminants.
- ❖ **Surface passivation of CQDs is performed to reduce the detrimental effect of surface contamination to their optical properties.**
- ❖ effective surface passivation is an essential step in order to produce CQDs with high fluorescence intensities.
- ❖ CQDs whose surfaces are unpassivated or “naked” might emit colourful fluorescence, but their quantum yields are generally low

Anilkumar's group introduced the concept of crosslinking surface passivated CQDs for better optical performance. They showed that crosslinking of the passivating PEG1500N on the surface of CQDs results in the formation of fluorescent particles that contain multiple CQDs in covalently-bound clusters

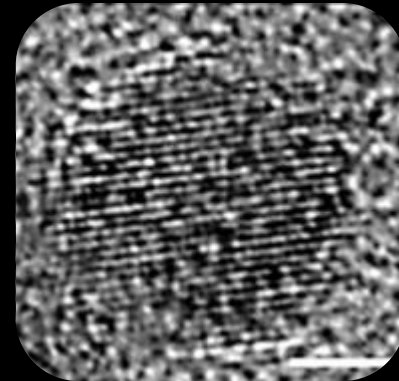
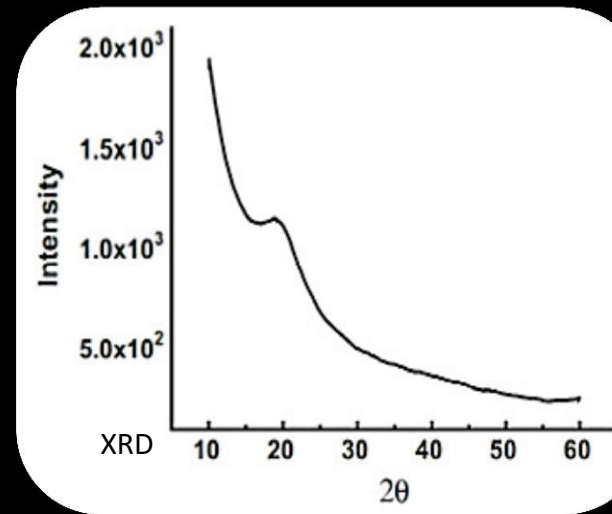
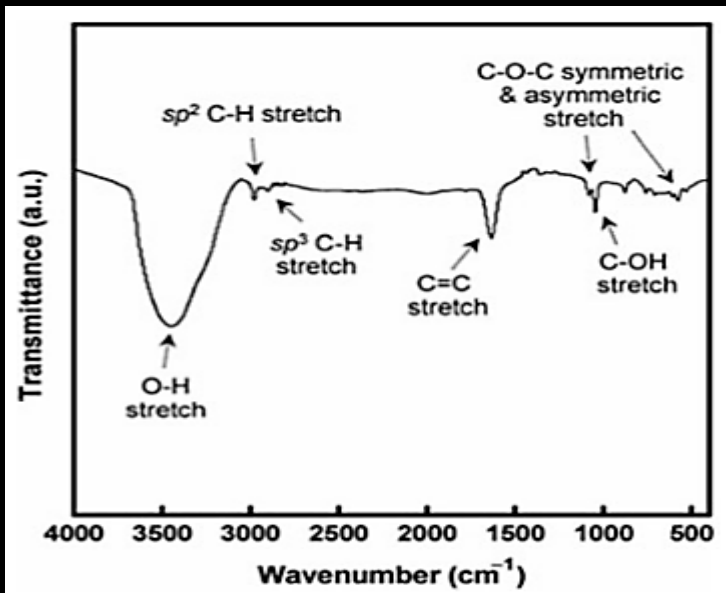


Crosslinking of PEG1500N-functionalised CQDs by reaction with dimethyl pimelidate in a pH 8 phosphate buffer



## 4. Characterization

- The morphology of the samples observe by transmission electron microscopy (TEM) and atomic force microscopy (AFM)
- Photoluminescence (PL) and photoluminescence emission (PLE) spectra were recorded using a fluorescent spectrophotometer
- Ultraviolet-visible (UV-Vis) absorption spectrum record using a UV-Vis-NIR spectrophotometer
- Light source for the fluorescence microscopy observations was a halogen lamp or a mercury lamp with a fluorescent filter cube
- X-ray diffraction (XRD)



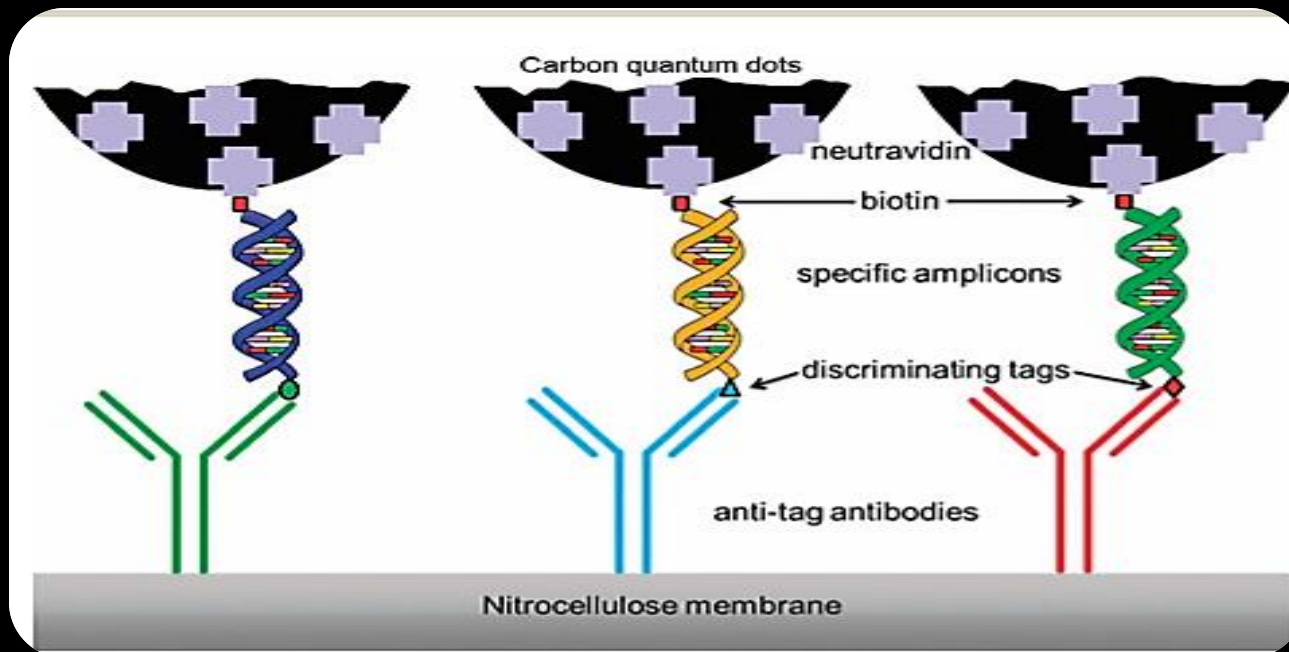
## 5. Applications of CQDs

### 5.1 Chemical sensing

One of the first attempts of utilising CQDs in chemical sensing is the selective detection of  $Hg^{2+}$  in aqueous solutions and live cells

### 5.2 Biosensing

CQDs were shown to have higher sensitivity as labels in lateral flow assays (LFAs) in comparison to gold or latex nanoparticles



*Schematic illustration of NALFIA*



### **5.3 Bioimaging**

It has been demonstrated that surface passivating agents of low cytotoxicity can be used safely at high concentrations for in vivo imaging.

For example, PEGylated CQDs showed no noticeable toxic effects in vivo up to 28 days when intravenously injected 8–40 mg  $kg^{-1}$  (CQD/bodyweight) of the PEGylated CQDs into mice for toxicity evaluation

### **5.4 Nanomedicine**

- ❖ CQDs are also very attractive in nanomedicine because they do not show any visible signs of toxicity in animals and thus can be used for invivo studies.
- ❖ CQDs do not limit the activity of thrombin and do not lead to any blood coagulation

### **5.5 Photocatalysis**

The demonstrated capability of harnessing long wavelength light and energy exchange with solution species of CQDs offers an excellent opportunity for their use as photo catalysts in organic synthesis.

Smaller CQDs (1–4 nm) are effective NIR light-driven photo catalysts for selective oxidation of alcohols to benzaldehydes with good conversion efficiency (92%) and selectivity (100%), due to their excellent catalytic activity for H<sub>2</sub>O<sub>2</sub> decomposition and NIR light driven electron transfer property