

Citrus aurantium as an economical and massive source of carbon in CQDs synthesis for bandgap tuning in optoelectronic applications

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Abstract

As a promising quantum material, carbon quantum dots (CQDs) have been widely applied in almost every optoelectronics device and application but the conventional synthesis methods were not eco-friendly due to the use of toxic and heavy metals. We explored an entirely novel approach, utilizing citrus aurantium (bitter orange) as the carbon source and produced CQDs with 4–6 nanometers in diameter and blue, green, and orange emissions. For the purpose of bandgap tuning, we were able to increase the bandgap energy of CQDs by adding a certain amount of urea and polyethylene glycol to the precursor solution in the synthesis procedure. The bandgap energy of CQDs increased from 2.5 to roughly 3.8 eV. Our approach is thoroughly new which brings about a facile, eco-friendly, and low-cost synthesis method.

I Introduction

In recent decades, the application of semiconductor quantum dots was rather extensive in biosensing, bioimaging, laser, and optics due to their fluorescence emission[1][2]. Their sophisticated methods of synthesizing because of the utilization of heavy and toxic metals limit their function and make them less popular[3][4]. These limitations gave rise to the creation of non-toxic (CQDs) with similar emission properties. Therefore, there is an increasing demand for utilizing carbon nanomaterials and (CQDs) in several branches of science such as physics, chemistry, and biology due to their safe and superior optical characteristics[5][6]. The first invention of (CQDs) happened in 2004 by Xu[7] and that was the beginning of intensive research on the creation of fluorescence carbon nanomaterials. As Yang specified, the categories of carbon-based nanomaterials include graphene quantum dots (GQDs), carbon polymer dots, and carbon nanodots[8]. (GQDs) are semiconductors that are size-dependent and quite well known for their high carrier mobility, excellent chemical stability, and non-toxicity[9], [10]. They have been widely used in various applications including bio-sensing[11], bio-imaging[12], photodetectors[13] light-emitting diodes, and solar cells. There are two approaches for synthesizing of GQDs known as bottom-up and top-down. For instance, pulsed laser ablation (PLA)[14], oxidative /reductive cutting[15], and electrochemical cutting[16] are three examples of the top-down method. Although they are well-known and well-established there are some corrosive and severe reagents in the synthesis process that limit their application[17]. On the other hand, the bottom-up synthesis methods are surprisingly simpler than the top-down routes. Generally, the chemical reactions in almost every bottom-up method are exceptionally under control therefore we can have GQDs with different structures and photoluminescence properties. Hydrothermal[18], soft-template[19], and microwave-assisted[20] are some examples of famous bottom-up routes. In the hydrothermal synthesis method, GQDs crystalize and grow from a solution consisting of small precursor molecules with high pressure and temperature[21]. Some researchers used chemical carbon source ingredients such as citric acid, 1,5-dinitronaphtalene[22], and L-glutamic acid[23] and nitrogen sources for the purpose of producing N-GQDs in numerous applications. Dong et al synthesized GQDs using acid citric as a carbon source with blue color emission in 2012[24]. GU et al used ethylenediamine as a nitrogen source for the synthesis of GQDs[25]. Although the process of synthesizing using the hydrothermal method is somehow safe and eco-friendly the substances used in

the processes mentioned earlier are all inorganic or sometimes overpriced. Recently saving the earth from toxic materials is the priority in the industry. To this end, utilizing safe, natural, and low-cost accessible materials in the synthesizing process helps us achieve our long-term goal of having a safe environment as well as providing the opportunity for the industrialization of fluorescence quantum dots.

In this research, we have used the hydrothermal synthesis technique due to its facile process. Utilizing natural low-cost and accessible sources of materials, we have applied the novel idea of using citrus aurantium (bitter orange) as the carbon source. After successfully synthesizing CQDs, we were able to make a change in the bandgap energy of the synthesized sample by simply adding various amounts of urea and polyethylene glycol to the precursor solution. CQDs contain urea and polyethylene glycol labeled as CQDs-U and CQDs-PLG, respectively. Having a change in the bandgap energy, it makes it possible to use such bandgap engineered CQDs in numerous applications including solar cells, photodetectors, and sensor devices.

2 Characterization

The morphology of CQDs were investigated using transmission electron microscopy (TEM; Zeiss EM900). The crystal structure of CQDs were validated using X-ray diffraction spectroscopy (XRD; D8-ADVANCE) with Cu k (1/4 1.540 Å). The radiation of XRD ranges from 10° to 80° over Bragg angles. The functional groups on the surface of CQDs were studied using a Fourier-transform infrared spectroscopy (FTIR; Tensor II, Bruker). We have performed UV-Vis spectroscopy (LAMBDA 365, Perkin Elmer) of CQDs to analyze the absorption and transmission of the sample. The fluorescence spectroscopy of CQDs was done by Agilent; Varian Cary Eclipse.

3 Experimental details

Carbon quantum dots synthesis

We have synthesized CQDs through hydrothermal method. 12 cc of Citrus Aurantium (bitter orange) liquid juice was filtered by filter paper (Whatman 12.5 cm ASHLESS 40). It was then poured into a 25 mL Teflon lined autoclave with steel cover and heated in an electric furnace in 200 °C for 24 hours. After the heating process, the final bright brown solution was purified by 0.22 µm (FilterBio) sterile Syringe filter. In the next stage, the purified solution was centrifuged at 12000 rpm for 20 minutes. In the final step the impurities were separated from the solution and the CQDs then redispersed into DI water and the final product dialyzed against 500 mL of DI water through a dialyzing bag in a container, stirred for 24 hours. For synthesizing of CQDs-U, before the heating process we have added 1 g, 3 g, and 5 g of urea in three individual synthesizing process. For synthesizing CQDs-PLG, 0.3 g and 0.5 g of Polyethylene glycol have been added to the precursor solution before the heating process in two individual synthesizing.

4 Results and discussion

We have performed XRD characterization to study the crystal structure of the aqueous CQDs solution. Figure 1 depicts the X-ray diffraction peaks and a wide diffraction peak close to $2\theta = 25^\circ$ is visible and it is related to the crystal phase of graphite. There is also another peak around $2\theta = 9^\circ$ which is assigned to the (001) plane of graphitic nitride carbon[26]. Considering XRD analysis CQDs have been successfully synthesized. Another Characterization which verifies the CQDs is energy dispersive X-ray (EDX). Figure 1.b illustrate the EDX graph and table showing the existing elements CQDs aqueous solution. The majority of the solution is Carbon and Oxygen.

We have characterized the functional groups on CQDs surface using Fourier-transform infrared spectroscopy for the verification of our successful CQD synthesise. As we can see in Fig. 2.a, the peak located at 3543 cm^{-1} is attributed to hydroxyl group (O-H)[27]. The absorption band at 2933 cm^{-1} is allocated to C-H stretching vibration[28]. There are also other peaks at 1707 cm^{-1} and 1567 cm^{-1} which are ascribed to C-O and C-C in carboxyl group. Accordingly, the available functional groups on CQDs such as hydroxyl, carboxyl and amide make CQDs water soluble[27].

Figure 2.b, shows Transmission Electron Microscopy of CQDs. The size distribution of CQDs is approximately less than 10 nanometers in diameter.

Another process used for detecting properties of these CQDs was Fluorescence test with results shown in the Figs. 3a, 3b, and 3c with pure CQDs, urea and polyethylene glycol, respectively which were excited in 285 nm wavelength and emitted about 400 nm.

As stated earlier, we have made a change in bandgap energy of CQDs by simply adding various amounts of urea and polyethylene glycol. In order to determine the changes in bandgap energy, we have used the Tauc method. In 1966, Tauc roughly calculated the bandgap energy of amorphous semiconductors using optical absorption spectra[29]. After a while two other scientists named Davis and Mott developed the Tauc method[30][31]. This method was derived from the fact that the energy-dependent absorption coefficient α can be demonstrated by the following equation[32],

$$(\alpha \cdot hv)^{(1/\gamma)} = B(hv - E_g)$$

1

Where h is the plank constant, ν is the frequency of the photon, E_g is the bandgap energy and B is a constant. γ is a constant factor that depends on the nature of electron transmission and whether it's direct or indirect and is equal to 2 or $\frac{1}{2}$ respectively[33]. In this study, we have synthesized CQDs with different amounts of urea and polyethylene glycol for the purpose of bandgap tuning. In our most recent attempts, we have used 1g, 3g, and 5g of urea in the synthesizing process in order to change bandgap energy of CQDs. Figure 4a shows the optical absorption spectrum of CQDs without any urea added. In contrast, Figs. 4b, 4c, and 4d illustrate optical absorption spectra of CQDs when 1g, 3g, and 5g of urea were added, respectively. Similarly, in Figs. 5a and 5b optical absorption spectra of CQDs when 0.3g and 0.5g of Polyethylene glycol were added is shown.

Then by Tauc method as it is obvious in Fig. 6, we were able to make the bandgap energy of CQDs larger by adding urea to the precursor solution. Figure 6a shows the bandgap energy of CQDs without any urea in precursor solution which is 2.5 eV. After adding 1g of urea, the bandgap energy of CQDs were increased and reached under 3.5 eV which can be seen in Fig. 6b. Moreover, the bandgap energy of CQDs have reached to 3.5 eV by adding 3g and 5g of urea to the precursor solution as it is illustrated in Fig. 6c and Fig. 6d.

The bandgap of CQDs have changed by adding Polyethylene glycol as well. Figure 7, shows the bandgap energy of CQDs with 0.3g and 0.5g Polyethylene glycol in the precursor solution which is a lot higher compared to CQDs depicted in Fig. 6a.

The PL spectroscopy shows that the synthesized CQDs can act as a suitable spectral converter in solar cells and optoelectronic devices. As it is obvious in Fig. 8, the PL spectroscopy shows the red shift when CQDs are illuminated by different wavelength. The inset numbers are excitation wavelength. CQDs can simultaneously absorb the UV region of the sun and convert these photons to a visible light which will ultimately increase the power of solar cells.

5 Conclusions

We have successfully synthesized an eco-friendly CQDs with quantum confinement using citrus aurantium (bitter orange) using a low-cost material and oversimplified synthesizing method. CQDs are able to convert the blue region of the solar radiation from 200 nm-350 nm to the red and visible region (400nm-500nm). Furthermore, the bandgap energy (eV) of CQDs were tuned by add in certain amount of Urea. In the final step, we added polyethylene glycol to the precursor solution for bandgap engineering.

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Figures

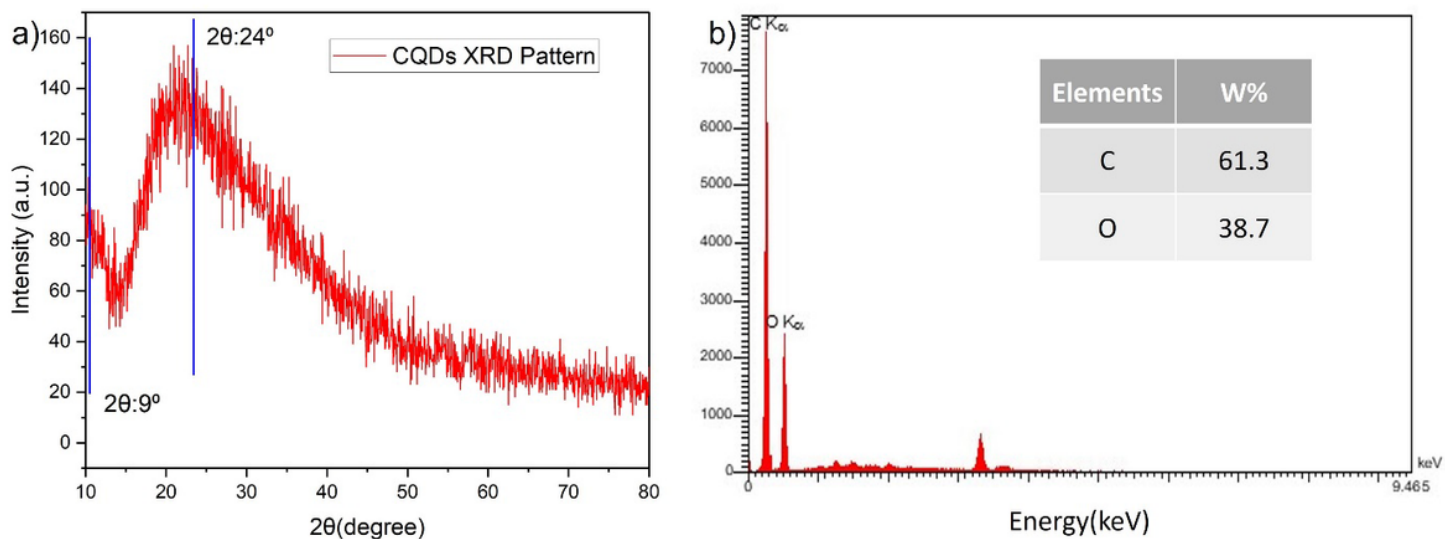


Figure 1

a) XRD spectrum of CQDs, b) (EDX) analysis of CQDs.

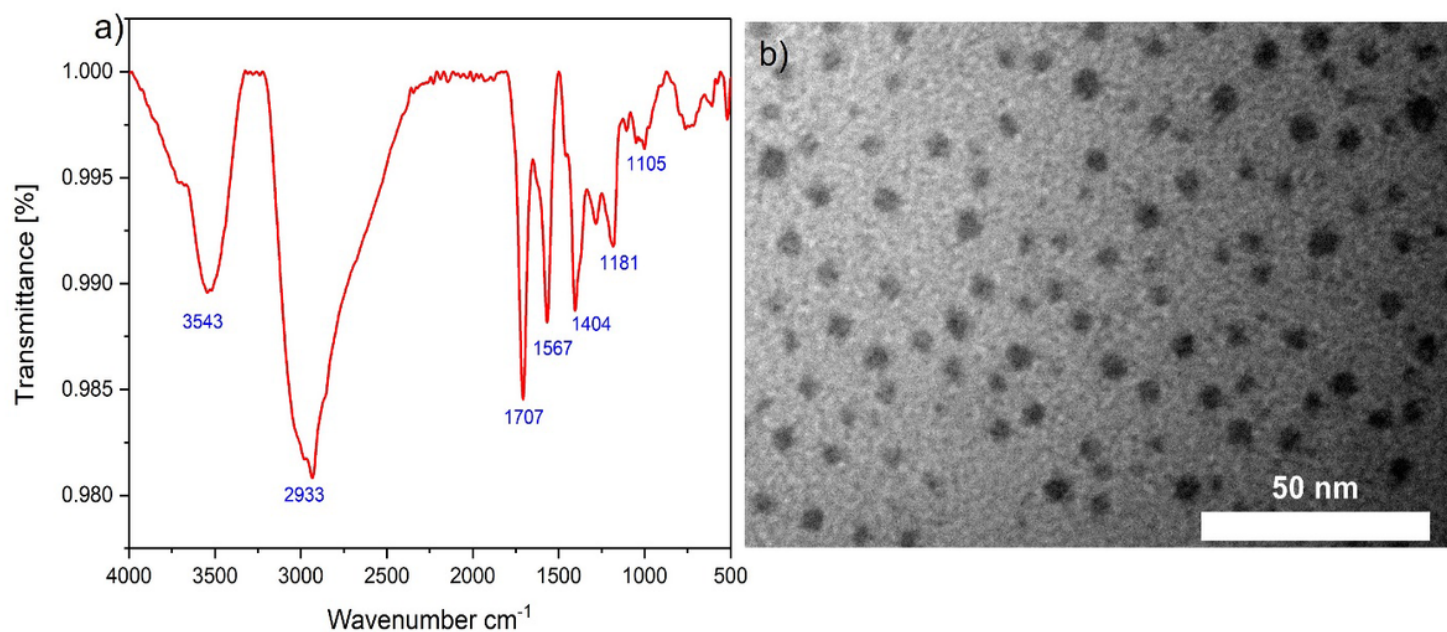


Figure 2

a) FTIR spectrum of CQDs, b) Transmission electron microscopy of CQD.

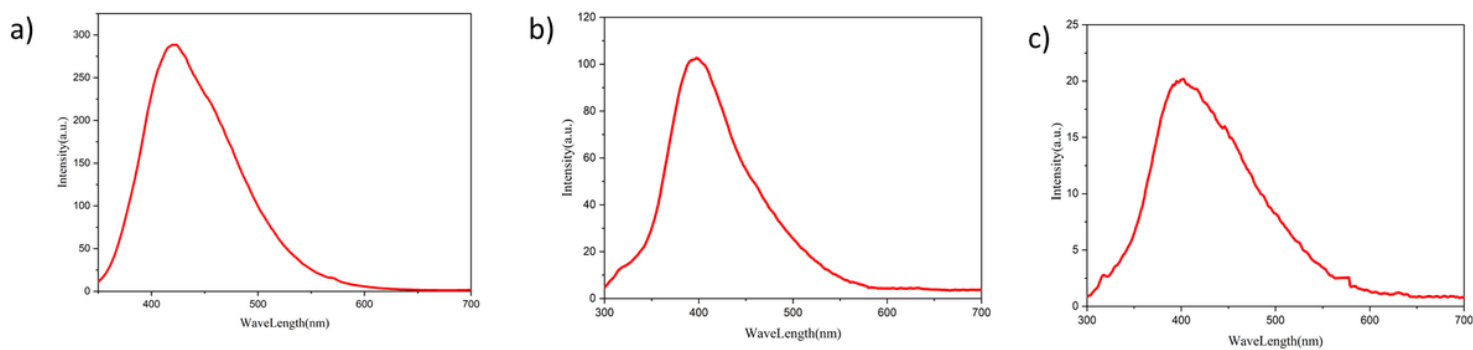


Figure 3

pure CQDs a) urea, b) polyethylene glycol in 285 nm and c) polyethylene glycol in 400 nm.

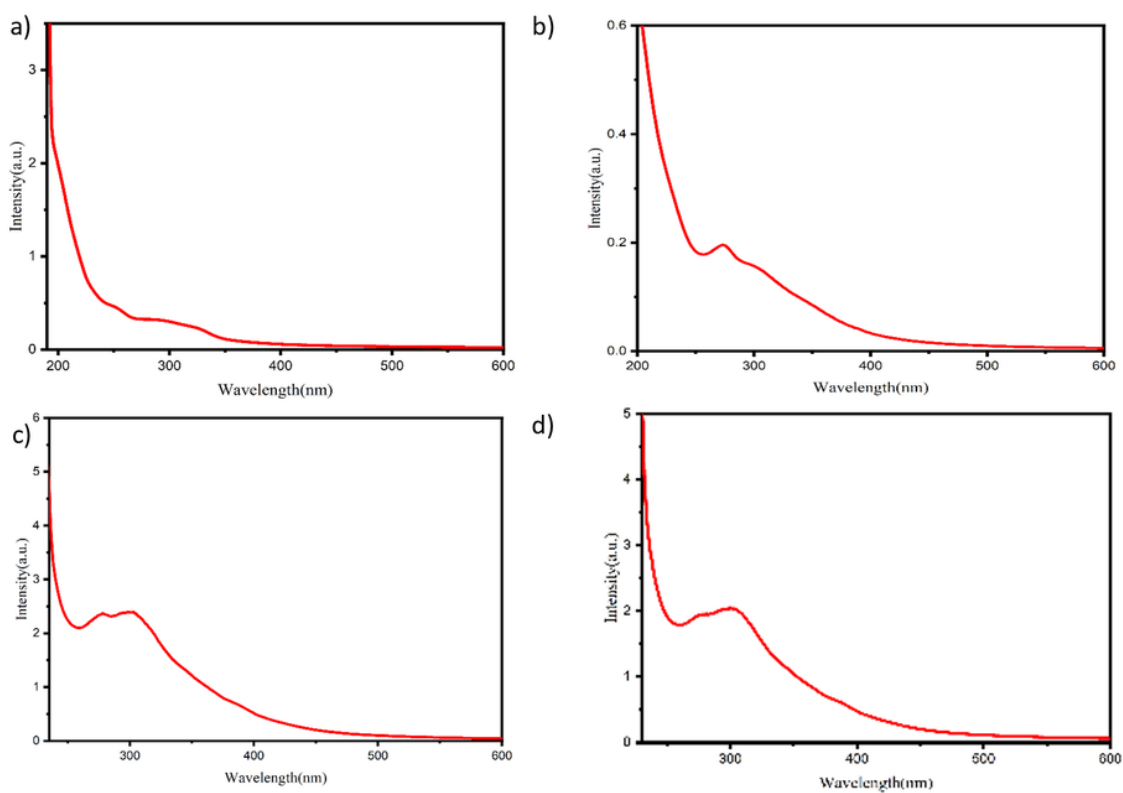


Figure 4

CQDs a) without any urea, b) 1gr urea, c) 3gr urea, d) 5gr urea.

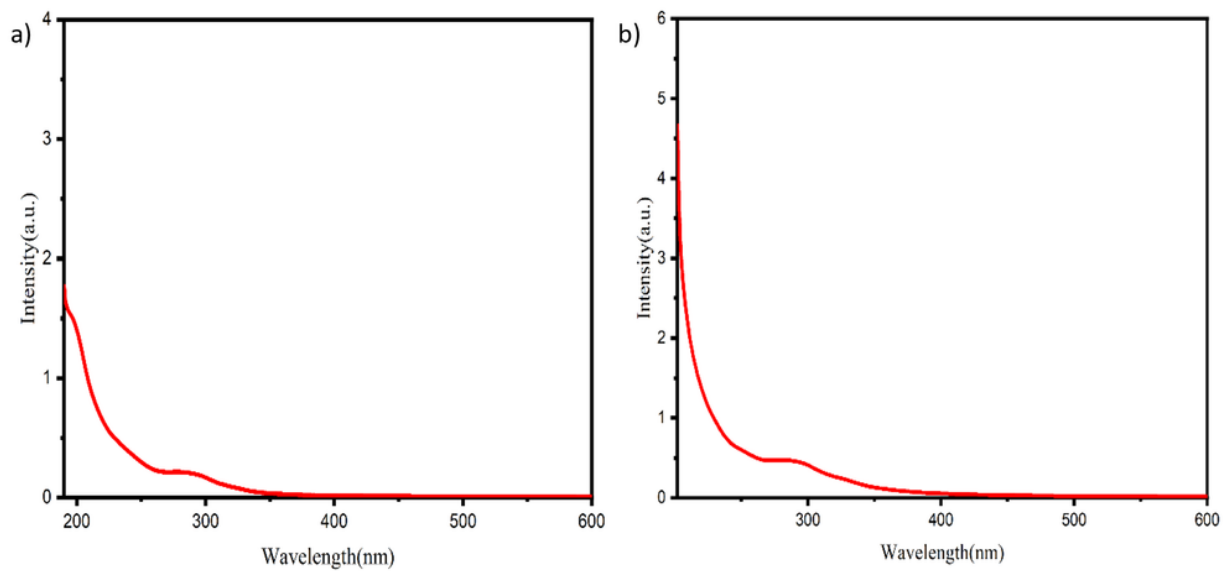


Figure 5

CQDs a) 0.3gr Polyethylene glycol, b) 0.5gr Polyethylene glycol

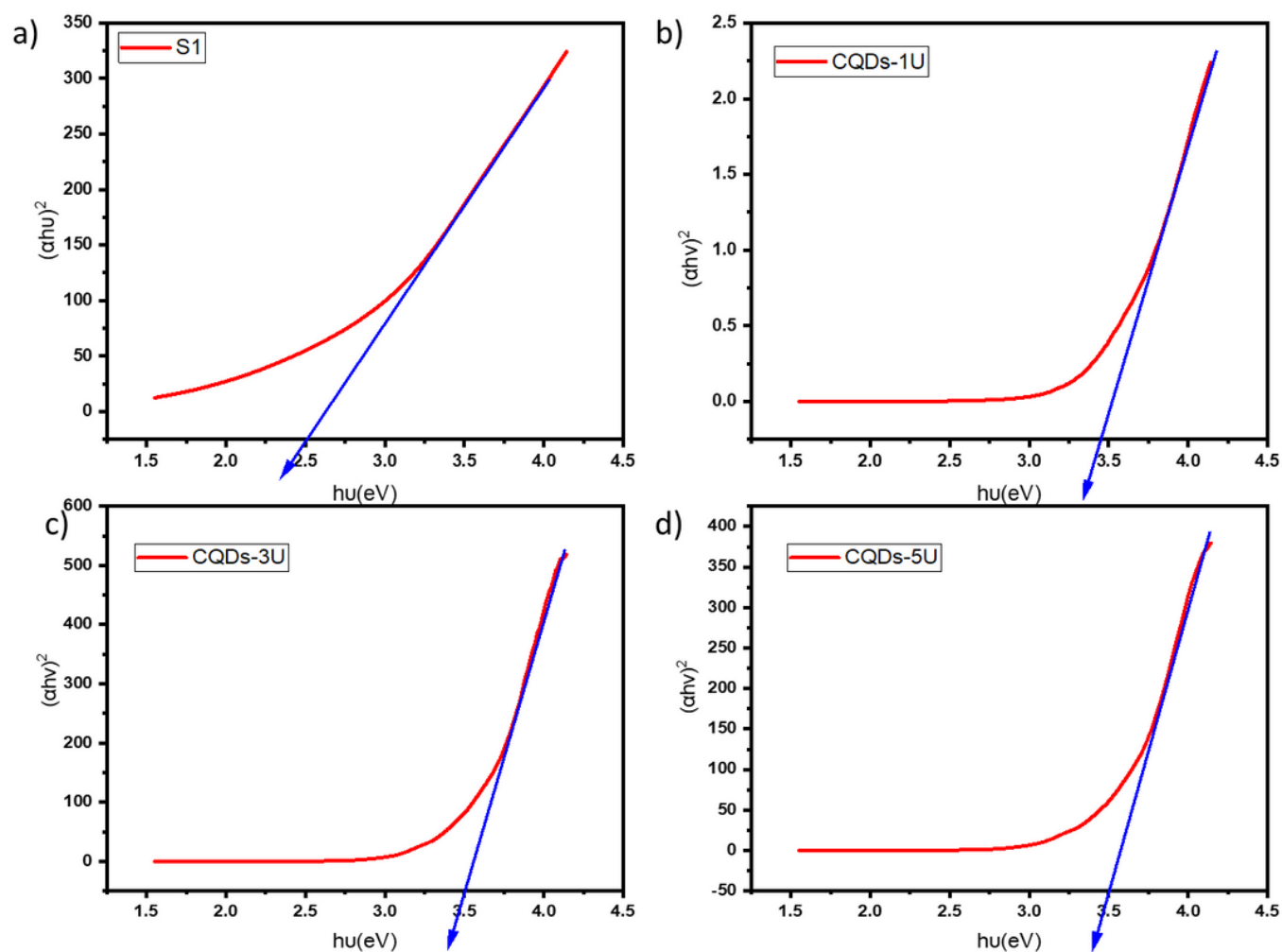


Figure 6

Bandgap energy determination using Tauc plot. a) Pure CQDs. b) CQDs-1U. c) CQDs-3U. d) CQDs-5u.

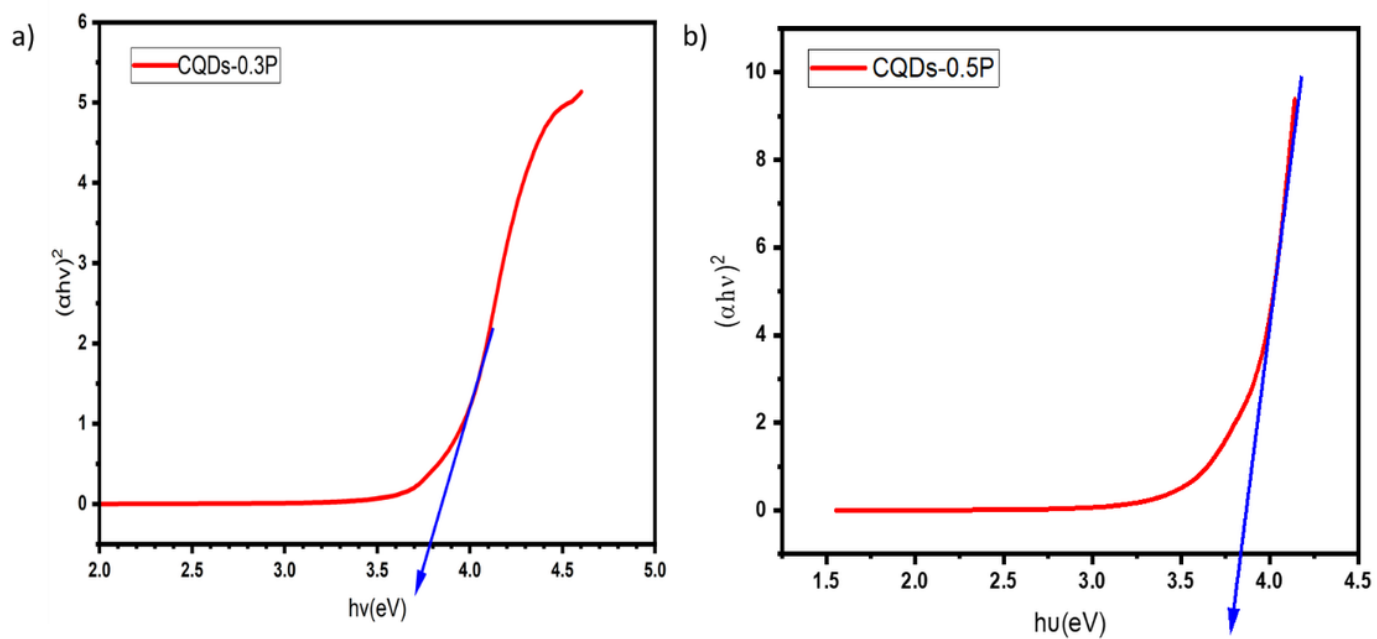


Figure 7

Bandgap energy determination using Tauc plot. a) CQDs-0.3P. b) CQDs-0.5P.

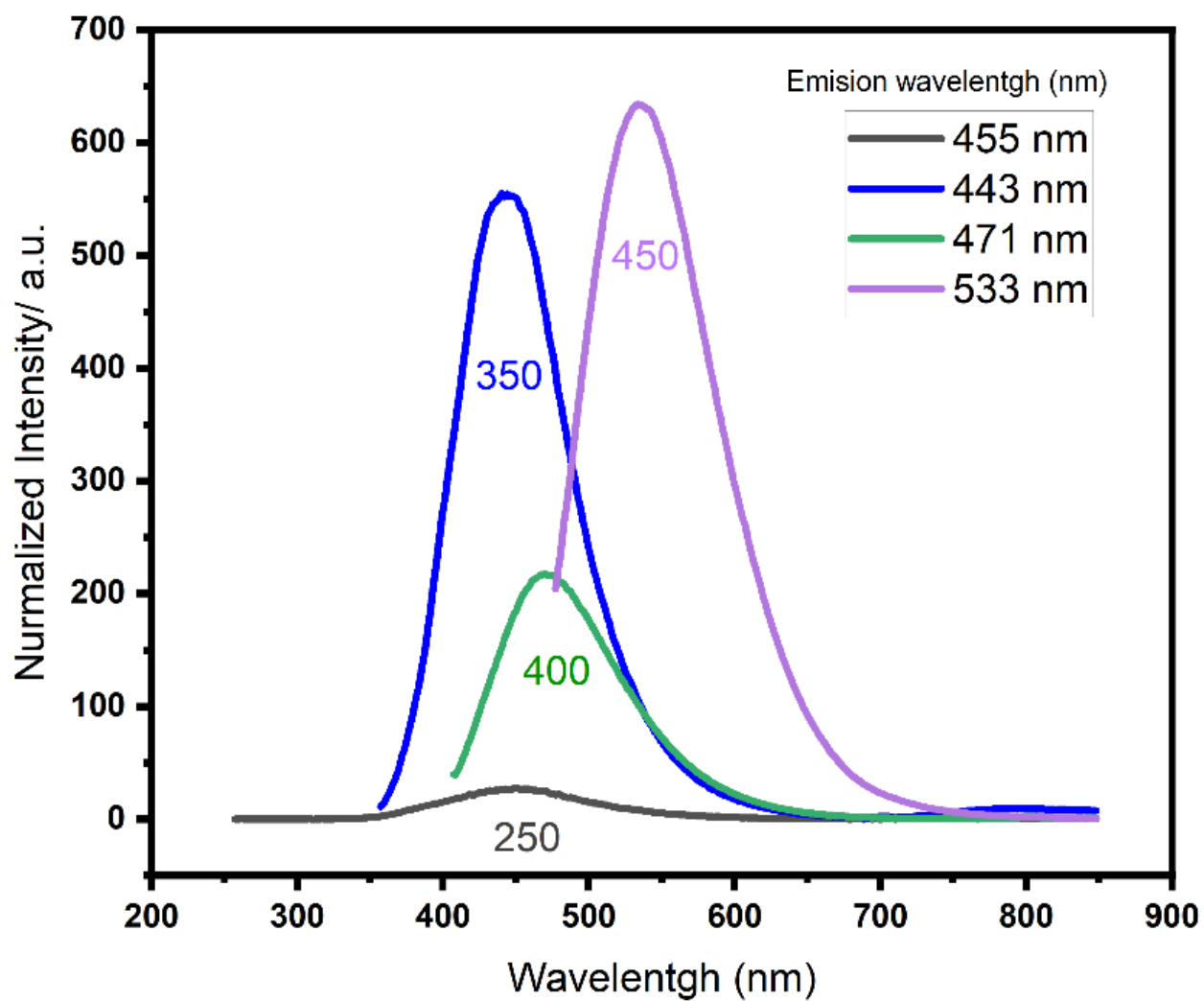


Figure 8

PL spectroscopy of CQDs.